The Principles of Thermodynamics

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N. D. Hari Dass

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Dedication

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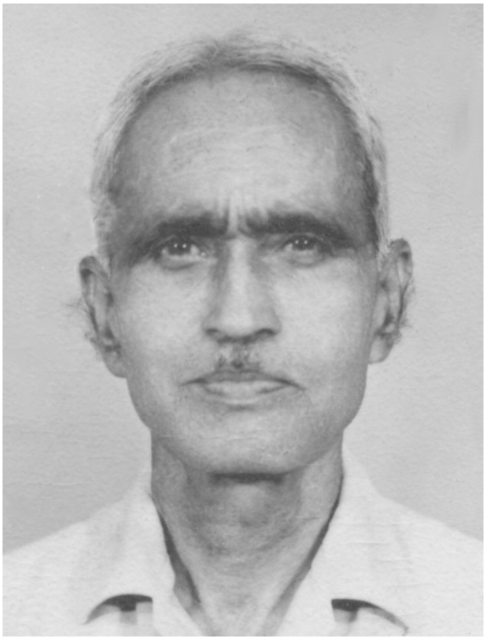

I dedicate this book to my beloved high school teacher Sri. H. Anantha Rao (1907-2011), who lived true to the spirit of science. He opened our minds to the wonderful world of physics. Till his last days he was preoccupied with science, and in particular whether modern science was addressing the right questions.

I also dedicate this book to my parents. To my mother, Venkatalakshmi, who, despite gnawing poverty, made the education of her children her prime objective in life. And to my father, Desikachar, who, despite being very orthodox religiously never hindered our choices in life.

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Preface

The great German physicist Arnold Sommerfeld, in the preface to his book *Thermodynamics and Statistical Mechanics*, had this to say: "*In contrast to classical mechanics, thermodynamics has withstood the quantum revolution without having its foundations shaken.*" A similar sentiment is echoed in the American physicist Arthur Wightman's tribute to Gibbs that "his contributions have survived 100 years of turbulent developments in theoretical physics." It is this resilience that makes a study of thermodynamics such a rewarding experience. In fact, not only did thermodynamics survive the revolutionary developments of quantum theory, it, in the hands of the great masters Planck and Einstein, played midwife to the very birth of quantum theory. Behind this resilience lies the great generality of the principles of thermodynamics. Usually when principles are too general, their effectiveness gets limited. But in the case of thermodynamics, its impact both on scientific thought as well as its practical impact have been unmatched by any other field of science. As for the latter aspect, the applications of thermodynamics range over physics, chemistry and engineering, and of late over biology and even black holes!

With the epoch-making developments in *Statistical Mechanics*, there is an increasing trend among physicists to treat thermodynamics as some sort of a second fiddle. This is unfortunate indeed as in reality the powers of thermodynamics remain undiminished. Of course, the two complement each other, making both of them even stronger. It is also unfortunate in another sense that young readers get the mistaken impression that statistical mechanics is easier while thermodynamics is nearly incomprehensible. This is partly because at that level, statistical mechanics is almost algorithmic, while thermodynamics seems to require constant revision of its basic tenets. In fact, one often needs, as for example in the case of magnetism, the guidance of thermodynamics in proper applications of statistical mechanics.

In this book the focus is entirely on what Pippard calls *Classical Thermodynamics*. My intention is certainly not to belittle the greatness of statistical mechanics. It is more to highlight the elegance, power, and conceptual economy of thermodynamics. To see how much of natural phenomena can be comprehended, even highly quantitatively, by thermodynamics on its own. I find it gratifying that Max Planck, Fermi, and Pippard have written their great books in a similar spirit. That this classical thermodynamics can be succesfully applied even to a manifestly quantum state like the Bose-Einstein condensate is yet another example of the resilience mentioned above.

All this granted, I am sure many would like to ask "Why yet another book on thermodynamics?." It is true that there are many many books on this subject, and some of them are classics. I would say, in response, that first of all there should always be space for more books. No two serious authors will have the same perspective and emphasis. But on a more serious note, I found, while teaching courses on this subject at the Chennai Mathematical Institute, that even the classics were not uniform in their choice of topics. By this I do not mean the applications part. They are too vast anyway to be included in any single book. I mean that even when it came to the basic aspects there was this non-uniformity. It was, therefore, my desire to distill in one book the essence of many of these classics, and more. It is unlikely that this book is ever going to replace the classics. But my hope is that it will single handedly complement most of them. As can be gleaned both from the Table of Contents and the extensive subject index, I have given detailed coverage to a number of basic topics. I have also included historical background without interfering with the scientific content, as I strongly believe that a history of ideas is as important as the ideas themselves. My second goal was to help enlarge the scope of thermodynamics for teaching purposes. My third goal was to produce a handy reference for experts. I hope I have succeeded, at least to some measure, in these aspects. Needless to say, I have not only relied on the great classics, but also on some pedagogically excellent sources, which I have described at the end of chapter 2. I have also included a reading guide to help the readers on the one hand, and teachers on the other.

Writing a book is a venture that can not be undertaken without the support and encouragement of many. Firstly, I thank my daughter Shantala for prevailing over me, time and time again, to write books to make my pedagogical skills available to a larger audience. I thank both her and my wife, Jayanthi, for all the difficulties on the personal front that had to be endured during the writing, and for the continuous enthusiasm they showed throughout. I thank Prof. Dr. Gmehling and Prof. Joerg Krafczyk of the Dortmund Data Bank for their immense help and permission to use their data on water. I thank David Fausel and CRC Press for permission to reproduce data on specific heats from the *Handbook of Chemistry and Physics*. On the production side, I thank Aastha Sharma, David Fausel, and Rachel Holt from Taylor and Francis for patiently dealing with my never ending queries. Shashi Kumar's continuous help with LaTeX related matters and style files played a vital role in the production of the manuscript. I thank him profusely for the same. I am indebted to Rama Murthy of Indian Institute of Science for his meticulous drawing of the figures, and for his patience with many redrawings. I thank my friends Sharada Babu and S.A. Prasad for their permission to use their father's photograph in the dedication. I thank my uncle Prof. M.V. Narasimhan for innumerable discussions on heat engines and entropy. Finally, I would like to thank the students of the 2010 batch of BSc Honours(Physics) at the Chennai Mathematical Institute for sensitizing me as to how to teach a subject like thermodynamics properly!

Chennai, February 2013 N.D. Hari Dass

Guide for readers and teachers

I have written this book with the objective that it can address i) beginning undergraduate students, ii) more advanced undergraduate or beginning graduate students, iii) teachers, and iv) experts and researchers. The entire material should be easily accessible to all except the beginning undergraduate students. In this guide, I wish to point out a practical road map to each one of these categories.

A basic knowledge of calculus is essential for all. My suggestion is to start with chapter 16; the beginning undergraduates must first master the first two sections of this chapter. After that, depending on their interest, they can master the rest of the sections. For the other categories, I would recommend reading this entire chapter thoroughly.

Teachers

Teachers can use this book in a variety of ways. They can use it to augment the courses they are already teaching by using selective portions of the book as per their requirements. They will benefit from the large number of solved examples and problems in each chapter. Alternately, they can split the material into two courses a) a beginning undergraduate course, and b) an advanced course.

For the beginning undergraduate course: the first three sections of chapter 1, all of chapter 2, skip sections 3.2 and 3.3 but otherwise cover all other sections of chapter 3, all of chapter 4, skip chapter 5 and chapter 6, cover all of chapter 7, skip chapter 8, cover all of chapters 9 and 10, cover only the first three sections of chapter 11, only the first two sections of chapter 12, skip chapter 13, cover the first two sections of chapter 14, and skip chapter 15.

For the more advanced course, whatever was skipped above can all be covered.

Students

Beginning undergraduate students can follow the same guidelines as given to the teachers above in designing a beginning undergraduate course. The more advanced students will be able to follow the entire book.

It is highly recommended to understand the solved examples as well as attempt as many problems as possible. It is also very important to follow the suggested reading at the end of chapter 2.

Experts and Researchers

This category should find the entire book very useful. In several places, reference has been made to original literature.

Solution manual

A solution manual will be made available in which solutions to all the problems will be given. For lack of space many important topics like chemical reactions, saturated solutions, surface tension of solutions, equilibrium in external force-fields etc. could not be adequately discussed in the main text. These have been addressed in the solution manual. At any time, the author may be contacted at ndhari.dass@gmail.com for your suggestions, comments, and any help.

1 The Beginnings

Like all sciences, the subject of thermodynamics too grew out of systematizing *empirical data*. Needless to say, data has no meaning unless viewed within a reasonably well-defined *conceptual framework*. The beginnings of such a framework is of course in day-to-day sense perceptions and experiences. The notion of *hotness* and *coldness* must have been around for a very long time. An important part of this experience is also the recognition that upon contact, the hotter body grows colder and the colder body grows hotter.

Another very important, though somewhat abstract, empirical notion is that of *equilibrium*. Taking the example of mixing, say, hot water with cold water, it was recognized that after some *reasonable time*, the bodies reach a common hotness, and left to themselves, would continue in that situation. In fact, experience tells us that this property of equilibrium holds even when several objects are brought in contact. So, for example, if three samples of water all with different hotnesses are mixed together, they would all reach the same hotness. This is true if instead of mixing the same substance at different hotnesses, one brings in contact totally different materials. For example, if a chunk of iron, a chunk of copper and a volume of water, all with different hotnesses, are brought together, they would all reach the same hotness eventually.

This leads to the following highly non-trivial property of thermal equilibrium: if bodies A and B are in thermal equilibrium, and bodies B and C are also in thermal equilibrium, then A and C are necessarily in thermal equilibrium. This obvious sounding, innocuous looking property is so essential for the consistency of the subject of thermodynamics that Fowler [18] has suggested elevating it to the status of a law, and consequently it is often called *The Zeroth Law*.

There are a few subtle points that are worth emphasizing in the context of thermal equilibria. In the example of the mixing two substances mentioned above, it is clear that some time has to elapse before equilibrium is reached. But how much time? This is strictly speaking beyond the purview of thermodynamics discussed in this book, which is called *equilibrium thermodynamics*. It turns out to be a very difficult question anyway. For example, if we live in a static universe (which we do not) and if the basic laws are laws of classical mechanics, the two systems will eventually go out of equilibrium! Of course, one has to wait for *super-astronomical times*, but in classical mechanics this is among the very few exact results. The phenomenon is called *Poincaré Recuurence*. So, one has to wait long enough for equilibrium to set up, but not wait too long. Even ignoring the Poincaré Recurrence, the very fact that systems are not perfectly isolated can also take them out of equilibrium.

The other point is that the nature of the *contact* between systems has to be qualified more carefully. Whatever has been said so far only holds when contacts are such that only heat can be exchanged between the two systems. Such conditions are usually called *constraints*, or more picturesquely called *walls*.

1.1 Temperature and thermometry

A real progress in this process of theorizing and conceptualizing was the recognition of the notion of *temperature* as a *measure of hotness*. The main bases for this concept are the following empirical facts: i) The fact that when bodies are in equilibrium they acquire the same hotness would mean that they will also have the same temperature. ii) The property of thermal equilibrium mentioned above has the important consequence that it would be possible to decide if two bodies are in thermal equilibrium without having to bring them into actual contact; this can be done by simply measuring their respective temperatures. If their temperatures are the same, they have to be in thermal equilibrium.

That raises the question as to how to *measure* the temperature of a body. Since the abovementioned aspects of thermal equilibrium do not depend on the relative sizes of objects, an important corollary is that by making one of the objects, to be eventually called a *thermometer*, very small, so that its contact with the bigger object does not in any appreciable manner affect the thermal condition of the bigger object, it would be possible to monitor the hotness of the bigger object by simply monitoring the hotness of the smaller system or, in other words, its temperature.

That still leaves open the question as to how to decide what the temperature of the smaller body, the thermometer, is. The empirical fact that heat affects the material state of bodies can be exploited for answering this. It can be done by measuring one of the properties of the thermometer, like its volume. For example, bodies expand upon being heated (mostly, but there are very important exceptions like ice on heating actually shrinks in volume). Therefore, properties like the volume of an object at some prescribed pressure can be used as a measure of its temperature. This is the basis of the so called *thermometry*.

But it may come as a shock to know that how this is to be done, i.e define the temperature of the thermometer in terms of, say, its volume, is essentially *arbitrary*. This can lead to troubling thoughts as to how a temperature scale that is fixed arbitrarily can play any role in a scientific theory. In particular, it can lead to worries as to how, say, two different scales of temperatures so defined can still be compatible with each other? We shall address these important concerns with an explicit model for a thermometer. But it is worth pointing out that such basic difficulties are necessarily there in every branch of physics. If we take time as an example, and a clock in place of the thermometer, questions like what defines the quantity one calls time and how exactly should the markings on a clock be determined are precisely the sort of questions we are encountering in thermometry!

Let $X(t)$ be some temperature-dependent property of some system as a function of its temperature t. It could, for example, be the volume of a gas under some fixed pressure P_0. But let us keep the discussion general and not specify what $X(t)$ is. The thermometer can essentially be thought of as a measuring device for X(t), the difference being that its readings give out temperatures in place of values of X.

The first thing one has to do is choose two *fiducial* points on the thermometer. In simple words this means we should mark two positions on the thermometer which correspond to the temperatures, according to this particular thermometer, of two standard states. For example, these can be taken to be the freezing point of water and the boiling point of water, both at one atmospheric pressure. Thus, thermometry is a relation giving t in terms of the higher fiducial temperature T_H, lower fiducial temperature T_L, where the scale agrees with some standard scale, along with the measured values of X at these three temperatures.

Let us *arbitrarily* mark the freezing point as 0 and the boiling point as 100 (as for example in the *Centigrade* scale; in the *Fahrenheit* scale these would be 32 and 212 respectively) on *all* thermometers. Let the values of the quantity X at these fiducial temperatures be X_0 and X_{100}. Next, one subdivides this interval in X-space into N *uniform* divisions with N+1 points. The value of X at the point labelled n is given by $X^{(n)} = X_0 + (n-1)/N\,(X_{100} - X_0)$. There should be no confusion between the numbers in the superscript and those in the subscript. The numbers in the subscript refer to the temperatures of the fiducial points (on the centigrade scale in this example), while the superscripts refer to the marker positions. The important point to bear in mind is that the markers on the thermometer corresponding to these values will also be *equally spaced* as the thermometer is just a measuring device for X.

So far we made several arbitrary choices, even after fixing the substance to be used in the thermometer as well as its property used for measuring temperatures. There is one more arbitrariness, which may come as a surprise to some. Even though we have N+1 equally spaced markers on the thermometer, it is not *necessary* to assign numerical values to these markers in a *uniform* way! These numerical values will be the 'temperatures' read out by the thermometer. Let us look at two concrete examples to clarify the situation.

1.1.1 Uniform temperature scale

The simplest is to adopt a *uniform* or *linear* scale. In this case, the numerical values attached to the markers (temperatures) are given by

$$\frac{t^{(n)}}{100} = \frac{\left(X^{(n)} - X_0\right)}{X_{100} - X_0} = \frac{n-1}{N} \tag{1.1}$$

Thus we can mark one hundred points separated by $\Delta t = 1$ or two hundred points separated by $\Delta t = 0.5$ etc. with $\Delta t = 1/N$ in general. The larger the number of subdivisions, i.e the value of N, the more accurately can the temperature be measured by this thermometer. We can work out the temperature dependence of X when this temperature scale is used:

$$X(t) = X_0 + \frac{X_{100} - X_0}{100}\, t \tag{1.2}$$

which says that X increases *linearly* with t. But it should be borne in mind that this linear behaviour of X is an artifact of the way this particular temperature scale was defined. It is easy to generalize these considerations when the fiducial temperatures are arbitrary, and even on an arbitrary scale and not just on the centigrade scale as exemplified here.

For many students, this can be a source of great confusion. Often it is asked, does X really vary linearly with temperature? The point is that this question does not have much content. To specify temperatures, one must say which scale of temperature has been used. Depending on that, the same physical quantity may show different temperature-dependence. In the above example, $X(t)$ varies linearly with temperature simply because the temperature scale was as defined in eqn.(1.1). But we have to show that physically sensible conclusions, like whether a body A is hotter than B, or whether C and D are in equilibrium etc. are indeed *independent* of the arbitrary definition of the temperature scale.

1.1.2 Non-uniform temperature scales

To clarify these, let us define another scale of temperature, and for ease of comparison take the same fiducial states, i.e freezing and boiling points of water at one atmosheric pressure. Let us still call these 0 and 100 degrees respectively. But instead of defining temperature according to eqn.(1.1), let us define it according to the admittedly more complex

$$\frac{t^*}{100} = \sqrt{\frac{(X - X_0)}{X_{100} - X_0}} = \sqrt{\frac{n-1}{N}} \tag{1.3}$$

Even according to this new scale, when $X = X_0$ the temperature $t^* = 0$ and likewise when $X = X_{100}$, $t^* = 100$. Therefore at the fiducial states, by design, all temperature scales agree. But they generally do not agree elsewhere. The temperature dependence of X according to the new scale is

$$X(t^*) = X_0 + (X_{100} - X_0)\left(\frac{t^*}{100}\right)^2 \tag{1.4}$$

Now we see that the same physical quantity X has a quadratic temperature dependence according to t^*-scale. It should be kept in mind that X_{100}, X_0 are physical values of X and are therefore *independent* of any temperature scale.

Suppose we have two bodies A and B, and that our thermometer shows values X_A, X_B when brought in contact with them. As already stressed, X_A, X_B in themselves do not depend on any temperature scale. Further, let $X_A > X_B$ when A is hotter than B. Then, according to the t-scale, $t_A > t_B$ and indeed t is a good measure of hotness. But it is easily seen that $t_A^* > t_B^*$ also, so that the t^*-scale, which has nothing to do with the t-scale, is also an equally good measure of hotness. Finally, if according to t-scale the two bodies are in equilibrium, i.e $t_A = t_B$, then from eqn.(1.2) $X_A = X_B$. But from eqn.(1.4), $t_A^* = t_B^*$. This means that even according to the t^*-scale, the two bodies are in equilinrium.

Finally, note that it is possible to convert from one scale to another:

$$\frac{t^*}{100} = \sqrt{\frac{t}{100}} \qquad \frac{t}{100} = \left(\frac{t^*}{100}\right)^2 \tag{1.5}$$

and this conversion is such that a given value of t corresponds to a unique value of t^*, and vice versa. Because of this, one can, without any loss of generality, always adopt the uniform scale. But it should be stressed that the natural scale to be adopted depends on the function $X(t)$. For example, if $X(t) = at^2$, it is obviously better to adopt the non-uniform scale(quadratic in this case).

1.1.3 Materials for thermometry

Can any physical quantity play the role of $X(t)$ as long as it is temperature-dependent? The answer is no. Before answering this in mathematical terms, note that water has a peculiar behaviour at $4\,^\circ\mathrm{C}$. Its density is *maximum* at this temperature, and decreases both as the temperature increases or decreases from this value. So if we had used the density (or equivalently the volume) of water in a *water thermometer*, we would have had the peculiar situation that the temperature would be ambiguous. More precisely, it is two-valued, one of them above $4\,^\circ\mathrm{C}$ and the other below. Hence the mathematical criterion for $X(t)$ to be admissible for thermometry is that $t = t(X)$ must be *single-valued* which also means that $X(t)$ itself must be a monotonically increasing or decreasing function of t. Here t can be with respect to some other thermometer. While we have illustrated these important properties of thermometry with just two examples, it is clear that there are infinitely many temperature scales all equally valid.

Clearly the temperatures so measured will depend on the material used in the thermometer, on how its properties depend on temperature as well as on the temperature scale chosen. An apparent circularity at this stage can be removed by using several types of thermometers, i.e depending not only on different materials but also on different properties used for thermometry. Then different thermometers can be *calibrated* against each other. The properties of the substances used in thermometers must, however, obey the general mathematical criteria spelled above.

It is very important to emphasize that though temperature is a measure of hotness or coldness of a body, there is no *absolute quantification* of hotness of a body. This is because of the inherent arbitrariness in the choice of a temperature scale.

It will also become clear that no one substance or one property will suffice to define a temperature scale with arbitrary range of parameters. At temperatures low enough that a certain gas will liquefy, a gas thermometer based on this gas can not obviously be used at low temperatures. In fact under extreme conditions of temperature and pressure, radically different methods of thermometry will come into play. Their design, the task of their accurate calibration etc. forms a fascinating part of thermodynamics.

For a very illuminating account of the history of thermometers, including the very early ones based on human physiology, see [47]. Thermometers based on gases at low pressures and average temperatures were found to agree rather well with each other best. We shall also see later that thermodynamics provides a very elegant way of defining a *universal scale of temperature* which is independent of all such material details.

Example 1.1: Comparing thermometers

Consider two constant volume thermometers, one of which is based on an ideal gas, and the other on a substance whose pressure at fixed volume follows the law $P(T) = aT + bT^2$*, T being the absolute scale. Find expressions for the two temperatures* T_1 *and* T_2 *in terms of T. Show that the temperature(on the absolute scale) at which the discrepancy between the scales is maximal is always the mid-point between the fiducial temperatures.*

Let us take the ideal gas law to be $P = cT$, where c depends on the molar fraction of the ideal gas used in the thermometer and its volume. Let the fiducial points for both the thermometers be at T_A, T_B with $T_A < T_B$. T_1 read on this scale is

$$T_1 = T_A + (T_B - T_A)\frac{P(T) - P_A}{P_B - P_A} = T \tag{1.6}$$

irrespective of c. Likewise, the temperature T_2 read on the thermometer with the second material is

$$T_2 = T_A + (T_B - T_A)\frac{P(T) - P_A}{P_B - P_A} = T_A + (T_B - T_A)\frac{aT + bT^2 - aT_A - bT_A^2}{aT_B + bT_B^2 - aT_A - bT_A^2} \tag{1.7}$$

It is easy to see that T_2 can be recast as

$$T_2 = T + b'(T - T_A)(T - T_B) \tag{1.8}$$

where b' is a constant depending on T_A, T_B and b/a (but not on b and a individually). Therefore the maximum deviation i.e $T_2 - T_1$ occurs at $T = (T_A + T_B)/2$. This is to be expected as everything is symmetric between T_A and T_B.

Example 1.2: Uniform and nonuniform scales

Consider two constant pressure thermometers both of which use an ideal gas as the material. One adapts a uniform scale while the other adapts a quadratic scale. Take the fiducial temperatures to be 0 and 100 on the celsius scale. If there are N subdivisions in both cases, find $T_1^{(n)}$ *and* $T_2^{(n)}$*.*

On the uniform scale the temperature corresponding to the marker n is

$$T_1^{(n)} = 100\,\frac{n-1}{N} \tag{1.9}$$

while on the quadratic scale

$$T_2^{(n)} = 100\sqrt{\frac{n-1}{N}} \tag{1.10}$$

Thus with 100 subdivisions the first nonzero marking will occur at a temperature of 10! Clearly, on the nonuniform scale one must take N to be sufficiently large. If the first nontrivial reading is to be at t=1, N should be 10^4. For that case, the second nontrivial reading will be at $t_3 = \sqrt{2}$, the next at $\sqrt{3}$ etc..

Example 1.3: A water thermometer

Water has its maximum density at $4^\circ\mathrm{C}$. *Denoting this density as* ρ_4 *and the density of liquid water at* $0^\circ\mathrm{C}$ *as* ρ_0, *the variation of density can be modelled as* $\rho(t) = \rho_0 + t(\rho_4 - \rho_0)/4$ *for* $0 < t < 4$, *and by* $\rho(t) = \rho_4 + (t-4)(\rho_0 - \rho_4)/4$ *for the range* $t \geq 4$. *Discuss the peculiarities of this water based thermometer.*

It is clear that density as a function of temperature is not single valued in this case. In fact, densities at temperatures $t+\tau$ and $t-\tau$(on the centigrade scale) are both equal. Thus a thermometer based on water will not be able to distinguish these temperatures when $\tau \leq 4$. However, when $\tau > 4$, i.e when $t > 8$, density becomes a single valued function of temperature and water qualifies to be a good thermometer material as per our earlier discussion. Else, one will have to use separate water thermometers for the respective temperature ranges above. However, it must be stressed that the differences in density are very small in practice. The density at $0^\circ\mathrm{C}$ is 0.9999 g/cc while the density at $4^\circ\mathrm{C}$ is 1.0000 g/cc (definition).

1.2 Ideal gas laws

We now turn to a discussion of the thermal properties of the so called *Ideal Gases*. An understanding of these is important from many different perspectives including their relevance for the *Gas Thermometers*. Historically, long before these empirically determined gas laws were established, thermometry had already reached a good degree of sophistication. The gas thermometer designs shall be based on these laws. At this stage it may be hard to motivate what one means by an *ideal* gas, but that should become clearer as we proceed.

The immediate temptation for a modern reader is to think of $PV = nRT$, where P and V are the pressure and volume respectively, while T is the temperature, n the number of *moles* of the gas, and finally R is the so called *Gas Constant* (it is said that the letter R is in honour of Regnault, whose work will appear prominently in any discussion on the development of thermodynamics). But one should resist that for several reasons, both historical as well as scientific. That this is so can immediately be seen on noting that temperatures in this equation refer to the *Kelvin* or *Absolute* scale, something that came much after the gas laws were discovered. Equally importantly, this single equation is a concatenation of three distinct, and equally important, laws of gases. Each of these is conceptually different and each was discovered at very different times. It is necessary to pay attention to these nuances to get a proper understanding of what is collectively called the ideal gas law. That will also turn out to be crucial to the understanding of gas thermometry.

Denoting temperatures by t (say, as measured by some thermometer according to some chosen temperature scale), the first relevant law in this connection is the *Boyle-Mariotte* law (Boyle 1658, Mariotte 1676; but in those days scientists often discussed their researches in monographs published many years after their work), which states that

$$P^{(i)}V^{(i)} = \theta^{(i)}(t) \tag{1.11}$$

This laws states that for a given mass of a gas, the product PV depends only on its temperature. In the above, we have labelled the gases by an index i to allow for the possibility that while for each species pressure is in inverse proportion to its volume, the product PV could vary from gas to gas.

In most modern texts, this point is glossed over and the product is taken to be the same for all gases. But careful historical accounts [42] have asserted that that was not what Boyle had claimed in actuality. Though Boyle was careful enough to clearly point out that the said relationship had only been established in a narrow range of pressures and temperatures, it appears as if his experiments were done only on air. Therefore the logical possibility that the functions $\theta^{(i)}$ could be different must be allowed for in a careful enunciation of the Boyle-Mariotte law.

For gas thermometry, it makes a considerable difference whether $\theta^{(i)}$ is different for different gases or not. In the physical ranges where $\theta(t)$ satisfy the conditions for consistent thermometry discussed above, if these products are not the same, any one of them can be used to construct a bona-fide gas thermometer, and in general these thermometers will not agree with each other, though all of them can be calibrated against each other. Further, as explicitly shown in the section 1.1 on thermometry, each of them can be brought to the linear form, a form associated with the text book formulations, by choosing the thermometer material appropriately. But mention had been made of the fact that a large number of gas thermometers agree rather well with each other. This is only possible if for this class of gases the function $\theta(t)$ is the same to a good accuracy. Boyle's law does not claim any such universality.

In fact, the source of that universality lies in yet another of the gas laws, the so called *Gay-Lussac-Charles's Law*. Gay-Lussac announced his results in 1802 in the journal *Ann. de Chimie* but even then he acknowledged the fact "..citizen Charles had noticed the same property in these gases 15 years ago.."[1]. Therefore, it is appropriate to call this law as the *Gay-Lussac-Charles's law*. But what exactly did this law claim, and what exactly is its impact on gas thermometry?

Unfortunately, textbooks and other modern accounts of this miss the essentials. They also wrongly attribute to this law conclusions that were never claimed, and what is worse, conclusions that obfuscate important scientific issues. For example, many of them claim that according to this law, 'for a given mass at constant pressure, $\frac{V}{T}$ is the same for all gases.' As commented before, the Kelvin scale was unknown at the time, and consequently this could not have been the original formula. Some others say that according to this law 'the fractional change in volume for a given mass of any gas at constant pressure is proportional to the change in temperature' while yet another source claims that according to this law 'the fractional change in volume at constant pressure for a change in temperature of $1\,^{\circ}\mathrm{C}$ is the *same* for all gases.'

Fortunately, the English translation of Gay-Lussac's original French paper is available [1]. He has recorded his claims in such a precise way as to be far more useful for the current purposes than any of the modern renderings. It turns out that Gay-Lussac did not study any detailed temperature dependence of volumes of gases at constant pressure, nor did he study the the fractional changes in volume per degree Celsius. What he did show was, in his own words, *All gases, whatever may be their density and the quantity of water which they hold in solution, and all vapors expand equally between the same degrees of heat.* In this context, *equal expansion* should be understood as the *ratio* of the change in volume to the original volume, and the phrase *same degrees of heat* meaning given initial and final temperatures. In fact, he studied the expansion as gases were heated, according to him, between temperatures of melting ice and boiling water. In other words, the precise statement of the Gay-Lussac-Charles's law should be taken to be

$$\frac{V_{100}^{(i)} - V_0^{(i)}}{V_0^{(i)}} = f(P)\,c(0,100) \tag{1.12}$$

for all gases when their masses are held fixed. Here $c(0,100)$ is a number that depends on the two temperatures of 0 and 100 on the centigrade scale. Combining eqn.(1.12) with the Boyle-Mariotte law of eqn.(1.11) would give

$$\frac{\theta^{(i)}(100) - \theta^{(i)}(0)}{\theta^{(i)}(0)} = f(P)\,c(0,100) \tag{1.13}$$

for all i. That is possible only if $f(P)$ is a constant independent of P, and $\theta^{(i)}(t) = \theta(t)$ for all i. Furthermore, $f(P)$ can be taken to be 1 without loss of generality and in that case $c(0,100) = \frac{\theta(100)-\theta(0)}{\theta(0)}$. Therefore, the true import of Gay-Lussac-Charles law is that the product PV is indeed the same function of temperature for all gases.

This has the profound consequence that if Gay-Lussac-Charles and Boyle-Mariotte laws are exact, *all gas thermometers* based on volumes of gases would agree with each other. Gases for which these laws are exact will be called *Ideal.* When any of the ideal gases is used as a material for a thermometer and a *linear* scale is chosen, $\theta(t) = \theta_0(1+\alpha t)$. In that case, the *equal expansion* of Gay-Lussac is simply 100α.

1.2.1 The Kelvin scale

Now we come to the second result of Gay-Lussac as declared by himself. according to him, the *equal expansion* for all the gases was found to be 100/266.66 on the centigrade scale [1]. Equating this to 100α yields $\alpha = 1/266.66$.Now, $\theta(t) = \theta_0(1+\alpha t)$ can be reexpressed as $\theta(t) = (\theta_0\alpha)(\alpha^{-1}+t)$. Hence, the temperature scale can be taken to be $T(t) = 266.66 + t$. The modern value of the zero of Kelvin scale expressed in Celsius is 273.13 as against Gay-Lussac's value of 266.66. But considering his times, his value is pretty close indeed. In terms of this new scale the gas law will take the form $PV = kT$.

This new scale was introduced by Lord Kelvin and hence carries the name *Kelvin Scale*. The Kelvin and centigrade scales are related by just a *constant shift*. Hence temperature differentials on both scales are the same. Whereas in the earlier scale, changes in volume at constant pressure were proportional to changes in temperature, in the Kelvin scale, volumes of ideal gases are themselves proportional to temperature. The zero on this scale has the interpretation of being the temperature at which volumes of *all* ideal gases vanish if the pressure is kept nonzero. It is yet another matter that before such a temperature almost every known gas becomes a liquid to which the gas laws are no longer applicable.

In reality neither of the above mentioned laws is exact and deviations, even if small, are frequent. Then the gas thermometers will not all agree with each other, and there is really no criterion to choose one over the other. For each of them, a Kelvin-like scale can be introduced, and for each of them their zero on the centigrade scale will be somewhat different. The same Lord Kelvin also showed how a temperature scale can be introduced without reference to any material, not even perfect gases (and therefore independent of any gas law), which shall be called the *Absolute Scale* of temperature. In practice, the Kelvin scales of ideal gases is very close to this absolute scale.

The last ingredient in the gas law is the *Avogadro's law* formulated in 1811. Avogadro's law, as formulated by him, said *equal volumes of gases under the same external conditions of pressure and temperature contain equal number of corpuscles.* In modern terminology Avogadro's *corpuscles* are the *molecules*. The seeds for this law were laid in Dalton's *law of multiple proportions* for chemical compounds and Gay-Lussac's *law of integral volume ratios* for gases .

Avogadro formulated this law with an atomistic view of matter. Though today we know that the nature of matter is indeed atomistic, at the time of Avogadro, and to even much later times, atomism remained a speculation. Even at the time of Boltzmann it remained so, and the first vindication of this age-long and profound conjecture came only in the wake of Albert Einstein's work on *Brownian Motion* in 1905. As emphasized earlier, the spirit of thermodynamics is to involve as little as possible of microscopic details, whether empirically well established or merely speculative, in its description. On the other hand, it would be futile to completely ignore the microscopic reality. Therefore, what is needed is a very minimalistic attitude towards microscopics.

With this in mind, the famous physical chemist Ostwald, a long time critic of atomism, suggested to use the concept of *moles* instead of molecules. A *gram-mole* of a gas would be a certain mass characterstic of the gas. For Hydrogen it is 2gms etc. The Ostwald reformulation of Avogadro's law would then read *equal volumes of gases under the same external conditions of pressure and temperature contain equal moles of the gas*. Stated this way, and with an operational way of determining the number of moles in a given mass, all reference to atomism has been removed. Another equivalent formulation is to say that all gases under the same external conditions have the same *molar volumes*.

As an example of molar volumes, consider Hydrogen gas whose molar weight is 2gms. The density of Hydrogen gas at $0\,^\circ\mathrm{C}$ and 1 atm. of pressure is about 9.0×10^{-2} g/liter. The molar volume is easily calculated to be 22.2 liter. What is remarkable is that a gram-mole of every gas occupies this very volume at the said pressure and temperature. This is really a first glimpse into the atomic nature of matter.

The final form of the ideal gas law after combining all the three laws is

$$PV = nRT \tag{1.14}$$

where n is the number of moles, T the temperature in Kelvin, and R the so called *gas constant* with a numerical value of 8.31 Joules/K.

1.2.2 Non-ideal gases

As already mentioned, in reality no gas is perfectly ideal and departures from the gas laws discussed earlier are the rule rather than the exception. Many alternative equations have been proposed, each with its positive as well as negative features. Here are just a few of the most prominent ones.

van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{1.15}$$

Clausius equation

$$\left(P + \frac{an^2}{T(V + nc)^2}\right)(V - nb) = nRT \tag{1.16}$$

Dieterici equation

$$P(V - nb) = nRT\, e^{-\frac{an}{VRT}} \tag{1.17}$$

Of these the van der Waals equation played a major role in explaining the liquefaction of gases. In a separate chapter we show how this equation provides a simple model for almost everything that one needs to learn and understand in thermodynamics.

1.3 Heat and specific heats

As we saw earlier a hotter body on contact with a colder body becomes itself colder, while at the same time the colder body gets hotter. So it is legitimate to think in terms of an *exchange of heat* between the two bodies. This is where the notion of *heat* enters the subject. The above process, then, is described as the hotter body giving up a certain amount of heat to the colder body. The concept at this stage is only intuitive and heuristic. A quantification of this concept and finally an elucidation of the *nature* of heat are among the prime objectives of thermodynamics.

The quantification is done through the following, arbitrarily chosen, criterion: the unit of heat is a Kcal or kilocalorie, and it is the amount of heat needed to raise the temperature of 1 Kg of water under one atmospheric pressure from $14.5\,^\circ\mathrm{C}$ to $15.5\,^\circ\mathrm{C}$.

For any body, the *specific heat* c is given by the amount of heat required to raise the temperature of 1 kg of the substance by 1K. Denoting the amount of heat by $\text{đ}Q$, the definition of specific heat is $c = \frac{\text{đ}Q}{dT}$. Note that while defining the calorie, the heat transferred to water was at the constant pressure of one atmosphere. It will turn out that the amount of heat required to raise the temperature of a body by a given amount depends on the external conditions. Consequently there are many types of specific heats. All this will be clarified in great detail as we go along.

1.3.1 Nature of heat

One of the most important questions in thermodynamics concerns the *nature of heat*. It is interesting that none of the gas laws required any understanding of heat for their formulation. In fact their statement only involves the mechanical notion of pressure, the geometrical notion of volume in addition to that of temperature and molar content. While temperature is a measure of hotness, it is not heat *per se*. This is indeed a fortunate circumstance as far as the gas laws are concerned, as their validity is not entangled with the correctness or otherwise of any particular *theory of heat*.

One of the earliest such was the *Phlogiston* theory. We shall not discuss this at all. For one thing, this theory was discarded long ago, and more importantly it had no *predictive power* whatsoever. The next serious contender was the *Caloric* theory, chiefly propounded by Lavoisier. Unlike the Phlogiston theory, the caloric theory was capable of making specific and some very sophisticated predictions. The fundamental and pioneering works of the genius Sadi Carnot were all based on this theory. We shall describe Carnot's seminal work in detail.

The basis of the caloric theory was the following: while heat may be added or subtracted from bodies, it is not obvious whether a concept of a *total heat contained* by a body in some thermodynamic state makes sense or not. The caloric theory claims it does. This theory goes further and states that heat is an indestructible fluid. Consequently, the total heat of a body is the sum total of all heat that has flown in and flown out, there being no other mechanism to alter the amount of heat in the body. More precisely, the caloric theory claims that *heat is a state function* very much like pressure, volume, temperature etc. This aspect of caloric theory can be expressed in a mathematically precise manner as then dQ is a *perfect differential*. We shall first describe Carnot's work based on this theory in detail, then discuss various arguments and experiments that were put forward in its criticism before going on to develop the theory of heat as understood by post-Carnot thermodynamics. Carnot's theory is remarkable in that even in a cyclic process where total heat absorbed has to be necessarily zero in accordance with the caloric theory, net work can be produced.

The modern theory of heat, in contrast, refutes the caloric theory by claiming heat can be created and destroyed by other agencies, principally work of various kinds like *mechanical, electrical, magnetic* etc. Since it can easily be shown that work can not be a state function, and in fact depends on the history of how one state was transformed to another as a result of work performed, it follows that heat can not be a state function either. The post-Carnot view is that heat is yet another form of energy interconvertible with other forms of energy like mechanical, electrical etc. Furthermore, the *new thermodynamics* specifies a precise conversion factor between heat and work, a development as revolutionary as Einstein's famous $E = mc^2$, in both its conceptual depth as well as its scientific impact. Subsequently, the principle of conservation of energy takes form as *the First Law of Thermodynamics*. Contrary to the impression created that heat can be freely and completely converted to work, thermodynamics imposes *an absolute upper limit* to the efficiency with which heat can be converted to work. This is the content of *the Second Law of Thermodynamics*, a law unsurpassed in its depth and a law that has impact even on the most modern branches of physics today.

Before turning to a description of Carnot's work, we shall introduce in more precise terms notions very basic to the thermodynamic description as *thermodynamic states and their transformations*, *constraints and walls*, and finally the notion of *reversible and irreversible changes*. Carnot uses all these notions in a precise manner in a way that is completely consistent with their post-Carnot meanings. It appears to the author that precise formulations of the notion of a state, of reversible and irreversible process may indeed be due to Carnot himself.

1.3.2 States and transformations

States: By a *Thermodynamic State* we shall mean the *equilibrium* states of a system. Though it would seem natural to include only stable equilibrium states, it turns out useful to include even unstable and metastable equilibrium states also in the thermodynamic state space. So, a thermodynamic state of a *single component system* is characterized by well defined values of temperature, pressure and volume. If it is a *multicomponent system*, in addition to P, V and T, additional parameters like the *molar fractions* are needed to specify the state. If the system is also *magnetic*, then the magnetic degrees should also be included.

Equations of State: These are relations between the parameters of a thermodynamic state that lead to a *complete thermodynamic specification* of the system. For example, in the ideal gas case $PV = nRT$ is one such equation. For a more structural meaning of these equations, please see chapter 6. There are as many equations of state as there are *independent* degrees of freedom.

Transformations: Any change of state is a *transformation*. The changes in the parameters during a general transformation could be anything subject to the equations of state. When the transformation connects states whose degrees of freedom are very close (neighbouring states), the transformation is called infinitesimal. For both kinds of changes (transformation) a further, very important, distinction should be made between so called *irreversible* and *reversible* changes.

Reversible and Irreversible changes: We can try to illustrate these concepts by considering a cylinder filled with a gas and fitted with a piston. Imagine the cylinder in contact with a *heat reservoir* which is nothing but a body much larger than the cylinder, kept at a constant temperature. We can imagine loading the piston with enough weights to completely balance the gas pressure. If we increase the pressure by a very small amount, the gas will quickly come to a new equilibrium position at a slightly smaller volume. This is an example of an infinitesimal transformation. Now reduce the pressure and the gas will start expanding; one can go on reducing the pressure gently so that after some large number of steps both the volume and pressure have changed substantially. This would amount to a change that is not infinitesimal.

Now imagine that there is friction between the piston and the cylinder walls. Irrespective of which way the changes are made, i.e increase of pressure or decrease of pressure, the moving piston will dissipate heat. So a sequence of changes in pressure $P \to P + \Delta P \to P$ will dissipate energy both ways, and even though the gas has been brought back to its original state, the surroundings have certainly undergone some change. When that happens, we say the change is *irreversible*. While reversible changes are always infinitesimal, infinitesimal changes can be both reversible as well as irreversible.

But for Carnot's times this would not be a good example as it presupposes that friction can lead to generation or *creation* of heat. Though admittedly correct from the point of view of modern thermodynamics, such an assertion would not be tolerated by the caloric theory. So we should characterize reversible and irreversible changes in a way that would be insensitive to the actual nature of heat. Such a characterization would be: *a reversible change, whether finite or infinitesimal, should be such that at the end of the combined operation of the original process and its exact reverse, no changes should have occurred in the surroundings.* Any process not fulfilling this will be deemed *irreversible*. Carnot indeed used such a refined notion in his seminal work.

In the specific example of the steam engine, he cited effects such as the heating of the boiler walls through conduction to be the ones that would spoil the reversibility of the changes made on the water-steam system. Clearly if the system is expanded to include not just steam and water, but also various surrounding elements including the boiler walls, the seemingly irreversible nature of changes to the subsystem of steam and water can be reconciled with reversible changes of the larger system. Precisely such nuances concerning reversibility and irreversibility also show up in the completely unconnected case of *Quantum Measurements*!

There is another aspect of irreversibility that is important to highlight; while reversible changes have necessarily to be slow (quasi-static) though the reverse is not true, i.e not every slow change is reversible, sudden changes are, as a rule, irreversible. Imagine reducing the pressure on the piston suddenly and by a large amount. The gas will go through various stages before eventually settling to a final equilibrium state. But the path from the initial state to the final is not representable as a sequence of intermediate equilibrium states. So in the, say, PV-diagram, an irreversible change will appear as a sudden jump. The conceptually cleanest characterization of irreversible changes is given in the context of the second law of thermodynamics, but in the present context that would be like putting the cart before the horse.

Walls and Constraints Very often, useful and interesting changes are such that some parameter is held fixed. For example, if we enclose gas in a box of fixed volume, only P and T are variable and because of the gas law only one of them is an independent variable. So the set of possible changes is *one-dimensional* in contrast to the full, *unconstrained* changes, which in this case are *two-dimensional*. Such changes are called *constrained* and the *constraint* in this case is $V = conct.$. As in this example, it is the walls that enforce the constraint, Callen picturesquely calls all constraints as arising due to *Walls* even though literally that may not be the case. Changes that maintain volume are called *isochoric*. Likewise, we can think of changes under constant pressure, called *isobaric*. Changes at the same temperature are called *isothermal*. Systems can also be completely thermally insulated from their surroundings and changes are then called *adiabatic* (care should be taken not to confuse this word with what is used in classical mechanics). Such changes are also called *isentropic*, i.e the constraint being constant entropy, but we have to wait till we have discussed the second law of thermodynamics for its justification. Lastly, it is possible to consider transformations that do not change the number of moles. In what follows, we shall focus only on such changes. We shall consider changes of molar concentrations while dealing with *phase equilibria*.

1.3.3 Some examples

We now present some examples, based on the ideal gas law, to illustrate the concepts discussed above. Let us start with *reversible isochoric* processes. Then the only independent variable for a simple single-component system is either P or T. Changing one changes the other. An observable associated with such changes is the *pressure coefficient* defined as $\beta_P = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$. For one mole of an ideal gas this can easily be worked out using the ideal gas law to be $\frac{1}{T}$. At close to freezing point of water this is close to $\frac{1}{273}$, the expansion coefficient used in gas thermometry.

Likewise, if we consider *reversible isobaric* processes, i.e processes under constant pressure, the independent variables are now V and T. An observable associated with such changes is the *expansion coefficient* defined by $\beta_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. It again follows from ideal gas law that this is also $\frac{1}{T}$, same as the pressure coefficient.

The observable associated with *reversible isothermal* processes is the fractional change of volume per unit change of pressure, i.e $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. It is defined with a negative sign as the volume is expected to *decrease* with increased pressure. Called the *isothermal compressibility* and denoted by κ_T, for ideal gases it equals $1/P$, as can easily be checked.

An example of an *irreversible isothermal process* is the mixing of two samples of a gas at the same temperature but each sample having different volume and different mass. Likewise, an example of an *irreversible isobaric process* is the mixing of two samples of gas at the same pressure but different temperatures. The last two examples bring out yet another aspect of irreversibility, namely a process is irreversible if it can proceed *spontaneously* but not its reverse.

Actually, there are relationships between quantities characterizing these different constrained processes. That follows from the *triple product rule* of partial derivatives:

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \tag{1.18}$$

On using the other very important property of partial derivatives, namely,

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1} \tag{1.19}$$

it is easy to show that

$$\frac{\beta_V}{\kappa_T} = P\beta_P \tag{1.20}$$

It is to be noted that these relations are valid for all thermodynamic systems whether they are solids, liquids, or gases. Among gases they hold for ideal as well as non-ideal gases. It is the existence of such very general relationships that makes thermodynamics so powerful. For example, knowing β_V, β_P would immediately determine κ_T without a need for its independent determination.

Example 1.4: Work by ideal gases

Calculate the work done by an ideal gas for i) an isothermal expansion from volume V_1 to V_2 at T; ii) an isothermal rarefaction from pressure P_1 to pressure P_2 at T; iii) from volume V_1 to V_2 during an isobaric process at P; iv) from temperature T_1 to T_2 during an isobaric process at P, and finally, v) from volume V_1 to V_2 during an adiabatic process.

For the ideal gas $PV = nRT$ where n is the number of moles present. The infinitesimal work done by the system is PdV, and the total work done is the integral of this along the path describing the process. Without specifying a path, it is meaningless to talk of the work done as the latter is path-dependent.

i) For isothermal processes T is constant. Since the question specifies the changes in volume, pressure P is eliminated in favor of V according to P=nRT/V. This gives the work done in going from V_1 to V_2 to be $W = \int nRT(dV/V)$ to be $nRT\ln(V_2/V_1)$. ii) In calculating the work done in this case, we should eliminate the volume in favor of pressure. This leads to $dW = -nRTdP/P$ and the total work done is $W = -nRT\ln(P_2/P_1)$. It should be recognized that this is the same expression as in i) but expressed in terms of the pressures. iii) It is trivial to find out the work done in this case as P remains constant, i.e $W = P(V_2 - V_1)$. iv) Now we eliminate V in terms of T to get dW=nRdT, therefore the work done is $W = nR(T_2 - T_1)$. v) In this case the adiabatic relation gives $PV^\gamma = c$, where the constant is determined by the initial pressure and volume. Straightforward integration yields $W = c(V_2^{1-\gamma} - V_1^{1-\gamma})/(1-\gamma)$.

Example 1.5: Work in arbitrary process

Show that the work done by a gas under arbitrary changes of temperature and pressure can be determined in terms of the coefficient of volume expansion α and the isothermal compressibility κ_T. As a corollary show that for isochoric (constant volume) processes $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\kappa_T}{\alpha}$. Verify this for an ideal gas.

The work done is always given by PdV. V can always be taken to be a function of T and P. Hence under arbitrary changes of T and P,

$$đW = PdV(T,P) = P(\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP) = P(V\alpha dT - V\kappa_T dP) = PV(\alpha dT - \kappa_T dP) \tag{1.21}$$

Thus knowing the coefficient of volume expansion α and the isothermal compressibility κ_T, one can always determine the work done under arbitrary changes dT and dP.

For isochoric processes $dV = 0$ and hence it follows from the above that $\left(\frac{\partial P}{\partial T}\right)_V = \alpha/\kappa_T$. For an ideal gas, it is easily seen that $\alpha = 1/T$, $\kappa_T = 1/P$ and

$$\left(\frac{\partial P}{\partial T}\right)_V = nR/V = P/T.$$

1.4 Sadi Carnot and the motive power of heat

Now we give a detailed account of Carnot's seminal work *Reflexions sur la Puissance Motrice du Feu* published in 1824, a clear three decades ahead of the formulation of the first and second laws of thermodynamics. Fortunately, the English translation *Reflections on the Motive Power of Heat* is available [5], making accessible to the English speaking world this great treasure of science, which, unfortunately, was ignored and antiquated even before its greatness was understood and appreciated. Its greatness was revealed to the world of science largely due to William Thomson (Lord Kelvin)'s epoch-making paper *Account of Carnot's Theory* which appeared in 1849 [71], nearly a quarter of century after Carnot's work was published. It is remarkable that Thomson himself was a young man at the time, having just embarked on his scientific career. The account given here is based both on the original work as well as Kelvin's paper.

Carnot's style of presentation would clearly be found cumbersome and confusing by the modern reader. It hardly has any equations, and almost all the chief results, of which there really are very many, are derived in a verbose and descriptive manner. Lord Kelvin's account is decidedly more modern both in its perspective, as well as in its presentation. It does make use of equations as well as of calculus. It gives a *mathematically precise* meaning to Carnot's axioms as well as his results. As a result of this clarity, Kelvin is able to show that Carnot's theory contains even more remarkable results like what has come to be known as the *Clapeyron Equation*. But even Kelvin's account may be found somewhat verbose. In this book, the author has given a *succinct* mathematical theory which covers all the principal conclusions of both Carnot and Kelvin. It also points out very clearly the experimental data that would have been acid tests for the Caloric theory, an objective that was at the heart of Carnot's work.

Carnot makes the *Caloric Theory* the cornerstone of his analysis, and says about the former:*'....This fact has never been called in question. It was first admitted without reflection, and verified afterwards in many cases with the calorimeter. To deny it would be to overthrow the whole theory of heat to which it serves as a basis. For the rest, we may say in passing, the main principles on which the theory of heat rests require the most careful examination. Many experimental facts appear almost inexplicable in the present state of this theory.* Nevertheless, he expresses his disquiet about this theory quite clearly in the course of his thesis. In fact, to quote him verbatim, *The fundamental law that we propose to confirm seems to us to require, however, in order to be placed beyond doubt, new verifications. It is based upon the theory of heat as it is understood today, and it should be said that this foundation does not appear to be of unquestionable solidity. New experiments alone can decide the question.*

The student of modern science may then wonder the usefulness or the need for going into details of a work based on what is now known to be incorrect, namely, the *caloric* theory. The answer is that even such a student would be amazed to find how many deep truths Carnot uncovered, based on wrong premises, that have nevertheless survived the later developments. It is indeed a valuable lesson on how scientific theories are to be assessed. If one had concentrated only on these highly non-trivial aspects, one may well have come to the conclusion, even to this date, that caloric theory may after all be right!

The other important lesson that such a student would learn from Carnot's work is the precision with which scientific questions can be formulated, and the objective way in which they can be answered. He introduced techniques of scientific enquiry which were very original then, and are novel even now! His focus was not so much on any actually practicable engine; rather, it was on narrowing in on the essentials of an ideal engine, conceivable in the simplest way, unencumbered by needless complications. It was a precursor *par execellence* to the later day *gedanken experiments*. In its simplicity and range of applicability, its closest intellectual equivalent is the *Turing Machine* of *Computer Science*. Finally, Carnot's work is a testimony to the true spirit of enquiry, honestly raising doubts about one's own work and demonstrating unswerving faith in experiments as the only arbiters of scientific truth. In fact, the author believes that one's grasp of thermodynamics in particular, and science in general, will be significantly enriched through an understanding of Carnot's work.

Before proceeding to a description of his work, it is worth making note of the milestones in the subject that were already known at the time of Carnot. The gas laws of Boyle-Mariotte, Charles-Gay Lussac, and Dalton were firmly established. Specific heat measurements by Clement and Desormes, as well as by Delaroche and Berard were used by him as important experimental inputs in his analysis. The fact that *sudden* compression of gases heats them up and equally, sudden rarefaction cools them was known to him, and quantitative details provided by Poisson were used in his analysis. In modern terminology, this refers to the so called *adiabatic* processes. Carnot was well aware of Laplace's work on the speed of sound, which had, in a crucial way, corrected the earlier calculations of Newton by correctly incorporating the adiabatic changes [35].

Carnot's objectives: His main objective was to investigate the *motive power* of heat. In modern usage, this means the ability of heat to provide mechanical work. The first important step in this direction was his recognition that the effects of heat can be manifold, like generation of electrical currents, chemical reactions, volume changes etc., and that to lay the foundations of a particular effect of heat, it is necessary to *imagine* phenomena where all other effects are absent. This is so that the relation between cause (in this case heat), and the effect (in this case mechanical work), may be arrived at through certain *simple* operations.

Therefore he focuses on systems where the sole effect of heat is in producing mechanical work. In particular, where the mechanical effects arise out of increases and decreases in volumes under varying conditions of temperatures and pressures. The two precise questions Carnot sets out to answer are:

(i)*What is the precise nature of the thermal agency which produces mechanical work and nothing else?*

(ii)*What is the amount of thermal agency needed to produce a given amount of work?*

With respect to the second question, he further raises the issue of whether there is any limit to the amount of work produced by a given amount of the *thermal agency*.

Cycles Carnot argued that as thermal agency not only produces work, but also alters the *state* of the system, it is in general not possible to *disentangle* the two aspects of heat from each other. For example, when we heat a gas at constant temperature, say, the gas expands leading to a change of state (to a new density) and at the same time work is performed by the expanding gas against the pressure. To circumvent this, Carnot envisages a *sequence of operations* that brings the body back to its original state. That way, the body having been returned to its original state, the work performed can be related *solely* to the thermal agency. Thus he introduced the novel notion of *cycles*. **It is very important to emphasize that in the caloric theory, the total heat absorbed or given out in a cycle has to be exactly zero**. Therefore whatever Carnot calls the *thermal agency*, it can not be the total heat absorbed.

Equivalently, *heat is also a function of the state only* and ought to be representable as a singlevalued function of the state $Q(V,T)$, $Q(T,P)$ etc. In particular dQ is a *perfect differential* and partial derivatives like $\left(\frac{\partial Q}{\partial V}\right)_T$ are perfectly meaningful mathematically. This will be in great contrast to the situation in post-Carnot development of the subject, which we shall name *the new thermodynamics*, for ease of reference.

Thermal agency according to Carnot Since in a cycle the body returns to its original state, and as per the caloric theory the amount of heat in a body depends only on its state, it follows that the total heat absorbed must necessarily be zero. What, then, is the *thermal agency* responsible for producing work at the end of a cycle, since it can not obviously be the heat absorbed?

Carnot observes, after a careful examination of various heat engines that perform work, that in all of them heat enters the engine at a higher temperature, and leaves at a lower temperature. So he asserts that it is this *fall* of the caloric from a higher temperature to a lower temperature that characterizes the thermal agency. Hence, according to Carnot, work arises *not due to an actual consumption of caloric, but to its transportation from a warm body to a colder body*. He then likens the situation to the manner in which a *water wheel* performs work. There the agency responsible for work is the water falling from a height; the work performed depends both on the *quantity of water* falling, as well as *the height* through which it falls. After the work has been performed, the amount of water is *unchanged*.

In fact, Carnot, in the light of the caloric theory, sees a perfect parallel between the water wheel and heat engines; the quantity of water of the former corresponding to heat or the 'quantity of caloric' of the latter, the height of fall of the former corresponding to the difference in the temperatures at which heat enters and leaves the engine. The caloric theory says that the amount of caloric, which is neither creatable nor destructible, is invariable, and in the water wheel the amount of water is likewise. The comparison continues to be apt even when we consider another subtle concept in Carnot's work, i.e reversibility, as we shall see soon.

Ideal Heat Engines and Reversibility The next important question raised by

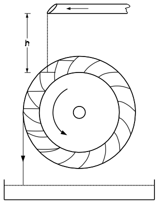

FIGURE 1.1 The Water Wheel

Carnot concerned the notion of *the most efficient* utilisation of the thermal agency in providing work. As is intuitively obvious, there should be no *wastages* of the thermal agency. The following ingenious criterion was found by Carnot: *the most efficient (perfect) engine is such that, whatever amount of mechanical effect it can derive from a certain thermal agency, if an equal amount be spent in working it backwards, an equal reverse thermal effect will be produced.* This laid the foundation for the all important notion of **reversibility** in thermodynamics, and for that matter, quite generally in physics. Recall our earlier characterization of a reversible change to be such that at the end of the combined operation of the original process and its exact reverese, no changes should have occurred in the surroundings. Clearly, Carnot's criterion ensures this.

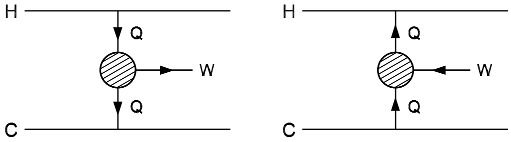

FIGURE 1.2 A heat engine and its reverse in Carnot theory.

This criterion for reversibility can in principle allow irreversible changes of a type where *less work* done in reverse could restore the original thermal agency. It would be irreversible by the earlier criterion that the original operation combined with the reverse would supply work to the surroundings at no cost of thermal agency. But such an irreversible process can not be allowed as it amounts to a *perpetual machine* which can supply *indefinite* amount of work at *no cost.* Hence the irreversibility must be such that, when run in reverse, it must take *more* work to restore the original thermal agency. However, it is clear that perfectly reversible engines permit the construction of *perpetual machines*; but they can not perform any useful work. In practice, perfect reversibility is anyway not possible to achieve, and even perpetual machines of this limited kind are not possible.

Quite obviously, the reverse process should first of all be a *physically realizable* process. Taking the water wheel as the example, clearly the reverse process, i.e of pumping water from a lower level to a higher level, is certainly physically realizable. Now if the wheel mechanism and other mechanisms involved in the water wheel are such that no work is dissipated in them, clearly the reversibility criterion of Carnot will be fulfilled. In the case of the steam engine, wasteful effects like conduction of heat through the walls of the boiler, for example, will degrade the efficiency for obtaining maximum possible work and therefore reversibility requires their absence.

Therefore, the first important criterion for a *perfect heat engine* according to Carnot is that it should be *reversible*. The criterion for reversibility enunciated by him is conceptually the *simplest* and *most straightforward*, with no hidden assumptions. For future reference, it is worth emphasizing that it is logically independent of the Second Law.

Universality of Ideal Heat Engines Just using the notion of reversibility, and that of *an ideal heat engine*, Carnot proved a far reaching result concerning the universality of all ideal heat engines. It is indeed a stroke of genius. The important question posed by Carnot was whether the maximum efficiency of ideal heat engines depended on their design or not. In other words, given *ideal* heat engines of many kinds, will some of them be more efficient than others or not?

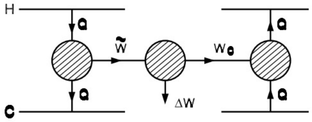

FIGURE 1.3 Universality of Carnot engines

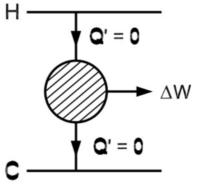

FIGURE 1.4 Universality of Carnot engines

It would appear at first sight that the answer to such a very general question will not be easy to find, but Carnot solves it in a truly ingenious manner. Suppose there are two ideal heat engines C, C' such that for the same thermal agency, i.e a certain amount of heat Q falling through the temperatures T_H, T_L with $T_H > T_L$, they deliver different amounts of work W, W' with, say, $W' > W$. Carnot considers splitting W' into $W + \Delta W$, and use W to work C *backwards*. Then, since C is ideal and hence reversible, run in reverse it will produce the same thermal agency as C but in reverse, i.e it will extract Q from T_L and deliver all of it to T_H. The net effect of running C' and the reverese of C together is then that no *net thermal agency* is used, yet there is net work ΔW produced. The cycles can be repeated *forever* producing work *indefinitely* out of *nothing*. This, Carnot argues, is *inadmissible* and will violate the very basis of physics.

Consequently, Carnot arrives at what is perhaps one of the most remarkable scientific truths, namely, that *all ideal heat engines must deliver the same amount of work for a given amount of the thermal agency*. It would still be possible to construct perpetual machines but of the kind that perform no useful work.

The true import of this *universality* of all ideal heat engines is truly mind-boggling. For any given ideal heat engine, this *efficiency*, i.e the amount of work performed for a given amount of thermal agency (it should be carefully noted that *efficiency* has a different meaning in the new thermodynamics), will naturally depend on a number of properties of the substance employed in the engine. For example, in the case of steam engines, it would involve such details as the *latent heat*, density of both the liquid and vapor etc. Yet, the combined dependence has to be such as to yield a universal efficiency. It has the further deep implication that, knowing the value of this universal efficiency for one substance, say, air, would allow determination of some property of another substance, say the latent of steam at some particular temperature, *without* the need for any experimental effort!

The only parallel one can think of is *Einstein's Principle of Equivalence* in the theory of Gravitation; there too, a *theoretical principle*, if true, would determine the behaviour of all systems under the influence of gravitation if one knew their behaviour in accelerated frames. In that sense, Carnot's universality is also a principle of equivalence, i.e the equivalence of all ideal heat engines. One may even say that it is conceptually on a firmer footing as its invalidation would lead to extraction of indefinite amount of work at no cost, and hence the end of all physics, whereas Einstein's equivalence principle could in principle have been found to be invalid experimentally!

The Carnot Cycle The cycle of reversible changes that Carnot envisaged as a means of addressing the question of efficiency of ideal heat engines consists principally of *four* stages in the following order: (i) an *isothermal dilation* at a temperature T_H, (ii) an *adiabatic dilation* leading to a cooling from T_H to $T_L < T_H$, (iii) an *isothermal compression* at T_L, and finally, (iv) an *adiabatic compression*. At the end of the fourth stage, the system is to return to its original thermodynamic state at the beginning of (i).

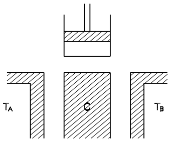

FIGURE 1.5 Schematic setup of a Carnot cycle

There is, however, a certain difficulty of an *operational* nature as the Caloric theory requires that the *heat absorbed* during the first stage must *exactly* match the *heat* *relinquished* during the third stage. In other words, while the end points B and C can be *freely* chosen, the end point D has to be so chosen that the last stage from D restores the system to its original starting point, and it is not clear how to identify such a D. To circumvent this, Kelvin, and Maxwell, suggested variants of the cycle, which we shall take up shortly.

Though Carnot discussed the cycles both for an *air engine* in which the working substance is any ideal gas, as well as the steam engine where the working substance at every stage is water and steam in equilibrium, let us discuss the cycle for the air engine first. This is because Carnot makes confusing statements about the realization of a *reversible* steam engine, even in an ideal sense. As Kelvin remarks in his commentary (he thanks Clapeyron for the clarification), there are no such difficulties and even for the steam engine, the same sequence of steps can be followed. The only thing to be kept in mind is that at all stages the temperature of the water equals the temperature of vapor.

Carnot overcomes the operational difficulties (i.e of ensuring that the heat absorbed during (i) exactly matches the heat relinquished during (iii)) as follows (see next figure): start with the system at $A'(P',V',T_H$ and let it, under isothermal expansion, go to B(P_B,V_B,T_H); then let (ii) be the adiabatic process taking B to *any* C$((P_C,V_C,T_L))$ such that C is at temperature T_L; in the next step, let (iii) isothermally take C to *any* state D$((P_D,V_D,T_L))$; and let the adiabatic process (iv) take D to A$((P_A,V_A,T_H))$ which is *at the same temperature* as the starting temperature T_H. The operational difficulty now manifests itself in that A need not necessarily be the same state as A', though both of them are at the same T_H. But the point of Carnot is that an isothermal dilation starting from A *has to* reach A', and from then on simply retrace the earlier path $A'B$. Now to get the Carnot cycle as prescribed earlier, all one has to do is identify the entire path $AA'B$ with the stage (i). Since no heat enters or leaves the system through the phases (ii) and (iv), it follows that the heat absorbed during (i) has to necessarily match the heat given out during (iii).

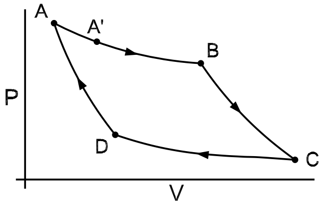

FIGURE 1.6 Construction of a Carnot cycle.

Carnot had also explicitly characterized stage (iii) to be such that it gives out all the heat the system had absorbed during (i). Kelvin points out that spelled that way, this is the only part of the specification of the cycle that is explictly sensitive to the correctness of the Caloric theory. Kelvin sought to free the description from this by requiring the end point D of stage (iii) to be such that the fourth stage takes it to the starting state of (i). Nevertheless, this does not solve the operational problem of locating such an end point. Maxwell's prescription, which is completely operational, was to start from *some* B at T_H, take it to *some* C at T_L via an adiabatic dilation, take the system from C to *any* D, also at T_L, through an isothermal dilation, take D to *some* A, as long as it is at T_H, and finally an isothermal dilation from A *has to* take it to B. It should be noted that this is pretty much the same strategy that Carnot also advocates.

The cycle for an ideal steam engine can also follow the same four stages with the important difference from gas engines being in the fact that isothermal trajectories are also *isobaric*, i.e at constant pressure. This is because the vapor pressure of *saturated vapor* depends only on the temperature. This fact, as beautifully analyzed by Clapeyron [6] , actually allows the universal Carnot efficiency to be evaluated entirely in terms of physically observable properties of the water-steam system, as will be discussed shortly.

The cycles are shown for the steam engine, as well as the gas engine in the next figure. For both of them, ABC is the expansion phase and CDA the contraction phase. A part of both of these is isothermal (AB,CD), and the other adiabatic (BC,DA). During the isothermal phases, for a given volume, the pressure during the expansion(say, at P_2) is always higher than the pressure during contraction (at Q_2). No such easy comparison is available during the adiabatic phases. By drawing the verticals P_1Q_1, P_3Q_3 it is seen that at a given volume, the pressure during the expansion is *always* higher than the pressure during contraction, as shown in the next figure.

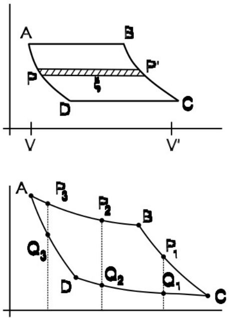

FIGURE 1.7 Carnot cycles for air and steam engines.

Hence the mechanical work done *by the system* during expansion is greater than the work done *on the system* during contraction. This way, Carnot concludes that *net work* is done by the system at the end of the cycle. Kelvin uses the graphical method to show that the work done is the same as the *area* of the curve ABCDA. The graphical methods are originally due to Clapeyron. For the modern student, that the area in the PV-diagram represents the work is a straightforward consequence of calculus, but in the beginnings even this was a novel way of looking at things.

Carnot's style of analysis As already mentioned, Carnot hardly made use of equations in his analysis, which were mostly verbal, augmented at most by simple arithmetical manipulations. Nevertheless, he made so many far reaching conclusions with remarkable precision. We shall demonstrate this by a finer mathematical analysis whose conclusions, as shown, coincided with his assertions made verbatim. But, to the modern reader, following Carnot's logic, though impeccable, would indeed be tiresome. We illustrate this by his analysis of the relationship between *specific heats of ideal gases*, as an example.

First of all, he uses the Gay-Lussac law to argue that when a given mass of a gas is heated *at constant pressure* from $0\,^{\circ}\mathrm{C}$ to $1\,^{\circ}\mathrm{C}$, the *fractional increase* in its volume is the *same* for all gases and equals the fraction $\frac{1}{267}$(the modern value would be closer to $\frac{1}{273}$). Therefore, the gas initially at $(P, V, 0\,^{\circ}\mathrm{C})$ would go to $(P, V + \frac{V}{267}, 1\,^{\circ}\mathrm{C})$ the difference in heat between these two states is by definition the *specific heat at constant pressure* (for the given mass). He also uses the *experimental data* of Poisson that under an *adiabatic compression* which raises the temperature of air by $1\,^{\circ}\mathrm{C}$, its volume decreases by a factor of $\frac{1}{116}$. Therefore, the heat content of the gas at $(P, V, 0\,^{\circ}\mathrm{C})$ and at $(P', V - \frac{V}{116}, 1\,^{\circ}\mathrm{C})$ are the same (here P' is the pressure the gas would have at $1\,^{\circ}\mathrm{C}$ when its volume is $V - \frac{V}{116}$). On the other hand, if the gas had been heated at *constant volume*, the heat required to raise the temperature by $1\,^{\circ}\mathrm{C}$ is, by definition, *the specific heat at constant volume* (again for the given mass). Hence, the specific heat at constant volume is *also* the difference in heat between the states $(P'', V, 1\,^{\circ}\mathrm{C})$ and $(P', V - \frac{V}{116}, 1\,^{\circ}\mathrm{C})$. Now these two states are at the *same* temperature but at *different volumes.* Carnot observes that the difference in their heat must be *proportional* to the difference in the volume $\frac{V}{116}$. On the other hand, by similar reasoning, the specific heat at constant pressure will equal the difference in heat between the states $(P', V - \frac{V}{116}, 1\,^{\circ}\mathrm{C})$ and $(P, V + \frac{V}{267}, 1\,^{\circ}\mathrm{C})$; these are also at the same temperature, and therefore, the difference in their heat must also be proportional to the difference in their volume, which is now $\frac{V}{116} + \frac{V}{267}$. It should be emphasized that the proportionality factor is the *same* as before. Let us call it X, for ease of reference.

From this rather verbose analysis, he rightly concludes that the ratio of the specific heat at constant pressure to the specific heat at constant volume is $1 + \frac{116}{267}$, i.e the constant pressure specific heat is always greater than the constant volume specific heat. This is usually attributed to *First Law*, but Carnot's analysis shows that it is much more general. What is even more striking is his conclusion about the *difference* in these two specific heats. By the reasoning given above, this difference must be $X\,\frac{V}{267}$. While the number $\frac{1}{116}$ was for air only, the number $\frac{1}{267}$, by Gay-Lussac law, is the *same* for all ideal gases. Thus, the difference in the specific heats is completely *insensitive* to the details of the individual gases. In fact, a little introspection shows that Carnot need not have used Poisson's data at all!

In the next step of the reasoning, too, Carnot displays absolute brilliance. He considers two ideal heat engines working with *different volumes* and just by using some properties of the ideal gas equation such as that for a given fractional change of pressure at the same temperature produces the same fractional change of volume etc., he demonstrates that $X \cdot V$ is the *same function of temperature* for all gases. Thus, the difference in the specific heat at constant pressure and the specific heat at constant volume being equal to $X\,\frac{V}{267}$, *it is the same for all ideal gases* at a given temperature, and is independent of the density.

Introduction of symbolic manipulation already makes the above arguments, though correct, more *transparent*. Let us, for ease of presentation, consider *one mole* of a gas. The heating at constant pressure, leading to an increase of temperature by $1\,^{\circ}$C, and the adiabatic compression for air also leading to an elevation of the temperature by $1\,^{\circ}$C can be described by the simple equations

$$Q(P,V+\frac{V}{267},1)-Q(P,V,0)=C_P \qquad Q(P',V-\frac{V}{116},1)=Q(P,V,0) \tag{1.22}$$

The heating by one degree at constant volume is likewise described by

$$Q(P'',V,1)-Q(P,V,0)=C_V \tag{1.23}$$

It immediately follows that

$$\begin{aligned} C_V &= Q(P'',V,1)-Q(P',V\frac{115}{116},1)\approx\left(\frac{\partial Q}{\partial V}\right)_T V\frac{1}{116} \\ C_P &= Q(P,V\frac{268}{267},1)-Q(P',V\frac{115}{116},1)\approx\left(\frac{\partial Q}{\partial V}\right)_T V(\frac{1}{116}+\frac{1}{267}) \end{aligned} \tag{1.24}$$

We have symbolized Carnot's principal axiom that *heat is a state function* by using $Q(P,V,T)$. The factor X introduced earlier is precisely $\left(\frac{\partial Q}{\partial V}\right)_T$.

1.4.1 Infinitesimal and finite cycles

In the above, changes of volumes and temperatures were very small. Let us now discuss Carnot's novel, and extremely useful, concept of *infintesimal reversible cycles*. These are reversible cycles where each of the four stages is infinitesimally small. He argues that any *finite reversible cycle* can be shown to be *equivalent* to a large number of suitably chosen infinitesimal cycles. We illustrate how two Carnot cycles operating between the same two temperatures T_H, T_L can be combined into a single Carnot cycle. Consider two such cycles $A_1B_1C_1D_1A_1$ and $A_2B_2C_2D_2A_2$ as shown in the next figure, such that the state A_2 is the same as the state B_1, and D_2 the same as C_1. We can represent each cycle by the *ordered* set of its segments; for example, $A_1B_1C_1D_1A_1$ can be represented by $A_1B_1, B_1C_1, C_1D_1, D_1A_1$. A segment B_1C_1 is to be understood as the *thermodynamic reverse* of the path A_1B_1.

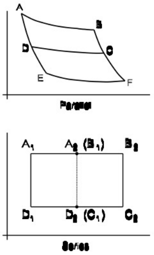

FIGURE 1.8 Composing Carnot cycles

Now the two cycles can be composed by considering the sequence of paths $A_1B_1,B_1C_1,C_1D_1,D_1A_1)+A_1B_1(A_2)+(A_2B_2,B_2C_2,C_2D_2,D_2A_2)+A_2(B_1)A_1$. On the one hand, this is the sum of the two given Carnot cycles on recognizing that $A_1B_1(A_2)$ *cancels* $A_2(B_1)A_1$ due to perfect reversibility of the ideal cycles. On the other hand, in the total path, the segment B_1C_1 cancels D_2A_2, leading to its reorganization as $A_1A_2,A_2B_2,B_2C_2,C_2D_2(C_1),C_1D_1,D_1A_1$ which is the *composite cycle*. This can be repeated for composing cycles operating between different combinations of temperatures. It is very important to notice that reversibility is the key to this composition of cycles.

The abovementioned way of composing Carnot cycles can be, by borrowing an obvious analogy from electrostatics, called a composition in *series*, and is shown as the bottom part of figure 1.8. However, one can also introduce the notion of composing Carnot cycles in *parallel*. In such an arrangement, the lower temperature of the first cycle would be the same as the higher temperature of the second cycle etc.. This is shown as the top part of the same figure.

Gas Engine Now we present the analysis of Carnot's *gas engine*, not in his original prosaic style, but in the succinct mathematical form used by Kelvin . As explained above, it suffices to analyze an infinitesimal cycle. Let (P,V,T) be the initial state and let dQ be the heat absorbed during the first isothermal stage, and let dV be the corresponding increase in volume, so that the state B at the end of the first stage is (P(1-$\frac{dV}{V}$),V(1+$\frac{dV}{V}$),T). The mean pressure during stage (i) is therefore $P(1-\frac{dV}{2V})$ and the work done during this stage is $dV\cdot P(1-\frac{dV}{2V})$. We need to calculate to second order in accuracy.

During the second stage, let $\delta P, \delta V and \delta T$ be the decrease in pressure, increase in volume, and decrease in temperature, respectively. Hence the state C is $(P(1-\frac{dV}{V})-\delta P, V(1+\frac{dv}{V})+\delta V, T-\delta T)$. It is a good approximation, as can be checked easily, to treat the corresponding variations during (iii) and (iv) to be the same as during (i) and (ii). The ideal gas law, for one mole of gas, then requires

$$-V\,\delta P + P\,\delta V = -R\,\delta T \qquad (1.25)$$

In fact, adiabaticity further restricts these variations, but as Kelvin has rightly remarked, it is not necessary to know them. The mean pressure during (iii) is therefore δP less than the mean pressure during (i), and the net work done during the isothermal stages is simply $dV\delta P$. The mean pressure during (ii) is therefore $P(1-\frac{dV}{V})-\frac{\delta P}{2}$. The mean pressure during (iv) is likewise $P\frac{dV}{V}$ *more* than that during (ii), and the net work done during the adiabatic stages is $-P\frac{dV}{V}\delta V$. The *total* work done during the cycle is, therefore, $(V\delta P - P\delta v)\frac{dV}{V}$. On using eqn.(1.25), this can be simplified as $dW = \frac{R}{V}\delta T\,dV$. Following Kelvin , this is further reexpressed as

$$dW \equiv \mu(T)\,dQ\delta T = \frac{R}{V\left(\frac{\partial Q}{\partial V}\right)_T}\,dQ\delta T \qquad (1.26)$$

This is the result that Carnot sought to find, and it expresses the *motive power* dW that the *thermal agency* $dQ\delta T$ will give rise to. According to the powerful *universality* argument of Carnot, the function $\mu(T)$ is the *same* universal function no matter how the heat engine is designed, or with what substance. For ideal gases, the above mentioned derivation yields $\mu(T) = \frac{R}{V\left(\frac{\partial Q}{\partial V}\right)_T}$.

1.5 Steam engines and the Clapeyron Equation

As already mentioned before, Carnot seems to have been under the impression that for steam engines, a fully reversible cycle can not be maintained. He based this on the premise that after the steam has condensed to water at the lower operating temperature, the water would have to be heated to be at the starting point of the cycle. It was Clapeyron, in 1834, two years after the untimely death of Carnot (he died in a cholera epidemic at the age of 36), who showed that the ideal steam engine can also be thought of as a reversible cycle with the same four stages that Carnot had given for the gas engine, provided important features of liquid-vapor equilibrium are taken into account. One of these is that in the P-V diagram for steam engines, the isotherms are at constant pressure because saturated vapor pressure depends only on temperature. The other is that water can absorb heat to become steam *without* any change of temperature. The adiabatic curves are basically the same as the P-T diagrams of coexistence. We now present Clapeyron's analysis of the motive power of steam engines. In this work, Clapeyron puts to use, in an eloquent way, his *graphical method*, which we have already discussed.

Again, let us consider only an infinitesimal cycle EFGH shown as a horizontal strip in the figure. The work done is given by the area of this strip which is, to a good approximation, the length EF multiplied by dP which is the thickness. The length EF is essentially the change in total volume of the system upon absorbing the amount of heat dQ. If $l(T)$ is the *latent heat* (in the modern sense, i.e amount of heat required to convert unit mass of water at temperature T to unit mass of steam at the same temperature; in Carnot's times the phrase *latent heat* was used in a different sense), the mass dm of water converted to steam is $dm = \frac{dQ}{l(T)}$. The increase in volume of steam is therefore $dV_{steam} = \frac{dm}{\rho_s}$, where ρ_s is the density of steam. No heat is lost to the water as neither its pressure nor temperature changes. However, there is mass loss of water, also by dm. This leads to a decrease in the volume of water by $dV_{water} = -\frac{dm}{\rho_w}$, where ρ_w is now the density of water. Both the densities depend on T. Therefore, $EF = dV = dm(v_s - v_w)$, where v_s, v_w are the *specific volumes*, i.e volume per unit mass of steam and water, respectively. Consequently, the work done during the cycle is $dW_s = EF \cdot dP = \frac{1}{l(T)}(v_s - v_w)\, dPdQ$. This can be rewritten as follows:

$$dW_s = \left\{\frac{v_s - v_w}{l(T)}\frac{dP(T)}{dT}\right\} dQdT \quad \to \mu(T) = \left\{\frac{v_s - v_w}{l(T)}\frac{dP(T)}{dT}\right\} \tag{1.27}$$

Now one can appreciate the true powers of the universality of ideal heat engines propounded by Carnot. According to it, $\mu(T)$ is the *same* function of temperature for *all* substances. The implication for steam-water coexistence can be deduced by rewriting the above equation as

$$\frac{dP(T)}{dT} = \mu(T)\frac{l(T)}{v_s - v_w} \tag{1.28}$$

This is the famous *Clapeyron Equation* and it has been obtained from the Caloric theory! The missing ingredient, however, was the function $\mu(T)$, and even Clapeyron bemoans the lack of reliable experimental data that would determine it. Regnault's careful work on steam [60], which Kelvin made use of at the time of his commentary on Carnot's work, would only start to become available in 1847, the full descriptions completed as late as 1870.

Returning to the specific heats of ideal gases, one gets

$$(C_P - C_V)(0) = \frac{R}{267\mu(0)} \tag{1.29}$$

We shall now go a step beyond Kelvin and give a completely mathematical treatment of Carnot's work.

Mathematical treatment of Carnot theory The starting point of Carnot's considerations was the *Caloric Theory*, which states that heat is a property of the system. More precisely, it states that *heat is a state function*, and mathematically this amounts to the existence of the *heat function* $Q(V,T)$. It can equally well be expressed as $Q(P,V)$ or $Q(P,T)$. As we have already seen, for ideal gases $V\left(\frac{\partial Q}{\partial V}\right)_T = \frac{R}{\mu(T)}$. The *Holy Grail* of Carnot theory is the determination of both $Q(V,T)$ and $\mu(T)$. Of course, knowing Q(V,T) for ideal gases at once gives $\mu(T)$ which holds for *all* substances. We develop the mathematical theory for ideal gases here, but it can be extended to arbitrary cases.

Let us consider specific heat at constant volume C_V (we consider one mole of the substance). By definition, the heat dQ required to raise the temperature by dT is $C_V(V,T)dT$. We leave open the possibility that the specific heats could depend on (V,T). In the caloric theory

$$C_V dT = Q(P'',V,T+dT) - Q(P,V,T) = \left(\frac{\partial Q}{\partial T}\right)_V dT \to C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{1.30}$$

But Carnot finds it more useful to understand C_V in terms of heat required to change volumes *at constant temperature*! That he does by invoking the properties under *adiabatic* changes. Let $\delta_{ad}V$ be the change in volume, under adiabatic changes, corresponding to a change $\delta_{ad}T$ in temperature. For air, considered by Carnot for which he quotes the experiments of Poisson, $\delta_{ad}V = -\frac{V}{116}$ when $\delta_{ad}T = 1\,^\circ\mathrm{C}$. The mathematical expression for adiabatic changes in the caloric theory is

$$Q(P,V,T) - Q(P',V+\delta_{ad}V,T+\delta_{ad}T) = 0 \to \left(\frac{\partial Q}{\partial V}\right)_T \delta_{ad}V + \left(\frac{\partial Q}{\partial T}\right)_V \delta_{ad}T = 0 \tag{1.31}$$

This is the same conclusion reached by Carnot, namely, *the heat absorbed at constant temperature in expanding by a small volume is the same as would be required to raise the temperature, at constant volume, by a degree by which the temperature would have increased under adiabatic compression by the same volume.* What is noteworthy is that Carnot arrives at it through only verbal manipulations!

The second important assertion by him, again proved only verbally, is that *the heat given out, at constant temperature, only depends on the fractional increase in volume and not on the increase in volume itself.* To arrive at that conclusion, he makes use of his result on the universality of ideal heat engines. In the mathematical formalism this emerges as follows:

$$dq = \left(\frac{\partial Q}{\partial V}\right)_T dV = \frac{R}{\mu(T)} \frac{dV}{V} \tag{1.32}$$

In fact, Carnot enunciates this result for *finite* changes as well (also proved verbally!): *When a gas varies in volume without change of temperature, the quantities of heat absorbed or liberated by this gas are in arithmetical progression, if the increments or decrements in volume are found to be in geometrical progression.* To see this in our mathematical formulation, simply integrate eqn.(1.32), to give,

$$Q_2 - Q_1 = \frac{R}{\mu(T)} \ln \frac{V_2}{V_1} \tag{1.33}$$

Though Carnot used Poisson's data for air on adiabatic changes, he could well have made that analysis more general as the law for adiabatic changes, in the form, $PV^\gamma = const.$, appears to have been known to Laplace, whose work on speed of sound is cited by Carnot. But, as can be seen now, the mathematical theory of the caloric gives the equivalent of this relation even when the specific heats are not constant.

To address this and other related issues, let us turn our attention to the specific heats within the caloric theory. One of the differential forms of the fundamental axiom of the caloric theory can be expressed as:

$$dQ = \left(\frac{\partial Q}{\partial P}\right)_V dP + \left(\frac{\partial Q}{\partial V}\right)_P dV \tag{1.34}$$

Other equivalent forms using (P,T) or (V,T) as independent variables may also be used. From the definitions $C_V = \left(\frac{\partial Q}{\partial T}\right)_P$ and $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$, it immediately follows that for ideal gases

$$C_P = \left(\frac{\partial Q}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \left(\frac{\partial Q}{\partial V}\right)_P \qquad C_V = \frac{R}{V} \left(\frac{\partial Q}{\partial P}\right)_V \tag{1.35}$$

The ratio, γ, of C_P to C_V in the caloric theory is given by

$$\gamma(V,T) = \frac{C_P(V,T)}{C_V(V,T)} = \frac{V}{P} \frac{\left(\frac{\partial Q}{\partial V}\right)_P}{\left(\frac{\partial Q}{\partial P}\right)_V} = \frac{V}{P} \left(\frac{\partial Q}{\partial V}\right)_P \left(\frac{\partial P}{\partial Q}\right)_V \tag{1.36}$$

Using the triple product rule of partial derivatives, one obtains

$$\left(\frac{\partial Q}{\partial V}\right)_P \left(\frac{\partial P}{\partial Q}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_Q \rightarrow \frac{\delta_{ad} P}{P} + \gamma(V,T) \frac{\delta_{ad} V}{V} = 0 \tag{1.37}$$

Which is incidentally the same equation for adiabatic changes in modern thermodynamics too. Therefore, this particular equation does not care what the nature of heat is.

Let us evaluate $\left(\frac{\partial Q}{\partial V}\right)_T$ for an ideal gas directly from eqn.(1.34):

$$\left(\frac{\partial Q}{\partial V}\right)_T = \left(\frac{\partial Q}{\partial V}\right)_P + \left(\frac{\partial Q}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = \frac{P}{R}C_P - \frac{P}{R}C_V \tag{1.38}$$

Combining this with the expression for $\mu(T)$, one gets the remarkable equality

$$C_P - C_V = \frac{R}{\mu(T)T} \tag{1.39}$$

This is the mathematical derivation of Carnot's result for the specific heats; and the difference can only depend on temperature, with C_P always *greater* than C_V. Carnot had concluded that if $C_P - C_V$ was a *constant*, the specific heats must have a *logarthmic* dependence on volume. In our mathematical framework, this case amounts to fixing $\mu(T)$ to be $\frac{1}{T}$ i.e hence $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{RT}{V}$, whose solution is $Q(V,T) = RT\ln V + f(T)$ with $f(T)$ being arbitrary. Therefore, $C_V(V,T) = R\ln V + f'(T)$ and $C_P(V,T) = R\ln V + f'(T) + R$. One can likewise explore the consequences of a *constant* C_V. It is easy to see that this would imply $Q(V,T) = C_V T + f(V)$, $f(V)$ being arbitrary. Then, $C_P = C_V + f'(V)\frac{R}{P}$. But $C_P - C_V$ can only be a function of T which fixes $f'(V) = \frac{A}{V}$ with A a constant. Consequently $C_P = C_V + \frac{A}{T}$.

Finally, we present the differential form of the caloric axiom for ideal gases in a form that is closest to the present day first law. For that, we take (V,T) as the independent variables:

$$dQ(V,T) = \left(\frac{\partial Q}{\partial T}\right)_V dT + \left(\frac{\partial Q}{\partial V}\right)_T dV = C_V(V,T)dT + \frac{R}{\mu(T)}\frac{dV}{V} \tag{1.40}$$

Carnot was very particular in his views about the importance of subjecting his conclusions to rigorous experimental tests. He correctly foresaw specific heat data to be the most important ones for this purpose. But the state of the art of these experiments were not fine enough, and in fact, the data of Clement and Desormes which made Carnot see some evidence for a logarthmic volume dependence were later found to be incorrect. It is undoubtedly clear that had Carnot lived to see greater precision in these experiments, he would have been the first to abandon the caloric theory, and perhaps the first to have formulated the first and second laws of thermodynamics! After all, the important ideas of Carnot and Clapeyron, in the hands of Clausius, paved the way for these developments. However, despite his great contributions, particularly the concepts of reversible cycles, universality of efficiencies, and of maximum of attainable efficiencies, it can not be said that he knew of even the broad contours of the first and second laws as understood today. For a critical assessment, the reader is referred to [23], and to [65] for a different view.

1.6 Problems

Problem 1.1 Consider three gases with $(P_1, V_1), (P_2, V_2)$ and (P_3, V_3). It is found that when the first two are in equilibrium the following condition is satisfied: $P_1V_1 = (P_2 + a/V_2^2)(V_2 - b)$, while the equation satisfied when the first and the last are in equilibrium is $P_3(V_3 - c) = P_1V_1\, e^{-d/V_3P_1V_1}$. Find the respective equations of state and identify them.

Problem 1.2 At very high temperatures the emissivity of a blackbody varying as aT^4, where T is in absolute scale, is used for thermometry. Devise both a uniform and a suitable non-uniform scale thermometer based on this. Which of the non-uniform scales will agree best with the absolute scale?

Problem 1.3 Show that constant volume thermometers using an ideal gas as well as a van der Waals gas both yield the same temperature scale when uniform scales are adopted. What is the relation of this common scale to the absolute scale? Does this happen with constant pressure thermometers using the same materials?

Problem 1.4 Thermocouples are bi-metallic junctions where a voltage difference arises as a function of temperature. A thermometer is to be built out of a thermocouple whose voltage varies linearly from 0 mV to 50 mV as the temperature is varied from $0\,^\circ$C to $400\,^\circ$C. What is the temperature of the device when the output voltage is 10 mV?

Problem 1.5 Two thermometers are constructed with uniform scales, one of which is based on a metal whose resistance varies with T as $R(T) = R_0(1 + aT + bT^2)$, and the other based on a thermocouple whose voltage varies as $V(T) = V_0(1 + cT^2 + dT^3)$. Determine the temperatures T_1, T_2 on them in terms of T. Find the values of T at which they differ most from the absolute scale. Find T where they differ from each other maximally.

Problem 1.6 It is believed that since birth radiactivity alone was responsible for raising the internal temperature of earth by at least 2500 K. If the average coefficient of volume expansion of the internal part of earth is roughly $3.0 \cdot 10^{-5} K^{-1}$, estimate by how much the radius of earth has increased since formation.

Problem 1.7 A mercury in glass thermometer is such that the change of area A of the capillary with temperature is negligible. The coefficients of volume expansion of mercury and glass are respectively α_m and α_g. If the volume of mercury that just fills the bulb at $0\,^\circ$C is V, show that the length of the mercury column in the capillary at t$\,^\circ$C is given by $L(t) = (V/A)(\alpha_m - \Delta 3, 1/3)$.

Problem 1.8 Calculate the work done by one mole of gas in expanding from V_1 to V_2 a) isothermally, and b) isobarically for i) ideal gas, ii) a van der Waals gas, and iii) a gas obeying the Clausius equation.

Problem 1.9 Calculate the net work done when one mole of an ideal gas is heated at constant volume till its temperature is tripled, then cooled at constant pressure to the original temperature, and finally expanded isothermally to the initial state.

Problem 1.10 Repeat the above problem when the gas obeys the van der Waals equation of state.

Problem 1.11 Calculate the work done in isothermally compressing the rubber band of problem 4.8 from L_0 to $L_0/2$.

Problem 1.12 The molar specific heat at constant volume of a substance is experimentally determined to be $\frac{3R}{2}$. What, according to Carnot theory, is its Clapeyron equation?

2 First Law—The $E = Mc^2$ of Thermodynamics

There is a tendency, particularly among physicists, to view *the first law of thermodynamics* as merely a consequence of *the energy conservation principle* of mechanics. That is to some extent a valid perspective today, when *atomism* has been firmly established and when thermodynamics is seen as the *effective* description of a very large number of these *microscopic constituents* in terms of a very few macroscopic *thermodynamic degrees of freedom.* But such a perspective would hardly have been justified at the times (middle of 19th century) when the first law was established. At that time, atomism was only a conjecture, however appealing. The true experimental vindication of atomism came only with experiments on *Brownian Motion*, immediately after Einstein's path-breaking work in 1905.

In fact what the first law achieves, in effect, is the *recognition* of a *new form of energy*, i.e *heat*, and equally importantly, establishes a *conversion factor* (the mechanical equivalent of heat) between this new form of energy and the older known forms of mechanical energy. Hence this author likens this development, in a precise scientific sense, to the *revolutionary* developments of *the Special Theory of Relativity* of Einstein, where too a new form of energy was recognized, i.e *mass*, and furthermore its conversion factor to the older known forms of energy was established through the famous $E = mc^2$. Actually, the first law achieves the recognition of *two new forms* of energy, namely, *heat* and *internal energy*! We shall have more to say on this later on. Recognizing new forms of energy is where the revolution is; the rest is *evolution*!

Once a new form of energy has been recognized, only then a new *manifestation* of the energy conservation principle assumes meaning and significance. In $E = mc^2$ such a manifestation takes, among other things, the dramatic form of *nuclear energy*, with enormous impact (of both positive and negative types) for science and society. It can be said, without any exaggeration, that the impact of first law on science and society is no less than that of $E = mc^2$. It is clear that without the establishment of a conversion factor, no *quantitative* expression of this manifestation would have been possible. In this chapter we describe in detail the makings of this revolution.

2.1 The fall of the caloric

Doubts about the correctness of the caloric theory had come to many minds. But most of these remained only as opinions, not at a level to be taken seriously as scientific *hypothesis*. The earliest important development is undoubtedly due to Benjamin Thomson (1753-1814), also known as Count Rumford. He passed away nearly a *decade* before Carnot published his *Reflections*.

As a *cannoneer* for Bavaria, he had noticed that vast amounts of heat would be generated while boring the cannon barrels. While this in itself may not be in contradiction with the caloric theory, what Rumford found was that heat could be extracted on an almost *continuous* basis, as long as the boring went on. This fact would certainly cast some doubts on the caloric theory, and made Rumford suspect that the heat output was actually *correlated* with the work done in boring. He conjectured that heat was *motion*. What made his ideas scientific was that he attempted to *quantify* this relationship, i.e he tried to measure the *conversion factor*.

One of the first such *quantitative* results he obtained was that two horses employed for 2 hrs 30 mins. would generate enough heat to melt 26.6 pounds of ice at 180 ° F (temperature scale used was *Fahrenheit*). Joule later argued that this represented 1034 foot-pounds of mechanical work based on Watt's claim that the power delivered by a horse was equivalent to 33,000 foot-pound. Horsepower or Hp is still used as a unit of power. Watt was also among the early doubters of the caloric. He expressed doubts, in the context of the steam engine, that all the heat absorbed at the boiler would pass to the condenser. But again, this was only a doubt expressed and not a serious critique of the caloric.

For that matter, even Rumford's demonstration, which today would be clearly taken as evidence that work can be converted to heat, can not, in any systematic manner, be shown to contradict the caloric. This, as carefully analyzed by Kelvin in his commentary on Carnot's work, would require it to be shown beyond any doubt that the caloric did not flow from other parts of the cannon, or that it did not flow into the cannon from outside. Kelvin in fact analyzes Joule's experiments on thermoelectricity wherein he had observed heating of a conductor upon passage of electricity. He points out that even there, careful experiments would be necessary to rule out cooling in other parts, in which case the heat observed would merely be consequences of the *redistribution* of the caloric.

Another important observation of Rumford was that heating caused no change of weight in an object; the caloric theory would consequently require that heat as a material object should be *weightless*. This too, while not constituting a conclusive test against the caloric, raised the level of discomfort against it.

What perhaps came as a death blow to the caloric theory was the experiment of Humphrey Davy (1778-1829) in 1799 (two years after Carnot's birth!) wherein he rubbed two pieces of ice against each other whereupon both ended up melting [10]. So the heat of melting could not have come from the caloric contained in either of the ice cubes. But even this experiment has not been totally beyond reasonable doubts; as late as 1926, it has been pointed out that this experiment was not carried out in a *vacuum* [2], as has been popularized!

2.2 The path to the first law

Though many thoughts pointing to the so called *first law* can be found in the literature, the works and thoughts of *Robert Mayer, James Joule* and *Helmholtz* stand out in their relative clarity. We briefly discuss the essential thoughts of these *three musketeers of thermodynamics*. It is said that the three worked independently. The predominant theme is that of *energy conservation*, though it must be emphasized that a mere extension of this known concept in mechanics to thermodynamics can not be made that straightforwardly.

Robert Julius Mayer (1814-1878): Mayer is said to have explicitly stated that *energy is generally conserved*, and to have equally explicitly claimed that heat and mechanical energy are *interconvertible*. In a paper written in 1841, but never published in any scientific journal, Mayer said *'motion is converted into heat,'* thereby directly questioning the caloric theory.

He made his criticism of the caloric very precise and succint by his declaration, in a brochure in 1845 (according to Ingo Müller [47]), that *'the heat absorbed by the vapor is always bigger than the heat released during condensation. Their difference is the useful work,'* in the context of the steam engine. There could not have been a clearer assertion of the interconvertibility of heat and work, and was a clear forerunner of the events leading to both the first and second law. Nevertheless, it still amounted to only an opinion.

Mayer also came up with a way of estimating the *mechanical equivalent of heat*. He did this by *interpreting* the difference between the specific heat C_p at constant pressure and C_v the specific heat at constant volume as *the work done against the pressure of the gas*. By using data on specific heats of Delaroche and Berard, and Dulong's value for the ratio of the two specific heats, he concluded the conversion factor to be such that *'the fall of weight from 365 metres heats the same weight of water by* $1\,^\circ\mathrm{C}$. This figure was eventually refined by Joule.

We have already seen that even caloric theory predicts that C_p is larger than C_v, and that the same data of Delaroche and Berard could not rule out these specific heats from being consistent with Dulong values. So clearly Mayer's calculation is *no proof* of the incorrectness of the caloric theory, or more precisely, no proof that heat and work were interconvertible. It was only an interpretation of the specific heat data *on the premise* that heat and work are interconvertible. The caloric theory, which would deny such an interconversion, would interpret the very same data in a completely different way.

James Prescott Joule (1818-1889): Joule took the journey towards the creation of thermodynamics that much further. As already mentioned, he discovered in 1843 the thermoelectrical phenomenon whereby passage of electricity through a conductor heats up the latter [72]. The interpretation of this effect in the caloric theory is obscure at best. Even in this context Joule had begun to wonder whether the mechanical power needed to run the generator was the eventual source of the heat developed in the conductor. But Joule is best known for the very careful experiments he performed to first show that mechanical work could be converted to heat, and then for the careful measurement of the mechanical equivalent of heat. His setup was essentially comprised of falling weights turning paddles in a liquid, which would heat up the liquid through *friction*. By carefully measuring the rise in temperature of the liquid, and correlating it to the equally carefully measured heights through which the weights fell, he arrived at the following conversion factor: *the heat required to raise by* $1\,^\circ\mathrm{F}$ *one pound of water is equal and may be converted to a mechanical force which can lift 838 pounds to a vertical height of 1 foot* [47]. He refined these values through more measurements and in 1845 had given it as 772 pounds. The modern statement of this conversion factor is

$$1calorie = 4.18Joules \tag{2.1}$$

where a Joule is $1Kgm^2/s^2$. Joule too was a firm believer in the conservation of energy and that heat is the motion of particles.

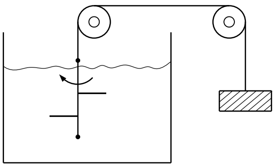

FIGURE 2.1 Joule's apparatus for mechanical equivalent of heat.

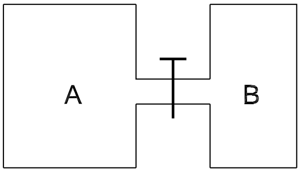

FIGURE 2.2 Joule's free expansion experiments.

Around 1845, a few years before Clausius gave the final, and complete, formulation of the first law, Joule performed an experiment of deep significance, namely, his experiment on the so called *Joule Expansion*. In the earlier versions of this experiment, performed by Joule alone, gas occupying a volume at some temperature was allowed, without any heat exchange with the environment, to expand into a region of *vacuum*, as shown in the figure. What Joule observed was that there was no change of temperature, though the volume had increased. A few years later (around 1852), Joule and Kelvin performed a *variant* of this experiment, the so called *porous plug experiment*, which showed a tiny *drop* in temperature. Gay-Lussac had performed the same experiment, even before Joule, but had not noticed the drop in temperature. Joule and Kelvin could observe the change because of the progress they had made in measuring small temperature differences.

The Joule expansion effect provides a second characterization of an ideal gas as one for which the temperature difference is strictly zero. It is very important to appreciate that this is *independent* of the *equation of state* $PV = nRT$. The significance of Joule expansion will be explained later in the context of both the first and second laws.

Herman Ludwig Ferdinand von Helmholtz (1821-1894): Helmholtz was also a firm believer of the atomistic view and of the conservation of energy. He made the very astute, and subtle, observation that at the microscopic level there is really no friction but only a *redistribution of energy*. As a consequence, he argued that *perpetuum mobile* was impossible. We have seen that Carnot had clearly stated this long ago without necessarily committing to an atomistic world view.

Though all these made contributions that were very pertinent for the formulation of the first law, none of them really came close to it. In particular, none of them even conceptualized *internal energy*, the bedrock of the first law. That task, as well as the task of giving a precise mathematical expression to the first law, was beautifully undertaken by **Rudolph Julius Emmanuel Clausius (1822-1888)**. He formulated the first law in 1850 [7, 8, 9]. It is said that **William John Rankine (1820-72)** had also given a formulation in 1850.

Clausius formulated both the first and second laws, more or less simultaneously, in 1850. This has led some to erroneously state that the origins of the first law too lay in the issues of the efficiency of heat engines. It is important to make a clear logical separation between the foundations of these two pillars of thermodynamics. The foundation of the first law lay in Clausius taking the *equivalence between heat and energy* to its logical conclusions, culminating in its precise mathematical expression. On the other hand, the second law concerned itself with the far more subtle issue of *the possible directions* for the interconvertibility between these two forms of energy. The first law says *absolutely nothing* about this.

This brief historical account would be woefully incomplete without mention of **James Clerk Maxwell (1831-1879), Josiah Willard Gibbs (1839-1903)** and **Ludwig Boltzmann (1844-1906)**. Indeed Gibbs is clearly the third of the *Thermodynamic Trinity*, after Carnot and Clausius. Working largely by himself, at a time of little tradition of theoretical physics in his country, this American scientist produced his monumental work on thermodynamics *On the equilibrium of heterogeneous substances* in 1875 [19]. This is one of the most influencial scientific works. In it, Gibbs introduced the concept of the *Chemical potential*, which, along with his *phase rule* (also in this work), revolutionized physical chemistry. It is a historical travesty that Gibbs chose to publish this in the obscure *Transactions of the Connecticut Academy*. This, along with its 'abstract style and difficult representation,' according to Ostwald, made this great work practically unknown for a long time. His contributions, in the words of A.S. Wightman, 'have survived 100 years of turbulent developments in theoretical physics.'

Gibbs also laid the foundations for *Statistical Mechanics* and made significant contributions to its development. His brilliant concept of *ensembles* has indeed changed the very complexion of this subject. His book *Elementary Principles in Statistical Mechanics* [20] is famous for its enormous impact. Einstein is said to have considered Gibbs as among the greatest men and most powerful thinkers.

Interestingly, even the beginnings of Statistical Mechanics can be traced to the works of Clausius on *kinetic theory*. His 1857 work on the diffusion of molecules greatly influenced Maxwell to undertake a major study in 1959 that culminated in his pioneering work on velocity distributions. This in turn was a major influence on Boltzmann who went on to formulate kinetic theory extensively. Kinetic theory morphosed into what is currently understood to be Statistical Mechanics. Therefore it would be fair to call Maxwell, Gibbs and Boltzmann the *Statistical Mechanics Trinity*.

2.3 The first law of thermodynamics

We shall present here the main essence of Clausius's formulation of the first law. The starting point is the *paradigmatic shift* that heat and mechanical work are interchangeable; obviously, this marks a fundamental departure from Carnot, who based his *Reflections* on the premise that heat can neither be created nor destroyed. Therefore, according to Clausius, at the end of a *reversible cycle* the net amount of heat absorbed *must equal* the net work performed, i.e $\Delta Q = \Delta W$, whereas for Carnot $\Delta Q = 0$ while $\Delta W \neq 0$.

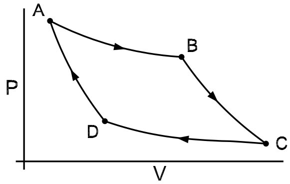

FIGURE 2.3 A Carnot cycle

Almost everything else follows just from this initial departure, which is of course a very radical departure. It is immediately obvious that *heat can not be a state function* as was the case in the caloric theory. If it were, dQ would have been a *perfect differential* and ΔQ would have been zero, as in Carnot theory. That ΔW is not zero is anyway familiar from mechanics where in general the work done around a closed path is nonzero, and additionally depends on the path. In the thermodynamic context, if the pressure P is a function only of volume (which can not be true in general), can dW be a perfect differential.

At this stage, all that can be said is that

$$đQ = dW + dU \tag{2.2}$$

where dU is a perfect differential, and therefore U is some state function. It is not even necessary at this stage for U to be nonzero. But Clausius not only showed that U has to be necessarily *nonzero*, he derived the integrability conditions for U in a physically transparent manner. The reader is referred to Ingo Müller's book [47] for more on the original papers of Clausius.

It is worth remarking at this stage that Clausius maintained the *conceptual edifice* that Carnot had created, i.e concepts of cycles and reversibility. In fact, Clausius goes to great pains to explain that he would like to keep as much as possible of the structures that Carnot had introduced. This is a great tribute to Carnot indeed. Clausius makes use of the fact, as done by Carnot and Kelvin too, that addition of heat can alter both the temperature and volume of a system

$$đQ = M(V,T)dT + N(V,T)dV \tag{2.3}$$

By definition, $M = C_V(V,T)$. Clausius then considers an infinitesimal cycle, a concept pioneered by Carnot. During the isothermal expansion let $\delta_T V$ (since the cycle is infinitesimal, the isothermal contraction in the third stage can also be taken to be the same) be the change in volume. The heat absorbed during this stage is therefore $dQ_{AB} = N(V,T)\delta_T V$. For what follows, where the final quantities of interest are *second order* in the variations, it is better to express this as $dQ_{AB} = \frac{1}{2}(N(V,T) + N(V + \delta_T V))\delta_T V$. This amounts to taking the *mean value* prescription for $N(V,T)$.

Likewise, the heat relinquished during the third stage CD is $-\frac{1}{2}(N(V + \delta_T V + \delta_Q V, T - \delta_Q T) + N(V + \delta_Q V, T - \delta_Q T))\delta_Q V$. We have denoted the changes during the isothermal stages by δ_T and those during the adiabatic stages by δ_Q. The stages BC and DA being adiabatic, $dQ_{BC} = dQ_{DA} = 0$. Writing these conditions out explicitly, the expressions for the work done during the four stages can likewise be written down, and the total work done during the cycle is given by

$$\Delta W = \left(\frac{\partial P}{\partial T}\right)_V \delta_Q T \delta_T V \tag{2.4}$$

The total heat absorbed during the isothermal stages can be seen to be

$$\delta Q = \left(\frac{\partial N}{\partial T}\right)_V \delta_Q T \delta_T V - \left(\frac{\partial N}{\partial V}\right)_T \delta_T V \delta_Q V \tag{2.5}$$

This can be simplified on noticing that the adiabaticity condition $dQ_{BC} + dQ_{DA} = 0$ becomes

$$\left(\frac{\partial C_V}{\partial V}\right)_T \delta_Q T \delta_T V = \left(\frac{\partial N}{\partial V}\right)_T \delta_Q V \delta_T V \tag{2.6}$$

The final result for the net heat absorbed during the cycle is, therefore,

$$\Delta Q = \left\{\left(\frac{\partial N}{\partial V}\right)_T - \left(\frac{\partial C_V}{\partial V}\right)_T\right\} \delta_T V \delta_Q T \tag{2.7}$$

There are some features of this calculation that are worth emphasizing; firstly, all quadratic variations of the type $(\delta_Y X)^2$, where X, Y stand for (V,T) and (Q,T) respectively, vanish identically. This is the advantage of using the mean value method. Secondly, a naive estimate for the work done may have looked like $dPdV$, but the calculation shows the need for a more careful treatment which shows the work done to be as given by eqn.(2.4).

Equating ΔQ with ΔW as per the new paradigm, and in complete contradiction of the caloric view point, one gets

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial (N - P)}{\partial T}\right)_V \tag{2.8}$$

Clausius interpreted this as an *integrability condition* for the *perfect differential dU* where

$$dU(V,T) = C_V(V,T)dT + (N(V,T) - P(V,T))dV \tag{2.9}$$

culminating in the mathematical formulation of the *first law*:

$$đQ = dU + PdV \tag{2.10}$$

In this demonstration the work done was purely *mechanical*, but empirically it is known that heat can manifest in other forms of energy like electrical work for example. So it is natural to generalize the above equation to

$$đQ = dU + dW \tag{2.11}$$

which shall henceforth be taken as *the first law of thermodynamics*. Several comments are in order at this stage. On rather general grounds, Clausius has demonstrated the existence of a hitherto *unknown* state function U. That it is not identically zero is guaranteed by something as general as a nonvanishing C_V. In contrast, in the caloric theory a nonvanishing C_V did not imply the existence of such a state function. There, the only state function was the heat Q.

So the most important consequence of the interconvertibility of heat and work is this new state function. Kelvin named it *internal energy*. That name suggests itself from the new perspective of the equivalence of heat and energy. But it is indeed hard to immediately connect this new notion of internal energy to other known forms of energy like, for instance, mechanical energy. The fact that today we identify the internal energy with the energy of the atomic constituents of matter should not be brought to have any bearing in this purely thermodynamic context. In fact, Sommerfeld takes the view that the existence of internal energy should be viewed *axiomatically* without any attempt to link it to the concept of energy in mechanics, and calls this *the first part* of the first law. Once its existence is given, the power of thermodynamics lies in extracting many deep truths without ever bothering further about the *nature* of internal energy.

2.4 Some applications of the first law

We now consider various applications of the first law. Processes where some quantities are held *fixed* occur frequently in the description of a variety of circumstances. For example, many processes take place where the pressure is fixed to be that of the atmosphere. These are *constant-pressure* processes, also called *isobaric*. Likewise processes taking place at some given temperature are also common. They are called *isothermal*.

In the description of the atmosphere, a very important process is where a packet of air is transported through, say, convection. Hardly much heat is transferred to the packet during the course of its transport. This is an example of an *adiabatic* process. In this particular instance, as the rate of heat transfer is *extremely slow*, the name *adiabatic* here may remind one of a similar name in mechanics referring to *slowly varying* parameters. But in thermodynamics, the word *adiabatic* simply means transformations with no exchange of heat. For example, quickly opening a valve controlling a pressurised gas and reclosing it will still be an adiabatic process, though happening very fast. The reason is that things happen so fast that no appreciable heat transfer takes place. Of course, whenever something is happening very fast, something else will be happening very slow!

2.4.1 Internal energy of ideal gases

Let us first discuss a very important implication of first law for ideal gases. In section 2.2 we discussed Joule's experiment on *free expansion* of gases. In particular, it was noted there that for ideal gases the temperature remained the same for adiabatic changes when no work was done during expansion. In other words, when $dQ = dW = 0$, $dT = 0$ for ideal gases. But by first law, when both dQ and dW vanish, so must dU. In other words

$$0 = dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{2.12}$$

That is, for ideal gases $U(T)$ is a function only of temperature T. It should, however, be stressed that $dU = 0$ for free expansion of *all* gases, even if they are not ideal. In those cases U will not be a function of T alone, and changes in volume will induce changes in T under free expansion.

2.4.2 Isochoric changes

These are constant volume processes and are indeed very familiar. All changes, for example, to a gas enclosed in a container are changes of this type. For the ideal gas, these changes are characterized by $P/T = const.$ In other words, the pressure is in direct proportion to the temperature T. For all systems

$$\text{đ}Q = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\} dV \rightarrow dQ|_V = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT \tag{2.13}$$

The specific heat C_V at constant volume is, by definition, the *heat capacity* $\frac{dQ}{dT}$ in the limit $dT \rightarrow 0$. This is one of the most important *observables* in thermodynamics. For ideal gases for which U is a function of T only, $dU = C_V(T)dT$.

2.4.3 Isobaric changes

These too must be very familiar. All changes occurring when the system is under, say, atmospheric pressure, are examples of this. For ideal gases these changes are characterized by $V/T = const.$, i.e the volume is in direct proportion to T. For ideal gases, the first law, in the light of previous remarks and the gas law $PV = RT$, can be rewritten in the form

$$\text{đ}Q = C_V(T)dT + PdV = C_V(T)dT + RdT - \frac{RT}{P}dP \tag{2.14}$$

For isobaric processes this takes the form

$$dQ = (C_V(T) + R)dT \equiv C_P(T)dT \tag{2.15}$$

The specific heat C_P follows its definition as $C_P = dQ/dT|_P$. Thus, first law leads to an extremely important result that for ideal gases

$$C_P(T) - C_V(T) = R \tag{2.16}$$

The analog of this for van der Waals gases is worked out in chapter 12.

Example 2.1: Land and Sea Breezes

The specific heat of rocks and generally of soil is roughly only a fourth of the specific heat of water. Use this to explain the phenomenon of land and sea breezes.

The amount of solar heating, determined by the amount of heat received from the sun per unit area is more or less the same both over the land and the sea. Both for liquids and solids there is no appreciable difference between C_P and C_V. During day time, the soil reaches a much higher temperature than the ocean water as the specific heat of former is less than that of the latter. It should be noted that the temperatures do not simply rise uniformly in time. Both the soil and water reradiate till they reach equilibrium (at different temperatures). Because of the higher land temperature, air over the land gets hotter and lighter. Consequently, this hot air rises to reach upper parts of the atmosphere. This creates a low pressure over the land, to fill which the cooler air over the ocean rushes towards the land. This is the cool sea breeze.

At night, when the source of heating from the sun is not there, the soil cools much faster, again owing to its much lower specific heat. The ocean, on the other hand, loses its temperature relatively slowly. This reverses the situation from what existed during the day in the sense that it's the land that is cooler than the ocean at night. Therefore, it is the air over the ocean that gets hotter and lighter(relatively speaking), rising to upper atmosphere. The air from the land rushes towards the ocean, creating the land breeze.

2.4.4 Adiabatic changes in an ideal gas

By the condition of adiabaticity, one has $dQ = 0$, and since the gas is ideal, the first law requires

$$0 = dQ = C_V(T)dT + PdV \tag{2.17}$$

Now there are a variety of ways of realizing these conditions, depending on the independent variables one chooses. Let us start with the case where these have been chosen to be (V,T). We can use the ideal gas law to eliminate P and rewrite the adiabaticity condition as

$$C_V(T)dT + \frac{RT}{V}dV = 0 \quad \rightarrow \frac{C_V(T)}{R}\frac{dT}{T} + \frac{dV}{V} = 0 \tag{2.18}$$

In cases where C_V is a constant, this equation can be integrated to give

$$VT^{\frac{C_V}{R}} = const. \tag{2.19}$$

But in general, the adiabatic changes in an ideal gas are governed by

$$Ve^{\frac{S(T)'}{R}} = const. \tag{2.20}$$

where $S(T)'$ stands for $\int \frac{C_V(T)dT}{T}$. In the next chapter we shall see that this is one of the most important state functions in thermodynamics; it is the volume independent part of the *entropy* of an ideal gas.

2.4.5 Isothermal changes

We now turn to a discussion of the implications of first law for changes under constant temperature. Most generally

$$đQ = C_V(V,T)dT + \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}dV \quad \to \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}dV \qquad (2.21)$$

For an ideal gas many simple consequences follow. Firstly, pressure is inversely proportional to volume, i.e $PV = const.$; this is nothing but Boyle's law. As we saw earlier, U for ideal gases is independent of volume. Even for the general case for which C_V depends on temperature, for isothermal changes there is no change in internal energy and the first law gives $dQ = PdV$. In this case too, the heat Q is a state function! More explicitly

$$dQ = PdV \quad \to dQ = RT\frac{dV}{V} \quad \to Q = RT\ln V \qquad (2.22)$$

Heat was a state function for isobaric changes too. Recall that the defining feature of the Caloric theory was that Q was *always* a state function. Therefore, for isothermal and isobaric processes things are indistinguishable from caloric theory. There is no real conflict with the fact that heat is path-dependent; in these examples, the paths have been fixed.

2.4.6 Heats of transformation

A very important class of processes is where there can be absorption of heat or relinquishing of heat *without* any change in temperature. Such a form of heat is called *latent heat*. From first law it is clear that some other state variable must change. Indeed, in all such cases there is a change in the *phase* of the system. Let us cite some familiar examples. Ice at 273 K can absorb 80 cal/g of heat and turn into water, also at 273 K. But the density of ice being lower than that of water, there is a change in the volume of the system. Another example is that of water at its boiling point of 373 K. It can absorb 540 cal/g of heat to turn into steam, also at 373 K. Steam being a gas, has a much lower density (hence much larger volume per unit mass) than water. The worked example 2.3 should clarify the situation.

2.4.7 Enthalpy

For isobaric changes, first law implies that

$$dQ = dU + PdV = d(U + PV) \qquad (2.23)$$

i.e heat Q becomes a state function! Introducing the state function *enthalpy* H, defined as $H = U + PV$, the above equation has the interpretation that for isobaric changes $dQ = dH$. The significance of this follows from the fact that enthalpy is always a state function irrespective of whether one is dealing with constant pressure processes or not. Therefore the enthalpy for a given state can be determined unambiguously. For isobaric processes, it becomes meaningful to talk about the *heat of transformation* as the *difference* between enthalpies. The importance of this remark lies in the fact that heat, which is in general *path-dependent* quantity, can, for isobaric processes, assume a path independent meaning.

Enthalpy and gas flows

It turns out that enthalpy is a useful quantity even when changes are not isobaric. This is illustrated by the famous *porous plug experiment* of Joule and Kelvin. In this setup gas flows from a region of pressure P_1 to a region of pressure P_2 through a *porous* plug. The entire setup is thermally insulated so that there is no inflow or outflow of heat. There is a difference to this setup from the one for Joule free expansion; in the current setup, a *steady flow* is maintained from *external* sources. Also, here the gas expands against a pressure, and net work is done.

As emphasized by Pippard [54], the setup need not even be with real walls as long as conditions of steady flow and thermal insulation are fulfilled. For example, a pocket of air moving by convection over small distances over which the variation of the gravitational potential can be neglected will also behave as described below.

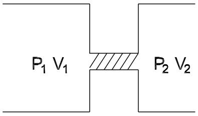

FIGURE 2.4 The porous plug experiment.

Consider the transfer of an amount of gas which occupies the volume V_1 on the left hand side, and V_2 on the right hand side. Therefore, on the left hand side of the plug the work done is P_1V_1 and on the right hand side it is -P_2V_2. Since $\Delta Q = 0$ it follows that the net change in internal energy must equal the net work done, i.e $U_2 - U_1 = P_1V_1 - P_2V_2$. But this is the same as the statement $U_1 + P_1V_1 = H_1 = U_2 + P_2V_2 = H_2$. That is, enthalpy is conserved through the flow!

It should be appreciated that the circumstance just considered is not one belonging strictly to the domain of equilibrium thermodynamics. The gas is certainly not in *mechanical equilibrium*. Nevertheless, there is steady state flow and that suffices to apply the thermodynamic notion of enthalpy.

When the pressure is variable, eqn.(2.23) changes to

$$đQ = dU + PdV = d(U + PV) - VdP = dH - VdP \tag{2.24}$$

It follows from either of them that $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ which is the precise analog of $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. For ideal gases for which C_V, and hence C_P from eqn.(2.16) are constants, it follows that $U = C_V T$ and $H = C_P T$.

Joule coefficient and Joule-Thomson coefficient

The Joule effect, i.e cooling upon free expansion, and the Joule-Kelvin effect, i.e the porous plug experiment (throttling) discussed before can be quantified through the Joule coefficient η and the Joule-Thomson coefficient μ_{JT}. In the adiabatic free expansion the internal energy U does not change but there is an increase in volume accompanied by a change in temperature (in general; for ideal gases there is no temperature change). Thus the quantity $\eta = \left(\frac{\partial T}{\partial V}\right)_U$. This coefficient is also defined as $\eta = \left(\frac{\partial T}{\partial P}\right)_U$ by some. On the other hand, in the porous plug experiment or the Joule-Kelvin process, it is the enthalpy that does not change. The relevant measure of this effect is the Joule-Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$. Both these are *irreversible* processes (see for example problem 3.2). Another important difference is that while in Joule expansion no work is performed, in the Joule-Kelvin process work has to be done on the system.

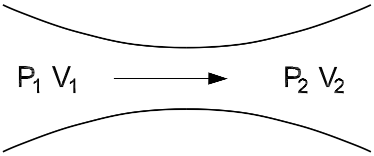

FIGURE 2.5 Enthalpy and flows.

Example 2.2: Enthalpy and flows.

Consider adiabatic gas flows. Use the Euler equation for fluid flows to show that, for an ideal gas,

$$\frac{v^2}{2} + V(\vec{r}) + H = const. \tag{2.25}$$

where H is the enthalpy, $\vec{v}$ *the flow velocity and V the external potential.*

The Euler equation is

$$\vec{\nabla}\frac{v^2}{2} = -\frac{1}{\rho}\vec{\nabla}P - \vec{\nabla}V(\vec{r}) \tag{2.26}$$

where $\vec{v}, P, \rho$ are respectively the velocity, pressure and density of the fluid. Since the flow is adiabatic, $P = c_1\rho^\gamma$, with γ the ratio C_P/C_V, and c_1 a constant. Using this

$$-\frac{1}{\rho}\vec{\nabla}P = -c_1\vec{\nabla}\frac{\gamma}{\gamma-1}\rho^{\gamma-1} = -\vec{\nabla}C_P T \tag{2.27}$$

where we also made use of the ideal gas equation $P = RT\rho$. Putting everything together, and identifying $C_P T$ with the ideal gas enthalpy, the desired result follows.

Example 2.3: Boiling of water

Consider the process of boiling, say, 10 gms of water, at its normal boiling point of 373 K and 1 atm. of pressure; the density of water can still be taken to be approximately 1 gm/cc. The density of steam at this temperature is, on the other hand, about $6.0\,10^{-4}$ *gm/cc. Work out the changes in the three quantities in the first law, i.e work done, heat added, and internal energy.*

The atmospheric pressure is $1.01\,10^5 Pa$. The volume of steam is 16660 cc. Therefore, the work done against the atmospheric pressure is $P(v_s - v_w)$, which is $\Delta W \simeq 1.01\,10^5 \cdot 16650 Pa \cdot cc$ i.e 1.67 kJ. The heat absorbed, i.e the latent heat of vaporization, is 2260 J/gm (which translates to 540 cal/gm on using the mechanical equivalent of heat). Since 10 gms of water is being boiled, the latent heat absorbed ΔQ is 22600 J or 22.6 kJ.

According to the first law, the mismatch between these two must be due to the change in internal energy of 10 gms of H_2O in passing from water at 373 K to steam at 373 K. Therefore the change in internal energy ΔU is about 20.93 kJ.

The lesson to be learned from this example is that during boiling the internal energy of a given mass of steam at the boiling point increases in comparison to the internal energy of the same mass of water at the same temperature. At an atomistic level, this means that water molecules are less bound to each other in steam than in water.

Example 2.4: The velocity of sound

Newton gave a theory of sound velocities taking the air to be at the same temperature during the propagation of the sound wave. This was in disagreement with the observed values. Laplace corrected Newton's theory by treating the changes in pressure and density adiabatically. Work out the details of both these.

The velocity of sound as given by the Newton-Laplace formula is

$$v_s^2 = \frac{dP}{d\rho} \tag{2.28}$$

where ρ is the density of the gas. To obtain Newton's expression for this, we evaluate the required derivative under isothermal conditions. The ideal gas law gives $P = RT/M\rho$, where M is the mean molecular weight of the gas. For air, it is about 28.9. Hence the velocity of sound according to Newton is

$$v_s^{Newton} = \sqrt{\frac{RT}{M}} \tag{2.29}$$

Let us evaluate this for dry air at 293 K. Using the value of the gas constant R to be 8.314 J/K, one finds v_s^{Newton} to be close to 290 m/sec. But the measured value at this temperature was more like 343 m/sec. It was this discrepancy which was resolved by Laplace, to whose treatment we now turn.

Laplace's essential argument was that over the very short time scales involved during the passage of a sound wave through a medium, the heat exchanges are minimal, and the problem of sound wave propagation has to be treated by considering the changes to the medium as adiabatic. We derived the adiabaticity conditions for an ideal gas as a relation between V and T. But for the present purposes, it is more useful to get this relation in terms of P and V, or equivalently, between P and ρ. This has been given as a problem at the end of this chapter. When the specific heats are taken to be constant, this relation is

$$P = const.\rho^{\gamma} \tag{2.30}$$

where $\gamma = C_P/C_V$ and takes the value 1.4 for air. It is then easy to show that $dP/d\rho$ for adiabatic changes is actually $\gamma P/\rho$. The velocity of sound then becomes

$$v_s^{Laplace} = \sqrt{\gamma \frac{RT}{M}} \tag{2.31}$$

This marks a substantial correction to the Newtonian value and gives for the velocity of sound through dry air at 293 K to be 343.2 m/sec, very close to the observed value!

Example 2.5: The adiabatic and isothermal atmospheres

It is a well known fact that upper parts of the atmosphere are much cooler than lower parts. Explain this on the basis of an adiabatic atmosphere. How do these considerations change if the atmosphere is considered to be isothermal instead? Show that there is a characterstic height of the atmosphere.

The physics behind the aforementioned fact is that a pocket of air on rising to the upper parts expands adiabatically and therefore cools. The process is adiabatic because over the time scales involved, no significant heat transfer takes place. The atmosphere is on the whole in hydrostatic equilibrium. Consider a thin slab of thickness dz(z is the height of the atmosphere) and unit area. The mass of the element is ρdz and the gravitational force is $-\rho dz g$ where g is the acceleration due to gravity and it is negative because it is downwards. The downward force due to pressure of gas above the slice is -(P+dP), and the upward force due to pressure of gas below the slice is P. Hydrostatic equilibrium is reached when these three forces add up to zero:

$$\frac{dP}{dz} = -g\rho \tag{2.32}$$

Therefore, the pressure of the atmosphere always decreases with height.

If the atmosphere behaves adiabatically, $P = a\rho^{\gamma}$(a is a constant). Hence the equilibrium equation, after using the ideal gas law $P = \frac{RT}{M}\rho$, can be rewritten as

$$\frac{dT}{dz} = -\frac{\gamma-1}{\gamma}\frac{gM}{R} \tag{2.33}$$

Hence for an adiabatic atmosphere, temperature decreases linearly with height. Using g= 9.8 m/s^2 along with the values of M and R given above, the rate of decrease is 9.8 K/km. Actual rate is smaller than this.

If, on the other hand, we treat the atmosphere isothermally, we have $P = (RT/M)\rho$ and the hydrostatic equilibrium condition becomes

$$\frac{dP}{dz} = -\frac{gM}{RT}P \qquad P(z) = P(z=0)\,e^{-\frac{gM}{RT}z} \tag{2.34}$$

In other words, the pressure (and hence the density) of an isothermal atmosphere falls off exponentially with height. The scale of fall-off is determined by the length scale $L = \frac{RT}{gM}$, which can be called the *height* of the atmosphere. Its numerical value is about 8.8 km! Of course, the atmosphere is far from being isothermal.

2.5 Problems

Problem 2.1 Consider the melting of 100 gms of ice at 273 K and 1 atm. of pressure. The densities of ice and water under these conditions are, respectively, 0.92 gms/cc and 1.0 gms/cc. The latent heat of fusion of ice is 80 cal/gm. Apply the first law to determine the heat absorbed, the work done, and the change in internal energy. Do you expect the internal energy per unit mass of water to be greater or lesser than that of ice, and why?

Problem 2.2 Show that the conditions for adiabatic changes of an ideal gas are governed by $\frac{dP}{P} + \gamma(T)\,\frac{dV}{V} = 0 \qquad \frac{dP}{P} - \frac{\gamma(T)}{\gamma(T)-1}\,\frac{dT}{T} = 0$, and that they can be integrated to $PV^\gamma = const.$ and $P = const.T^{\frac{\gamma}{\gamma-1}}$ when the specific heats are constant.

Problem 2.3 Show that for an atmosphere in hydrostatic equilibrium, the heat Q is a state function at each height, i.e Q(V(h),T(h),h). Also show that H+gh-Q=const. Apply this to the problem of the adiabatic atmosphere. The quantity H+gh is sometimes referred to as the *dry static energy*.

Problem 2.4 An empty container is filled adiabatically at temperature T_0 at pressure P_0 with dry air. A volume V_0 is transferred from outside. Calculate the final temperature of the air inside the container. Give a physical reasoning for the rise in temperature.

Problem 2.5 Chemists find the so called *enthalpy diagrams* very useful. These diagrams show various products of formation like H_2O from H_2 and O_2 etc. along with their enthalpies, called *enthalpy of formation*, at, say, atmospheric pressure. Draw such a diagram for H_2 and O_2 taking the enthalpy of the uncombined constituents to be 0 when enthalpy of formation is as follows:H_2O_2(-188),OH^-(-230),H_2O(vapor)(-242) and H_2O(liquid)(-285). Calculate the heat released when these are transformed into each other.

Problem 2.6 Consider a Carnot cycle operating with an ideal gas of constant specific heats C_V, C_P. The cycle starts at P_0, V_0 and goes through the following stages: an isothermal expansion to $2V_0$, a subsequent adiabatic expansion to $4V_0$, an isothermal compression to such a volume that an adiabat can connect this third state to the original state, and finally an adiabatic compression to the original state. Separately calculate the total heat given out, and the total work done during the cycle. Are they equal? Why?

Problem 2.7 In the Clement-Desormes experiment for measuring the ratio γ of specific heats for an ideal gas, one starts with the gas at some initial pressure P_1 and temperature T_1 in a container which is then allowed to adiabatically decompress to a pressure P_2 and temperature T_2 by quickly opening and closing a valve. The gas is then heated at constant volume till it reaches the original temperature T_1, but at a different pressure P_3. Show how γ can be determined from a knowledge of P_1, P_2, P_3. What fraction of the gas was lost to outside during the adiabatic decompression?

Problem 2.8 Show that any two points on the P-V plane can be connected by a combination of an isochore and an adiabat of the type PV^γ (note that the system need not be an ideal gas). If the heat Q discharged by a system during isochoric compression from P_i to P_f is given by $A(P_f - P_i)$, calculate the internal energy difference $U(P,V) - U(P_0,V_0)$ for arbitrary values of P_0, V_0, P, V(Callen)(V).

Problem 2.9 Consider the air in a room, which is not airtight, being isobarically heated to a higher temperature. If air is treated as an ideal gas, show that the total internal energy of the air within the room does not change despite the heating. Since the air escaping from the room goes to merely heat the outside and hence that amount of heat is wasted, is there still any benefit to this way of heating?

Problem 2.10 A medium size iceberg weighs about 100,000 metric tons. If the energy received from the sun is 2 cals/sq.cm in a minute, how long will it take to completely melt such an iceberg if all the solar energy incident on 1 square km is used for it? The latent heat of fusion of ice is 80 cal/g. Considering that the cross-sectional area of such icebergs is about 1000 square metres, how long will this iceberg last in its journey?

Problem 2.11 What fraction of ice will still remain after 1 Kg of ice has been supplied with 200 kJ of heat(all at 273 K)?

Problem 2.12 The specific heat of a solid substance near absolute zero has been found to vary with temperature as $C(T) = 2.0\,Te^{-3.0T}$ J/mol.K. How much heat will be needed to raise the temperature of 1 mol of this substance from 0 K to 10 K?

2.6 Suggested reading for this book in general

Though in this book the best of many sources has been distilled into one, it is nevertheless recommended that the reader consult as many different sources as possible. There are some outstanding textbooks on thermodynamics, as well as on statistical methods, but mostly books with thermodynamics as the main focus are suggested here.

1. Robert Resnick, David Halliday, and Kenneth S. Krane, *Physics, Vol. I* [61]. This is an excellent text with clear exposition and a large number of examples and problems. Highly recommended that beginners and others start with this.
2. Enrico Fermi, *Thermodynamics* [17]. This is a classic that is very clearly written and its particular speciality is the originality of presentation, and approaching problems from many different angles. It is an excellent source to get a deeper understanding of the thermodynamic potentials. It is also self-contained.

3. Max Planck, *Treatise on Thermodynamics* [57]. This is an excellent source book, with surprisingly few equations, but with plenty of insight. Planck's original works on the third law are beautifully explained here.
4. Arnold Sommerfeld, *Thermodynamics and Statistical Mechanics* [64]. Though only a small portion of the book is devoted to pure thermodynamics, this book is a must to get a clarity regarding the basic issues in thermodynamics. It also has a very good collection of problems along with their solutions in Sommerfeld's impeccable style.
5. Evelyn Guha, *Basic Thermodynamics* [22]. This short book is extremely clearly written. Whatever topics are covered, are covered well. It has a large number of very instructive worked examples, and good problems. Beginners and experts alike will find this very useful.
6. Y. V. C. Rao, *Engineering Thermodynamics Through Examples* [59]. This book illustrates many of the important concepts and results in thermodynamics. With over 750 very good worked examples, readers will benefit immensely from this source.
7. A. B. Pippard, *Classical Thermodynamics* [54]. This too is a classic and deals with a lot of subtle issues, and great attention is paid to essential details, though often in very fine print. Beginners may find this terse to read, but they should use it as often as they can.
8. L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I* [34]. In the typical Landau style, this is a great book for a deeper understanding of the subject. There are illuminating problems and worked examples. But it is hard reading at first!
9. Herbert B. Callen, *Thermodynamics and An Introduction to Thermostatistics* [3]. This is an indispensable source for a proper understanding of the logical structure of thermodynamics. This too has an extensive coverage of all the important topics. It has many problems and worked out examples. But it requires a certain mature understanding of the subject before its fine print can be adequately appreciated (and admired!)
10. M. N. Saha and B. N. Srivastava, *A Treatise on Heat* [63]. This is an old classic whose hallmark is the meticulous details that follow every discussion. This is also the place to get an accurate account of the various epoch-making experiments in thermodynamics.
11. R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* [18]. Considered as one of the authoritative sources in the subject.
12. Wolfgang Pauli, *Thermodynamics and the Kinetic Theory of Gases* [53]. This short but delightfully original account of thermodynamics is must reading. Some sections are terse but worth one's while.
13. Walther Nernst, *The New Heat Theorem* [50]. In this book, Nernst gives an extremely lucid and detailed account of the experiments and ideas that eventually led him to his postulate.
14. Dilip Kondepudi and Ilya Prigogine, *Modern Thermodynamics* [33]. This is a book with a more modern outlook on the subject, including non-equilibrium thermodynamics. It has a good coverage of the applications of thermodynamics to chemistry.
15. Joseph Kestin, *A Course in Thermodynamics* [31]. This book, apart from treating all the standard topics well, also includes a discussion of open systems.
16. Kerson Huang, *Statistical Mechanics* [26]. The main focus is on Statistical Mechanics, but has good chapters on thermodynamics too.
17. Sadi Carnot, *Reflections on the Motive Power of Heat* [5]. Though this work marked the essential beginnings of thermodynamics, my suggestion for the reader is to study it after gaining a reasonable mastery over modern thermodynamics, to avoid confusion between similar sounding concepts then and now. The English translation carries an expository article by Kelvin, which makes Carnot's ideas particularly transparent.

3 The Second and Third Laws

Soon after the first law, it became clear that while the first law, seen by many as a manifestation of the conservation law for energy when thermal phenomena were taken into account, while by some others like Sommerfeld [64] and Planck [57] as an axiomatic law recognizing new forms of energy to which an extended form of the conservation law can be applied, it still could not account for all *facts* of experience. For example, while first law could quantitatively forecast the amount of heat necessary to convert 1 gm of water at its boiling point to 1 gm of steam at the same temperature, it can not explain why 1 gm of steam does not *spontaneously* convert itself to 1 gm of water accompanied by an amount of heat (which can, however, be forecast by the first law). That the latter process does not take place is one of the facts whose explanation is beyond the first law.

Likewise, another *obvious* fact of experience, which even those untutored in ways of science would readily admit, is that heat *only flows* from a hotter body to a colder body though the reverse is in no sense contradictory to the first law. Oxygen and hydrogen can combine under the right circumstances to form water, but no one has observed water *on its own* relapsing to the original condition. Forget about something complicated as a chemical reaction, just mix hot and cold water to get water at an intermediate temperature, but has anyone witnessed the resultant water going back to the original mixture on its own? One can go on and compile a huge list of such *obvious facts*.

As beautifully explained by Planck, a common feature to these facts is that there is an element of *directionality* to them in that processes seem to proceed only one way spontaneously. To that extent, processes that would be put on par as far as the first law is concerned develop an asymmetry, making it meaningful to think of one of them rather than the other as the *initial* event.

Unlike the first law, where postulating the equivalence of heat and energy culminated in a complete description, including its succinct mathematical expression, the kind of *facts* mentioned above do not seem, at least on the surface, to have sufficiently common threads, apart from the directionality mentioned above, that could be used to give a comprehensive and quantitative description. So in essence, to paraphrase Max Planck, "*..when we pass from the considerations of the first law to that of the second, we have to deal with a new fact, and it is evident that no definition, however ingenious, although it contains no contradiction in itself, will ever permit the deduction of a new fact.*" Of course, the situation in this respect was not particularly different in the case of first law either; there too, the *new fact*, namely, that heat and energy are interconvertible, could never have been *derived*.

Rather than pretending to be able to derive the body of new facts embodying the second law, the question to be asked is whether one of these facts can be taken to be self-evident, and *all* other such facts can be derived from it consistently. Consistency would require that in fact *any* of the new facts can be taken as an axiom and all others ought to be derivable from it. But the main difficulty is in stating the *complete essence* of any one of such facts.

Historically, this was achieved most admirably through Clausius's formulation of the second law on the one hand, and Kelvin's formulation on the other. Planck and Maxwell added their formulations, which were essentially the same as these two, but stated differently, laying emphasis on one aspect rather than the other. All of them were expressions of *the impossibility* of the so called *perpetual machines of the second kind*. But in this chapter, we shall start with a very different approach; this is an extension of the perceptive remark by Sommerfeld that there are two *distinct* aspects of the second law. What he calls the first part is what can be called the *entropy axiom*, which postulates a state function that is now called *entropy*. To the author's surprise, the first part turns out to be fully equivalent to the entire second law! This will be explained in detail. As will be seen, the entropy axiom is not some arbitrarily picked postulate; for ideal gases, this is in fact a *consequence* of the first law. Before proceeding further, we take a brief, but crucial, detour into *perpetual machines*.

3.1 Perpetuum mobiles

As the name indicates, a *perpetuum mobile* is a machine that keeps running forever. For the purposes of our discussion we need to distinguish between *three* distinct types of perpetuum mobiles.

If there is a *reversible machine*, one can contemplate running a combination of this machine with its inverse. Whatever work is performed by the first in making certain thermodynamic transitions can be fed into the reverese engine, bringing the system to the starting point of the original machine. This can go on and on forever, constituting a perpetual machine that runs forever. Since all the work performed by the original machine has to be used to run the reverse machine, no *net work* can be performed by perpetual machines of this type. They do not violate any physical principles. A swinging pendulum in vacuum, without any frictional or dissipative losses, is indeed a perpetual machine of this type. While perpetual machines of this type are possible in principle, in practice it is impossible to devise a perfectly reversible machine, and no perpetual machines of this kind can ever be considered. Frictional and dissipative effects have to be strictly absent for their realization.

3.1.1 Perpetual machines of the first kind

Recall Carnot's ingenious argument that all ideal heat engines have to have the same efficiency. If not, running one of these ideal heat engines with the reverse of another ideal heat engine would lead to a net combination that would produce useful work without any thermal agency (in the caloric picture). Such a perpetuum mobile can in addition run forever, thereby producing limitless work for nothing. Carnot found that physically unacceptable as it implied lack of conservation of energy. Perpetual machines of this kind, which violate conservation of energy, will be called *perpetuum mobiles of the first kind*.

3.1.2 Perpetual machines of the second kind

Now let us consider machines that never violate the first law, and hence the conservation of energy in the extended sense described above. This still does not preclude a machine from drawing heat from a resevoir and convert it *completely* into work. Such machines will be called *perpetuum mobiles of the second kind.* If they existed, the almost limitless heat reservoirs available in the universe can be used to run such machines practically forever, producing work for 'free' so to say. Though such machines do not violate the first law, or equivalently, the conservation of energy, their existence certainly seems very implausible. Furthermore, combining such a machine with a 'normal' machine like a refrigerator(more on them later) would produce a situation where heat can flow from a colder body to a hotter body without expending any work. That too sounds very odd as in real life no such possibility has ever been observed!

Let us sharpen this notion by pointing out a few cases that may *superficially* appear to be examples of this kind of perpetual machine. Firstly, in any reversible cycle, first law demands $\Delta W = \Delta Q$, and it may appear that ΔQ has been completely converted to work. But closer examination reveals that not all of ΔQ has been extracted from a *single* reservoir. In fact, the heat drawn from the reservoir at a higher temperature has not been *fully* converted to work, and part of it has been *wasted* (from the perspective of a machine), and relinquished at some *lower* temperature. More precisely, ΔQ has not been extracted from a *single reservoir* or a *reservoir that is at the same temperature throughout* (this is to rule out the logically permissible description of the reservoirs at higher and lower temperatures as a *single* reservoir but whose temperature is not the same throughout).

Again, if we consider *isothermal expansion* of an ideal gas, clearly the heat absorbed is fully converted to work as per the first law, i.e $\bar{d}Q = C_V dT + PdV \rightarrow dQ = PdV$, and the heat has been extracted from a *single* reservoir. But this too will not qualify to be a perpetual machine of the second kind for somewhat subtler reasons. Firstly, the isothermal expansion changes the *state* of the system from (V, T) to (V', T); for it to act like a machine, the system will have to be eventually brought back to its original state whereupon it will expel part of the heat absorbed.

Both these examples serve to provide the following sharper meaning to what a perpetual mobile of the second kind can be:i) it has to absorb heat from a reservoir maintaining the same temperature throughout, i.e a *single* reservoir, ii) it should convert the heat so absorbed *fully* into work without affecting *any other changes*.

3.2 The entropy axiom: the first part of second law

3.2.1 A bonanza from first law for ideal gases

As we saw from the previous chapter, Joule's famous experiment on free expansion implies that for *ideal gases*, the internal energy U is a function of T only. In fact, this should be taken as an *independent* characterization of ideal gases from the gas law $PV = nRT$; it is independent because it can not be derived from the gas laws without further assumptions. Now let us consider $\frac{đQ}{T}$; according to the first law, considering only mechanical work,

$$\frac{đQ}{T} = \frac{dU(T)}{T} + nR\frac{dV}{V} = dA(T) + nRd\ln V \tag{3.1}$$

where $U = \frac{dA(T)}{dT}$. This is a *remarkable* result which states that for ideal gases, $\frac{dQ}{T}$ is indeed a perfect differential even though $đQ$ was not. This means that $\int \frac{đQ}{T}$ is yet another state function. The interesting question is whether this is just an *accident* valid only for ideal gases? Before attempting an answer to it, let us call $\frac{đQ}{T}$ as the perfect differential dS, where S shall be called *entropy*. Clausius introduced this concept in 1865, fifteen years after he formulated the first and second laws. The entropy for the ideal gas, from above, is

$$S = \int \frac{dU(T)}{T} + nR\ln V + S_0 \tag{3.2}$$

with S_0 being an *undetermined constant*. When C_V of the ideal gas is constant, this becomes

$$S = nC_V \ln T + nR\ln V + S_0 \qquad S = nC_P \ln T - nR\ln P + S_0' \tag{3.3}$$

The existence of entropy as a state function is what Sommerfeld calls *the entropy axiom*. We have seen that for ideal gases this is not really an axiom, and is in fact a direct consequence of first law when combined with the two laws for ideal gases. In general, U will not be a function of T alone and it is clear that the entropy axiom will not always be valid.

3.2.2 A consequence of the entropy axiom

To explore the status of the entropy axiom for other than the ideal gases, let us consider gases obeying the van der Waals equation that was introduced in chapter 1.

$$(P + \frac{an^2}{V^2})(V - nb) = nRT \tag{3.4}$$

If we consider in particular the so called *ideal* vdW gases, for which $C_V = const.$, it is not hard to see that for the choice $U(V,T) = nC_V T - \frac{an^2}{V}$, $\frac{đQ}{T}$ is again a perfect differential. This continues to be so as long as $U(V,T) = f(T) - \frac{an^2}{V}$, but for choices other than these, $\frac{đQ}{T}$ is indeed not an exact differential.

Therefore what the entropy axiom does on one hand is restrict the possible choices of internal energy. In fact, one can obtain a precise expression of this restriction by simultaneously demanding that dU as well as $\frac{đQ}{T}$ are perfect differentials. Taking (V,T) as the independent variables, these integrability conditions are, respectively,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V \tag{3.5}$$

and

$$\left(\frac{\partial}{\partial V}\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\frac{1}{T}\left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\right)_V \tag{3.6}$$

Simplifying this and using the previous equation, one arrives at one of the most important equations of thermodynamics, i.e

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3.7}$$

Eqn.(3.7) can be taken to be equivalent to the entropy axiom when the first law is valid.

When applied to an ideal gas for which $PV = nRT$, it is seen that this equation would require $\left(\frac{\partial U}{\partial V}\right)_T = 0$, which is the same as U being a function of T alone. Earlier we had shown the converse, i.e when U is a function of T alone, the entropy axiom is satisfied. In the vdW case too, the particular form of $U(V,T) = f(T) - \frac{an^2}{V}$ is indeed a solution of eqn.(3.7)!

The discussion of the entropy axiom so far seems rather mathematically oriented, without any obvious physical significance. Actually, the entropy axiom has very deep physical significance, perhaps one of the deepest in physics! To bring this out, we first demonstrate an *equivalence* between the entropy axiom, and *universality* of Carnot cycles.

3.3 Entropy axiom and universality of Carnot cycles

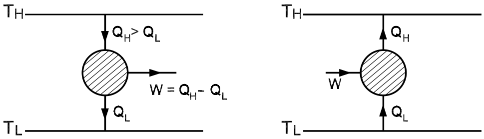

FIGURE 3.1 The Carnot engine obeying first law and its reverse

Recall that within the caloric theory, Carnot had reached the very important conclusion that all ideal heat engines *must* have universal *efficiency* if energy conservation (impossibility of perpetual mobiles of the first kind, according to Carnot) is to be respected. Now, with the new paradigm of interconvertibility of heat and work, it is pertinent to raise afresh the issue of the universality of all ideal Carnot cycles.

But unlike in the caloric theory, now the Carnot cycle is characterized by the amount of heat Q_H absorbed by the system at the higher temperature T_H, and the heat $Q_L < Q_H$ relinquished at the lower temperature T_L. Even in the new theory, the notion of efficiency can still be kept to mean the amount of work performed per heat absorbed at the higher temperature.

The important difference from the caloric theory is that the heat relinquished at the lower temperature is no longer the same as that absorbed at the higher temperature, but is in fact reduced by the amount of work performed. Consequently, the efficiency is given by $e = \frac{\Delta W}{Q_H} = \frac{Q_H - Q_L}{Q_H}$. What is not clear a priori is that in the new theory, the ratio $\frac{Q_L}{Q_H}$ is universal for all ideal heat engines.

What, if any, would go wrong if the efficiencies of all ideal heat engines were not the same? Precisely the same kind of analysis that Carnot carried out earlier can be done now too. The ideal Carnot cycle and its reverse are shown in the next figure. In the reverse engine, heat Q_L is absorbed at the lower temperature and $Q_H > Q_L$ is exhausted at the higher temperature after work equal to $Q_H - Q_L = eQ_H$ has been performed *on* the system. If there were two ideal Carnot engines C, C' with efficiencies $e, e' > e$, then a composite of C' with the reverse of C (see figure) would extract an amount of heat $(e' - e)Q_H$ from the lower reservoir and convert it *completely* to work W of the same magnitude, without expelling *any* heat at the higher reservoir. In other words, *a perpetuum mobile of the second kind* would be possible! This can only be avoided if the efficiencies of all ideal Carnot cycles, even in the new theory, are the same.

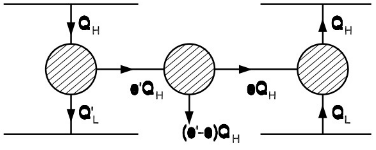

FIGURE 3.2 Universality of the Carnot cycles

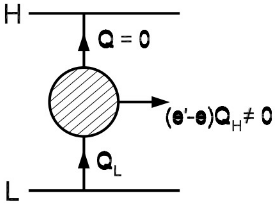

FIGURE 3.3 Universality of the Carnot cycles

This line of thinking, as Carnot had already demonstrated earlier, puts severe restrictions on efficiencies of *nonideal* (i.e not reversible) heat engines too. While the reverse of an irreversible (nonideal) Carnot cycle cannot be used, the argument can still be made use of with the irreversible Carnot cycle in combination with the reverse of a reversible cycle; therefore, if the efficiency of an irreversible cycle *exceeds* that of an ideal Carnot cycle, one can still construct a perpetual mobile of the second kind. Therefore one can conclude that *efficiency of an irreversible engine has to be necessarily lower than a reversible engine*.

We will now proceed to determine the conditions for the universality of ideal engines. We can just use the same calculus that Clausius used to establish the existence of internal energy U. So, considering an *infinitesimal Carnot cycle*, the efficiency de is given by $de = \frac{\Delta W}{N(V,T)\delta_T V}$. On using the results previously obtained, one gets $de = \frac{1}{N(V,T)}\left(\frac{\partial P}{\partial T}\right)_V \delta T$. Clausius is supposed to have been aware that for ideal gases $N(V,T) = P$. This is also what follows from Joule's experiment on expansions of ideal gases. In the light of the first law, this implies that for ideal gases U is a function of T only, and consequently $dU(T) = C_V(T)dT$. On combining this with eqn(2.11) one concludes that $N = P$. Therefore, for ideal gases

$$de = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V dT = \frac{dT}{T} \tag{3.8}$$

This is how Clausius fixed the universal Carnot function in the earlier Clapeyron equation to be $\mu(T) = \frac{1}{T}$ leading to the modern form of the Clapeyron equation which should aptly be called the *Clausius-Clapeyron equation*. However, to avoid confusion because of this equation being referred to in current literature as *Clapeyron equation*, we shall also continue with that practice with the understanding that the latter is a shorthand for the former. It is of course to be recalled that the earlier Clapeyron equation was based on the now defunct caloric theory, whereas Clausius derivation is what follows from the new theory of heat; it is just that many quantities (but of course not all) were insensitive to the actual nature of heat!

Now the requirement of universality of efficiencies of all ideal heat engines means that in particular they must equal the efficiency of all ideal heat engines based on ideal gases as the working substance, and one gets the extremely important consequence that $N(V,T) = T\left(\frac{\partial P}{\partial T}\right)_V$ *for all thermodynamic systems*! On the other hand, $\left(\frac{\partial U}{\partial V}\right)_T = N - P$. Therefore, universality of efficiencies of Carnot engines, in the light of the first law, requires that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3.9}$$

Lo and behold, this is nothing but the condition for the entropy axiom! In other words, *the entropy axiom is equivalent to the condition of universality of all Carnot engines*. This is the underlying physical significance of the entropy axiom. But since the universality is also equivalent to the impossibility of perpetual mobiles of the second kind, we draw the powerful conclusion that the entropy axiom, what Sommerfeld called the first part of the second law, is equivalent to the impossibility of perpetual mobiles of the second kind. But the latter is one of the formulations of the *second law of thermodynamics*, what Sommerfeld would have called the *second part of the second law*. Therefore, the entropy axiom is not just the first part of the second law, it is, at the same time, also its second part![24]

However, most people recognize second law in the form where it states that *entropy of a thermally isolated system never decreases*. As the system while executing a Carnot cycle is certainly not *thermally isolated* (except during the adiabatic stages), one can not immediately see the consequence of the second law, so formulated, for a Carnot cycle. Instead, we shall focus on the so called *Clausius inequality* which we shall later see to be equivalent to the form of the second law so stated. This inequality states that for *any* cycle, not necessarily reversible, the following is always true:

$$\oint \frac{\text{đ}Q}{T} \leq 0 \tag{3.10}$$

The equality holding only for reversible cycles. It is very important to stress that though $\frac{\text{đ}Q}{T}$ is a perfect differential, the integral of this over a path is the entropy difference between the endpoints only if the path is reversible. That is why even though $\frac{\text{đ}Q}{T}$ has been integrated over a closed path in eqn.(3.10), the rhs is not zero! Furthermore, the rhs can be *negative* so a naive interpretation of the integral as a change of entropy would actually imply an entropy decrease! We shall return to a fuller discussion of these subtleties shortly.

We shall now demonstrate that the entropy axiom, through its equivalence to the impossibility of perpetual mobiles of the second kind via its equivalence to the universality of ideal Carnot cycles, indeed yields the Clausius inequality, *without any further assumptions*. For that we make use of Clausius's own ingenious construction.

Consider an *arbitrary* cycle $\tilde{C}$, not necessarily a reversible one. In executing this, let the system start at A_1 and absorb an amount of heat $(\Delta Q)_1$ during the segment A_1A_2 at temperature T_1. The cycle is completed by absorbing $(\Delta Q)_2$ during A_2A_3 at T_2, and so on, till the system returns to its starting state A_1 by absorbing $(\Delta Q)_n$ during A_nA_1 at T_n. The sign of (ΔQ) can be positive or negative.

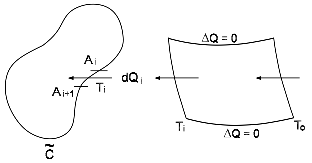

FIGURE 3.4 Proving the Clausius inequality.

Clausius's ingenuity lay in picturing the heat absorbed at each stage as the heat relinquished during a *reversible* Carnot cycle operating between some arbitrary temperature T_0 and the temperature of the stage of $\tilde{C}$ during which the heat was absorbed. Clearly, there are, in addition to the cycle $\tilde{C}$, n Carnot cycles $C_1, C_2, .., C_n$ operating between T_0 and the temperatures $T_1, T_2, .., T_n$. This is schematically shown in the figure for the stage A_iA_{i+1}.

So, the cycle $\tilde{C}$ starts at A_1 and at the same time C_1 starts at E_1 and goes through the reversible Carnot cycle by eventually delivering $(\Delta Q)_1$ to $\mathscr{C}$ during A_1A_2 at temperature T_1. It must therefore absorb $\frac{T_0}{T_1}(\Delta Q)_1$ from the reservoir at T_0. After $\tilde{C}$ and $C_1, .., C_n$ have been completed, all have returned to their original states; the total heat absorbed from the *single* reservoir at T_0 being

$$\Delta Q = T_0 \sum_i \frac{(\Delta Q)_i}{T_i} \tag{3.11}$$

and this is completely converted to work, with no other changes. If this heat were *positive*, we would indeed have realized a perpetual machine of the second kind. On the other hand, if this heat were *negative*, the work done would have been *on* the system, and this would only have amounted to a *refrigerator*, with no contradictions—the case when $\Delta Q = 0$ does not also contradict anything.

In conclusion, the entropy axiom is completely equivalent to a) universality of all ideal heat engines, b) the impossibility of perpetual machines of second kind, and consequently, c) Clausius inequality of eqn.(3.10). Later, we shall show how the form of second law stating that entropy of thermally isolated systems never decreases emerges from the Clausius inequality.

3.3.1 Ideal gas Carnot cycle

Let us consider a Carnot cycle whose working substance is an ideal gas. The states visited during the cycle are $(P_A, V_A, T_H), (P_B, V_B, T_H), (P_C, V_C, T_L), (P_D, V_D, T_L)$. We have already worked out the *infinitesimal* version of this cycle: in that case the efficiency was found to be $d\eta = \Delta W/Q_H = dT/T_H$, where Q_H is the heat absorbed from the higher tempeature reservoir and $\Delta W = Q_H - Q_L$ the work done by the cycle.

Earlier, in eqn. (3.8) we showed how Clausius had determined the efficiency of the *infinitesimal* ideal gas Carnot cycle to be $de = dT/T$. Now we show how the finite cycle works. Such a finite cycle is shown schematically in the adjacent figure. The first law tells that during isothermal changes $dQ = PdV = \frac{RT}{V}dV$. Hence the heat Q_H absorbed during the isothermal process at T_H is $Q_H = RT_H \ln V_B/V_A$. Likewise the heat relinquished at the lower end is $Q_L = RT_L \ln V_D/V_C$. Using the expression for entropy given in eqn.(3.3) the adiabaticity of the steps BC and DA requires $\ln V_C/V_B = \ln V_D/V_A$ and hence $\ln V_B/V_A = \ln V_D/V_C$ leading to $Q_H/T_H = Q_L/T_L$, with the resulting efficiency of the *finite* cycle being $\eta = (Q_H - Q_L)/Q_H = 1 - T_L/T_H$.

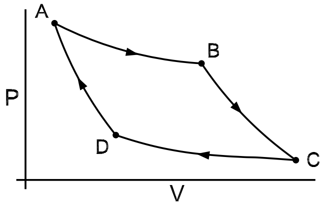

FIGURE 3.5 Finite Carnot cycle

During the isothermal stages $\Delta Q = \Delta W$. To compute the work done during the adiabatic stages, one uses (from first law) that during such changes $PdV = -dU$ and hence the work done during an adiabatic change is just the negative of the change in internal energy. But the internal energy for an ideal gas is a function of temperature alone according to eqn. 3.7. Hence the work done during BC is $U(T_H) - U(T_L)$ and that during DA is $U(T_L) - U(T_H)$, and these cancel each other exactly. Therefore at the end of the cycle too, the total heat absorbed equals the total work done.

Note that we have not assumed C_V to be a *constant*, so that the treatment given here is the most general. When C_V depends on temperature, it is not straightforward to get P as a function of V during adiabatic changes, so that an explicit evaluation of $\int PdV$ would have been very difficult. But that step has been circumvented by exploiting the fact that during such an adiabatic change $dW = -dU$.

3.3.2 Composition of Carnot cycles

Recall the earlier result that the efficiency of an *infinitesimal* Carnot cycle using an ideal gas as a working substance, and working between T and $T - dT$ is $d\eta = dT/T$. How then should one relate this to the efficiency $\eta = 1 - T_L/T_H$ of the finite cycle operating between T_H and T_L? Incidentally, the universality of all ideal heat engines makes these considerations applicable to any Carnot cycle, not necessarily the ones whose working substances are ideal gases.

A naive integration of $d\eta$ from T_L to T_H would give $\eta = \ln\, T_H/T_L$, a decidedly *incorrect* result! Infinitesimal cycles had been justified on the *correct* premise that finite cycles can be obtained, as a result of reversibility, by composing many infinitesimal cycles (in fact Carnot had initiated this concept). Therefore, something is amiss in the way the efficiencies have been compounded.

Carnot cycles in parallel and series To understand the intricacies better, let us introduce the notion of compounding Carnot cycles in *parallel* and in *series*.

Consider two infinitesimal Carnot cycles both of which are operating between the *same* temperatures T and $T - dT$. By composing these in *parallel* we mean a composite Carnot cycle, also operating between the same temperatures, and in such a way that the heat extracted by the composite cycle at the higher temperature is the *sum* of the heat extracted by the component cycles. Likewise for the heat relinquished at the lower temperatures. If Q_H, Q'_H respectively are the heat absorbed at T, the work performed by the components are $\delta W = \frac{dT}{T} Q_H, \delta W' = \frac{dt}{T} Q'_H$ and hence the total work done by the composite is $\frac{dT}{T}(Q_H + Q'_H)$. Therefore the composite has the same efficiency as the efficiency of the components(their efficiencies are the same as they operate between the same temperatures).

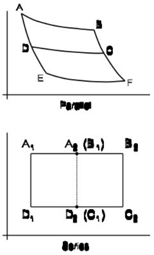

FIGURE 3.6 Carnot cycle compositions.

Now let us turn to Carnot cycles in *series*. We shall say two Carnot cycles are in series when i) the lower temperature of the first coincides with the higher temperature of the second, and ii) the heat relinquished by the first cycle at its lower temperature coincides with the heat absorbed by the second cycle at its higher temperature. If η_1, η_2 are the efficiencies of the two components and Q_H the heat absorbed at the higher temperature of the first cycle, the heat relinquished at the lower reservoir of the first cycle is $(1 - \eta_1)Q_H$. But this is the heat absorbed at the higher reservoir of the second cycle whereupon the heat relinquished at the lower reservoir of the second cycle is $(1-\eta_2)Q'_H = (1-\eta_1)(1-\eta_2)Q_H$. This means the efficiency of the composite cycle is $\eta_{12} = 1-(1-\eta_1)(1-\eta_2)$ and this is *not* $\eta_1+\eta_2$. In fact, the composition rule for the series case is $(1-\eta_{12}) = (1-\eta_1)(1-\eta_2)$. The efficiencies in a serially connected case is not the sum because the heat input for the second is not the same as the first, but is reduced.

More explicitly, if $Q_H(T)$ is the heat absorbed at the higher temperature T, the work done in an infinitesimal cycle is $dW = \frac{Q_H(T)}{T}dT$. So for the temperatures $T_H, T_1, T_2, \ldots, T_L$ characterizing many cycles connected in series resulting in a composite cycle operating between T_H and T_L, it follows that $\frac{Q_H(T_i)}{T_i}$ is *constant* equalling $\frac{Q_H(T_H)}{T_H}$; hence the total work done $W = \sum_i (dW)_i = Q_H(T_H)\frac{\sum_i dT_i}{T_H} = Q_H(1-\frac{T_L}{T_H}$ which is the result for the finite cycle obtained earlier!

Composition of the cycles in the caloric theory It is instructive to compare the above with what would obtain in the caloric theory, i.e for the cycles as originally envisaged by Carnot. Because there too the universality of efficiencies was valid, for cycles connected in parallel one would reach the same conclusion as above. But there is a dramatic difference for cycles in series; now the heat absorbed at the higher end of every component is the same! The rule for composing the efficiencies becomes $\eta_{12} = \eta_1 + \eta_2$ and one obtains, as shown by Kelvin,

$$\eta(T_H, T_L) = \int_{T_L}^{T_H} \mu(T)dT \tag{3.12}$$

Therefore, even if the efficiency of an infinitesimal cycle in caloric theory is chosen to be $\frac{dT}{T}$, to match the modern result, the efficiency of the *finite* cycle would have become $\eta(T_H, T_L) = \ln\frac{T_H}{T_L}$! Therefore, even though it is true that in both theories, a finite cycle can be obtained by composing many infinitesimal ones, the efficiencies compose differently.

3.4 Historical formulations of second law

As already indicated in the opening lines of this chapter, what was needed was a *succinct* postulate that would encompass the nearly countless circumstances of experience that lay beyond the scope of the first law. As stated, such a postulate, although differing in exact verbal details, was given by Clausius and Kelvin, and restated later by Planck and Maxwell. We begin with the postulate of Clausius:

Clausius Postulate *A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.*

The clause *only final result* is all important. Equivalently, the postulate of Clausius can also be restated as *heat can not, of itself, pass from a colder to a hotter body*, where again the phrase *of itself* is of critical importance.

As perceptibly noted by Fermi [17], this form of the postulate explicitly brings in the notion of *temperature*, which is in fact absent in the general formulation of the first law. As emphasized in the section on thermometry, though the numerical value of temperature is dependent on details of thermometry, the notion of whether a given body is hotter or colder than another given body is *absolute*, and is independent of thermometric details. Nevertheless, it may be worthwhile to give as precise a meaning as possible to this postulate.

One is to use, as done by Fermi, a well established phenomenon like conductivity to unambigously identify the hotter(colder) of the bodies. so, Fermi proposes to recast Clausius's postulate as: *If heat flows by conduction from A to B, then a transformation whose only final result is to transfer heat from B to A is impossible.*

Refrigerators It is also instructive to view the Clausius postulate as *the impossibility of perfect refrigerators.* Recall that in a *refrigerator* heat Q_L is actually extracted at the low temperature end and delivered as heat $Q_H > Q_L$ to the high temperature end. Of course, work needs to be done to make this happen and that is what the compressor does. So, in a precise sense, a refrigerator is *a reverse heat engine.* The efficiency of a heat engine $\eta = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H}$, but refrigerators are described by the so called *coefficient of performance* which is defined as *the amount of heat extracted per work done*, i.e $K = \frac{Q_L}{W}$. This is understandable as a good refrigerator is the one that extracts maximum possible heat per work done. Therefore, the higher the K, more efficient is the refrigerator. The formula for K is

$$K = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} \quad \to K = \frac{T_L}{T_H - T_L} \tag{3.13}$$

But the range of values of K is $0 \leq K \leq \infty$, whereas an efficiency is expected to lie in the interval $0 \leq \eta \leq 1$. It is, however, possible to define a refrigerator efficiency $e_R = \frac{K}{K+1}$ which lies in that range. What is the relationship between this refrigerator efficiency, and the efficiency η_R of the *heat engine* which is the reverse of the refrigerator? As can easily be checked, that relationship is $e_R + \eta_R = 1$, and not $e_R = \eta_R$! To grasp the significance of this, consider a *very inefficient* refrigerator, i.e one which expends a lot of work W in extracting very little heat Q_L from the cold chamber, thereby throwing out an enormous amount of Q_H at the hotter reservoir. The reverse of this inefficient refrigerator is the highly efficient heat engine which takes a large amount of Q_H, converting most of it to work and discarding a very small amount of Q_L at the cooler reservoir. Thus the process of reversal not only turns a refrigerator into a heat engine, and vice versa, but also changes their efficiencies into their complements in accordance with $e_R + \eta_R = 1$.

Now a perfect refrigerator is the one that transmits *all* the heat drawn at lower temperature to the higher temperature reservoir without the need for any work, i.e $W = 0$.But that is precisely what is forbidden by the Clausius postulate.

Kelvin Postulate *A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible.*

In other words, the Kelvin postulate is explicitly prohibiting perpetual mobiles of the second kind. In fact, the title of his paper on the second law was *The impossibility of a perpetual motion machine of the second kind.* The reader will now be able to appreciate the fine print in the concept of a perpetual mobile of the second kind that we so carefully elaborated. Just as we emphasized the notion of a *perfect* refrigerator, one can now appreciate that a perpetual machine of the second kind is nothing but a *perfect heat engine*. Therefore, the Kelvin postulate can also be restated as *the impossibility of a perfect heat engine*.

Though it is hard to immediately see any commonality between the Clausius and Kelvin postulates, we shall see that both are completely equivalent! Before demonstrating that equivalence, we state the postulate as restated by Planck and Maxwell.

Planck Postulate *It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight, and the cooling of a heat reservoir.*

Postulate of Maxwell *It is impossible, by the unaided action of the natural processes, to transform any part of the heat of a body into mechanical work, except by allowing the heat to pass from that body into another at lower temperature.*

Planck says that his restatement coincides fundamentally with those of Clausius, Kelvin and Maxwell, and that he has selected his form because of *its evident technical significance*. It is of course closer in form to Kelvin's postulate than Clausius's. Maxwell's formulation, on the other hand, preserves the essentials of both the Kelvin and Clausius forms. Therefore, we will be content to explicitly show only the equivalence of the Clausius and Kelvin postulates, as the equivalence to the Planck and Maxwell forms becomes obvious.

The perfect heat engine and the perfect refrigerator are schematically shown in the next figure. That the Kelvin postulate *implies* the Clausius postulate is schematically shown in the figure The argument is that, if the Kelvin postulate holds, one can envisage working a perfect heat engine with another heat engine which is driven by the complete utilization of the work output of the perfect heat engine. This will in effect result in a perfect regrigerator. That the Clausius postulate implies the Kelvin postulate can likewise be shown by working a perfect refrigerator in conjunction with a suitable heat engine to produce in effect a perfect heat engine, as shown schematically in figures.

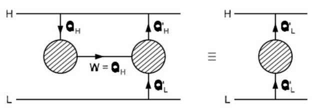

FIGURE 3.7 The equality of Clausius and Kelvin formulations-I

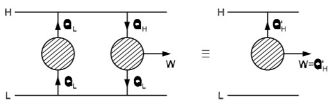

FIGURE 3.8 The equality of the formulations-II

3.4.1 Consequences of Clausius Inequality

Therefore, the above mentioned postulates are all equivalent to the impossibility of perpetuum mobiles of the first kind. We have already seen that that impossibility is equivalent to *the Clausius inequality*. Now we recount the argument of Clausius that his inequality leads to the famous formulation of the second law according to which *entropy of a thermally isolated system never decreases.*

First, let us consider the cycle relevant to the inequality to be *reversible*, i.e the whole cycle of operations can be performed in reverse. Operationally, this amounts to the replacement $\Delta Q \to -\Delta Q$. But the Clausius inequality, being true for *every cycle*, must hold for the reversed cycle too. In other words, for reversible cycles

$$-\oint \frac{\Delta Q}{T} \le 0 \to \oint \frac{\Delta Q}{T} = 0 \tag{3.14}$$

Now consider two states A and B connected by two different *reversible* paths I and II. Clearly a reversible cycle can be formed by traversing from A to B along I and returning from B to A along II. Then, eqn.(3.14) implies that for reversible paths I and II (with R denoting the reversible nature of the paths)

$$\int_{R,I} \frac{\text{đ}Q}{T} = \int_{R,II} \frac{\text{đ}Q}{T} = S(B) - S(A) \tag{3.15}$$

Since the paths I and II are *arbitrary*, the implication is that $\int_A^B \text{đ}Q/T$ is *path independent* and that it only depends on the states A and B. In particular, the integral has to be S(B)-S(A), and the differential dS of the state function S, called *entropy* by Clausius, is given by $dS = \text{đ}Q/T$.

It should be emphasized that in our approach, where the starting point itself was the existence of this function, defined precisely as above, this conclusion was built in. But in the historical approaches of Clausius and Kelvin, this powerful conclusion emerges from their innocuous sounding postulates! On the other hand, in the approach where the entropy axiom is the starting point, the postulates of Clausius and Kelvin (and consequently, those of Planck and Maxwell) follow as logical consequences, as shown earlier.

Now let us investigate the consequences of the Clausius inequality when one of the paths connecting A and B is *irreversible*. Then there is no obvious connection between the original cycle and the reversed cycle. Nevertheless, the Clausius inequality still holds for the cycle formed by going from A to B along the irreversible path, and returning from B to A along the reversible one. Hence

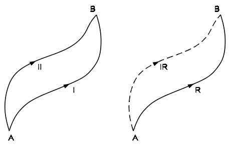

FIGURE 3.9 Reversible and irreversible cycles.

$$\int_{Ir,A}^{B} \frac{\text{đ}Q}{T} - \int_{R,A}^{B} \frac{\text{đ}Q}{T} \le 0 \qquad \int_{Ir,A}^{B} \frac{\text{đ}Q}{T} \le S(B) - S(A) \tag{3.16}$$

Some cautionary remarks are in order here. While one can sensibly talk about an integral along a reversible path, it is by no means clear what one means by such an 'integral' along an irreversible 'path'. First of all, when a set of irreversible transformations take the state A to a state B, there need not even be a path in the space of states (you can take it, for example, to be the P-V plane). Therefore, there is no sensible way to talk of an 'integral' along an irreversible path. What it means *operationally* is just summing $đQ/T$ over various segments of the transformation which may or may not form segments of a path in the P-V plane.

Secondly, if both A and B are given states, there is no big deal to eqn.(3.16) as we then exactly know both S(A) and S(B), and the above equation serves to say something about lhs and nothing useful about entropy per se. The meaning of the above equation is as follows: start with some state A of the system and imagine the outcomes of arbitrary sets of transformations, and consider the set of *all* states B that these transformations take A to. Then the difference in entropy between B and A must obey the above inequality.

In particular, let us *thermally* insulate the system and again consider all possible transformations; we must put $đQ = 0$ in the above due to the condition of thermal insulation, and one obtains

$$S(B) \geq S(A) \tag{3.17}$$

which says that the result of an *arbitrary* transformation of a thermally insulated system is such that its entropy *never decreases*. This is the famous *Second Law of Thermodynamics*. It must be emphasized that just requiring the entropy axiom, and nothing else, also guarantees this law.

For a reversible transformation, eqn.(3.15) with $đQ = 0$ yields $S(B) = S(A)$, i.e reversible transformations of a thermally insulated system maintain the system entropy. Furthermore, *irreversible transformations* of a thermally isolated system always increase its entropy. Thus at last we have a *quantitative* criterion for irreversibility. This criterion can also be stated equivalently as *irreversible processes can never enhance the efficiency of any heat engine*. Stated that way, it sounds intuitive and obvious, but the considerations of this chapter show that there is nothing really obvious about it.

3.5 Second law and irreversibility

What the second law can determine is the *directionality* of heat flow, something that the first law is incapable of doing. As a result, the second law discriminates between the *initial* and the *final* states of a general transformation of a system. Closely woven into this fabric is the notion of *irreversibility*. Furthermore, entropy as a state function provides a quantitative description of this directionality.

It is illuminating, and important, to introspect on these fundamental aspects. Let us consider the Clausius postulate which denies the possibility of a perfect refrigerator. But the reverse of a perfect refrigerator is the process by which heat spontaneously flows from a hotter body to a colder body (see fig. 3.11), and there is nothing impossible about that. Likewise, consider the reverse of a perfect heat engine, something forbidden by the Kelvin postulate (see fig. 3.10); this reverse is nothing but the process by which work is completely converted to heat, and again there is nothing forbidden about that. Stated differently, while perpetuum mobiles of the second kind are impossible, their reverses are commonplace!

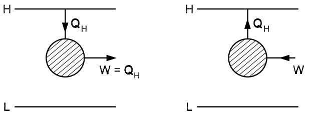

FIGURE 3.10 The ideal heat engine and its reverse.

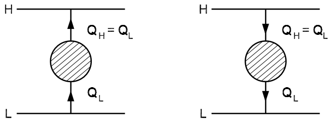

FIGURE 3.11 The ideal refrigerator and its reverse.

Therefore we see circumstances where certain processes are perfectly legitimate, but their reverses are absolutely forbidden. This is another way of saying that certain processes are *irreversible*. The nature and characterization of such irreversibilities is the body and soul of the second law. As Planck points out, the situation is dramatically different with perpetual mobiles of the first kind which in effect say that energy can neither be absolutely created nor absolutely created. But then, the reverse of the impossibility of a perpetuum mobile of the first kind is also an impossibility of the perpetuum mobile of the first kind!

A subtle manifestation of this also happens with the demonstration above that $S(B) \geq S(A)$. But what in this really distinguished B from A? To understand that, note that we composed the cycle by *first* going from A to B along the irreversible direction, and then returned from B to A along the reversible path. We could equally well have chosen the cycle by first going from A to B along the reversible path, and then coming back to A from B along the irreversible direction. The same arguments as before would now have given $S(B) \leq S(A)$! Is their a contradiction with what we obtained earlier? No, as far as the irreversible processes are concerned, in the first instance it was A which was the *initial* state, while in the second instance it was B that was the initial state, and in both cases the second law is saying the same thing, namely, $S(final) \geq S(initial)$. It is not that it is meaningless to consider the reverse of an irreversible path, it is that doing so interchanges the initial and final states, and second law discriminates between them. A similar issue does not arise with reversible processes.

Example 3.1: Extracting heat from a cold body

Find the minimum amount of work needed to extract 1 cal of heat from a body at 273 K(melting point of ice) and deliver to a room at 300 K(room temperature).

This example illustrates the heart of the second law, and is the way to understand why heat does not flow spontaneously from a colder body to a hotter body. If it could, no work would have been necessary in this problem, but we shall see that a minimum of work is needed. This can be viewed as a problem in refrigeration, as heat is being extracted at a lower temperature. The refrigerator that is most efficient, i.e the one with the largest coefficient of performance K, will be the one which will require the least amount of work for a particular amount of cooling. From eqn.(3.13) we see that for this case, $K = 273/27 \approx 10.1$

Again, by the definition $K = Q_L/W$, it is seen that the work needed in this case is $W = Q_L/K \approx 0.1 cal$. It should be noted that all temperatures have to be in the Kelvin scale. It is also seen that the higher the temperature of the room, the more work will be needed to transfer the same amount of heat.

It is also worth noting that the reverse of this refrigerator is a heat engine operating between 300 K and 273 K; the Carnot efficiency for that is $\eta_R = 1 - T_L/T_H = 27/300 \approx 0.09$. More generally, $\eta_R = (1+K)^{-1}$.

Example 3.2: Refrigerators as heaters

A refrigerator has to put out more heat than what it extracts from the cold chamber. Can this heat be effectively used to heat a room? Compare the heating power of a refrigerator with that of direct heating, say, by electricity or gas. Take the outside temperature to be 250 K(real cold!) and let it be desired to keep the interiors at a cozy 300 K. The option of direct heating is by supplying P_h kW(power in kilo-watts)

The idea is to make the entire outside at 250 K the 'cold chamber' of a refrigerator on which work can be done at W kW. The coefficient of performance for the required refrigerator is $K = 250/(300-250) = 5$. If the room were heated directly, the rate at which heat would be supplied is $\dot{Q}_H = W_h$. The amount of heat Q_H for the refrigerator can easily worked out to be $Q_H = (1+K)W_r$, where W_r is the work to be performed by the refrigerator. Hence $\dot{Q}_H = (1+K)\dot{W}_r = \dot{P}_h$. Thus the power required by the refrigerator, $\dot{W}_r$ is only 1/6 of the power for direct heating!

Example 3.3: Entropy and irreversibility-I

Consider mixing 100 gms of water at 300 K with 50 gms of water at 400 K. Calculate the final equilibrium temperature if the specific heat c of water per gm is 1 cal/gm/K. Calculate the change in entropy for this irreversible process.

This is a simple example of irreversibility, as the water so mixed will not, on its own, go back to the two samples we started with. Hence we expect the total entropy change to be positive. We can think of carrying out the steps in a thermally insulated vessel, so there is no exchange of heat with the outside world.

Since this is an irreversible process, eqn.(3.15) can not be used. In fact this example shows how, even for an irreversible path, the entropy difference between the initial and final states can be computed. The crucial fact to note is that entropy is a state function, and as long as we can find even one reversible path connecting the initial and final states of any process, even an irreversible one, we can then use eqn.(3.15) to compute the required entropy difference.

Since the whole system is thermally insulated, we have from first law $dU + PdV = 0$. The PdV term requires some discussion. It is possible to consider an arrangement that does not allow any changes in volume by, say, enclosing both samples in rigid containers of the right side, and only allowing heat to be exchanged between them. In that case the PdV terms are strictly zero. But in the case of liquids, the volume changes can be neglected to a good approximation. In that case the PdV terms can be neglected. But the distinction between the two circumstances should not be overlooked.

When volume changes are neglected, the specific heat in question can be thought of as c_v, and if this is taken to be constant, which is again a pretty good approximation for the range of temperatures considered, $dU = mcdT$. Therefore

$$\Delta U = 0 = 100(T_f - 300) + 50(T_f - 400) \qquad T_f = 333.33K \tag{3.18}$$

Now consider heating 100 gms of water from 300 to 333.33 K. When it is at the intermediate temperature $300 < T < 333.33$, the entropy gain upon heating by dT is $dS = 100c(dT/T)$. Therefore entropy gain is $\Delta S_1 = 100\ln(333.33/300)$ cal/deg. In the same way, the entropy loss on reversibly cooling 50 gms from 400 to 333.33 K is $\Delta S_2 = 50\ln(333.33/400)$ cal/deg. Hence the total change of entropy is $\Delta S = 10.535 - 9.116 = 1.419$ cal/deg. It is to be noted that entropy has the same units as the gas constant R, i.e cal/deg, which has the numerical value of 1.986 cal/deg.

Example 3.4: Entropy and irreversibility-II

Consider the same problem as in example 3.3, but now for an ideal gas; take the first sample to be one mole of the gas at T_L K, and the second one also one mole, but at T_H K. Compare the calculated entropy difference with the known expression for the entropy of an ideal gas as in eqn.(3.3)

Let us consider two versions, one where the volumes are fixed. Then the relevant specific heat is C_V, and the same calculation as in the previous example first gives $T_f = (T_H + T_L)/2K$, and, $\Delta S = C_V \ln(T_f^2/T_H T_l)$. The initial entropy, according to eqn.(3.3) being $S_i = C_V \ln T_L T_H + R\ln V_H V_L$ and final entropy being $2C_V \ln T_f + R\ln V_H V_L$, we see that the calculated entropy difference is (which it must be) the difference of the explicit values of initial and final entropies.

If, on the other hand, the volumes are allowed to change as for example in a constant pressure case, T_f still comes out the same as above but the directly calculated entropy difference comes out to be $C_P \ln(T_f^2/T_H T_L)$. The initial entropy now is $C_P \ln T_H T_L - 2R\ln P$, while the final entropy is $2C_P \ln T_f - 2R\ln P$, so the two differences again match.

The main lesson from this example as opposed to the previous one is that there only difference of entropy was calculated whereas now, being the ideal gas, we could use explicit expressions for entropy itself.

Example 3.5: Reversible and irreversible ice melting

How can a lump of ice at its melting point be completely melted into water reversibly? Compare it with its irreversible melting by, say, tossing into water at, say, a temperature 10 K higher.

Any reversible process, as the name indicates, can be made to proceed in both directions by suitably controlling the environment. Therefore one can reversibly melt ice by heating it with a reservoir whose temperature is very very slightly above the melting point of ice. The process can be reversed, i.e the resulting water refrozen by simply lowering the temperature of the reservoir to a temperature that is very very slightly below the melting point of ice. The reservoir can be taken to be at the same temperature as the melting point during such reversible melting. Reversible melting can be achieved by changing ambient pressures also.

The gain in entropy of ice is given by $\Delta S_{ice} = mlT_{melt}$ where m is the mass of the ice, and l the latent heat of fusion per gm. The entropy loss of the reservoir is equal in magnitude but opposite in sign as the temperature of the reservoir is the same as the temperature of ice, and the heat lost by the reservoir must exactly match the heat gained by ice. So the total entropy change is zero, as it should be for reversible changes.

In irreversal melting on the other hand, the temperature of the reservoir (the hotter water) is at a temperature greater than the temperature of ice by a finite amount. Hence the entropy loss by the reservoir is less than the entropy gain by ice, making the total entropy change positive, characteristic of irreversible changes. That this circumstance is irreversible may be understood from the fact no small lowering of water temperature is going to result in refreezing. However, dramatically cooling the water can result in refreezing but in such a process the entropy loss by water is lower than the entropy gain of ice, and again, the total entropy increases! Of course even in the so called reversible melting, in real life there is always some irreversibility, however small.

3.5.1 Second law and arrow of time

Does the fact that the entropy of a thermally isolated system never decrease have anything to do with the *arrow of time*? Irreversibility is the distinguishing feature of both of them. Existence of an arrow of time means time is not reversible, and that distinguishes *initial* and *final* states. We saw that the second law too distinguishes initial and final states. So it may appear that these two irreveribilities, i.e temporal and thermodynamic, are related.

But it would be hasty to draw any conclusions on this very knotty issue. Firstly, *time* has no role, whatsoever, to play in *equilibrium thermodynamics*. Therefore it is fairly obvious that the irreversibility brought forth by the second law does not directly have any bearing on issues of arrow of time. One may, somewhat crudely speaking, think of temporal evolution of states of a thermally insulated system and then imagine that second law of thermodynamics would imply that entropy is a *decreasing function of time*.

But within equilibrium thermodynamics there is no meaningful way of doing this, and this difficulty persists even when one passes on to *equilibrium statistical mechanics*. The only formalism where time makes its presence explicitly known is in Boltzman's *kinetic theory* and its modern variants. The celebrated H-theorem of Boltzman indeed attempts to answer this question, and while it answers affirmatively the relation between entropy and arrow of time in a manner that is satisfactory to most people, the extreme technical difficulties inherent in the theory are such that it can not still be taken as an unambiguous proof.

3.5.2 Entropy and disorder

Though the notion of disorder is again unwarranted within the strict confines of thermodynamics, it becomes a very powerful notion once we pass on to statistical mechanics. There the picture that emerges is that entropy is an indicator of *order*, suitably understood, of statistical systems. The higher the entropy, the more disordered the system is. Furthermore, most systems become more and more ordered as their temperature gets lower. In general the solid phase is more ordered than the liquid phase of the same substance, the liquid phase more ordered than the gas phase etc. There are interesting exceptions as for example He_3 where at around 0.3 K the liquid phase is more ordered than the solid phase. But even in that system at very low temperatures the relation between temperature and order reestablishes itself.

3.5.3 Entropy and information

The connection between entropy and order also suggests a connection between entropy and *information*. To appreciate this, note that a word with meaning in a language is an *ordered state* of alphabets, while alphabets thrown in at random, an obviously *disordered state* of alphabets, carries no meaning or information. Shannon was the first one to use an entropy-like notion to characterize information and this can easily be said to be one of the revolutionary developments in knowledge.

3.6 An absolute scale of temperature

We had earlier discussed the *Kelvin* scale of temperature in section (1.2.1). As already noted there, the manner in which this scale was introduced depended on the ideal gas assumption. Consequently, the Kelvin scale introduced that way explicitly depends on the material used for thermometry. In reality, no gas is ideal and even the small departure from idealness nevertheless introduces some material dependence to the temperature scales.

A question of fundamental importance then is whether even *in principle* it is possible to introduce a temperature scale that does not at all depend on the material introduced for the thermometry. The answer is in the affirmative, and what makes this possible is the deep property of the *universality* of the efficiencies of *all* ideal (in the sense of being perfectly *reversible*, and not in the sense that an ideal gas is the working substance) Carnot cycles (engines). Such a temperature scale, independent of the material used for thermometry, is called an *absolute scale*.

Before going into the details of such a scale, let us raise a question that ought to have occurred to anyone about the temperatures that we have so far referred to under so many different circumstances; namely, the scale according to which these temperatures are measured as after all the *numerical value* of temperature *depends* on the scale that has been used. One thing is clear though; the validity of the basic laws of thermodynamics can not be dependent on any particular temperature scale. In fact, the first law, in its purest formulation $đQ = dU + dW$, does not even refer to temperature explicitly! The second law, in whatever form one chooses to consider, does however involve temperature explicitly.

But as explained in the section (1.1), a change of temperature scale, of whatever complexity, is like a change of coordinates, and perfect differentials *transform* quite *unambiguously* under such transformations, *leaving the basic relations between perfect differentials unaltered.* All this really means is that all the thermodynamic relations hold good even when temperature scales are used that depend on the materials of thermometry, and no absolute scale need necessarily be used.

But what makes the notion of an absolute scale so powerful is that no single material will be adequate for use in thermometry for *all* temperatures, and many different scales may have to be used along with a knowledge of the precise map between them. An absolute scale avoids such difficulties.

Now let us turn to the explicit construction of such an absolute scale. Firstly, let us work with an *arbitrary* scale of temperature θ. Consider composing two Carnot cycles C_1, C_2 operating respectively between (θ_1, θ_2) and (θ_2, θ_3). Let Q_1 be the heat absorbed by C_1 at θ_1, Q_2 the heat given by C_1 at θ_2; since the cycles are composed in parallel (see section (3.32)), Q_2 is also the heat absorbed by C_2 at θ_2. Finally, let Q_3 be the heat given up by C_2 at θ_3. Therefore $Q_1 > Q_2 > Q_3$. Since the efficiency $1 - Q_2/Q_1$ is a *universal* function of θ_1, θ_2, even with respect to an arbitrary scale of temperature, it follows that Q_1/Q_2 is also an universal function of these variables. Let us call it $f(\theta_1, \theta_2)$. Likewise, $Q_2/Q_3 = f(\theta_2, \theta_3)$. Applying the same reasoning to the composite cycle C_3 operating between θ_1, θ_3, it follows that,

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3) \tag{3.19}$$

For this to hold for *every* θ_2, one must have

$$f(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \tag{3.20}$$

where $\phi(\theta)$ is yet another universal function. As it is clear that $f(\theta_1, \theta_2) > f(\theta_4, \theta_2)$ whenever $\theta_1 > \theta_4$, it follows that $\phi(\theta)$ is a *monotonically* increasing function of θ and furthermore, it is a *positive* function. Hence, from our discussions of section (1.1), it follows that ϕ itself qualifies to be defined as a temperature according to some scale. This is the absolute scale that we are looking for as $T = \phi(\theta)$ will be the *same scale* irrespective of the working substance used in the cycles. Hence for Carnot cycles $Q_H/Q_L = T_H/T_L$, when the absolute scale, as defined above, is used.

It is worth emphasizing that if θ is a particular parametrisation of the temperature scale based on some particular material used for thermometry, the function ϕ will depend both on the material and the parametrisation (refer to section (1.1) for an elaboration of these important discussions). This means that though T is in itself a scale that is independent of any material, the transformations $T \rightleftharpoons \theta$, depend on both of these.

Equality of ideal gas and absolute scales: In subsection (3.3.1) it was shown that for ideal gases, when the temperature scale is defined through $PV = nR\tilde{T}$, $Q_H/Q_L = \tilde{T}_H/\tilde{T}_L$. This scale is called the *ideal gas temperature scale*. Comparison with the absolute scale introduced above reveals that $T = a\tilde{T}$, i.e except for an overall constant multiplicative factor, these two scales are the same, and also the same as the Kelvin scale. The overall factor is often fixed by choosing the temperature of the *Triple point* in the water-ice-vapor system to be at 273.16 K.

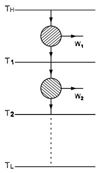

FIGURE 3.12 Absolute scale of temperature.

Uniform and nonuniform absolute scales We introduced the absolute scale above in a particularly simple way by choosing $T = \phi(\theta)$. Even with that choice, the problem of choosing a *uniform scale* for thermometry still remains. This is easily solved by arranging a number of Carnot cycles in *series* as shown in fig.(3.12). Then, in an obvious notation, if T_i are the various temperatures, as measured in absolute scale, one has $T_i/Q_i = const.$. Therefore, $T_i - T_{i-1} = c(Q_i - Q_{i-1}) = cW_i$.

Hence, if all W_i are chosen equal, one gets a uniform scale, or, if $W_i \simeq i^2$, one gets a quadratic scale etc. Clearly, there are many other ways of introducing scales that are nevertheless still absolute. In fact, scales introduced through $g(T) = \phi(\theta)$ are all absolute as long as the function g has no material dependence. As explained in the section 1.1, all such choices can be mapped to one another.

Absolute scales in caloric theory It is instructive to see how absolute scales would be introduced in the *caloric theory*, at least as a lesson in learning! As shown by Carnot, the universal efficiency in that theory took the form

$$\eta(\theta_H, \theta_L) = \int_{\theta_L}^{\theta_H} d\theta\, \mu(\theta) = w(\theta_H) - w(\theta_L) \tag{3.21}$$

Therefore, even in the caloric theory an absolute scale can be introduced via $T_{cal} = w(\theta)$. Again both uniform and nonuniform absolute scales can be introduced. For the particular choice of $\mu(t) = 1/t$, which we have seen to be the case for ideal gas in modern thermodynamics, this gives rise to Kelvin's famous *logarithmic scale*. Of course, even in this case the efficiencies for *finite* cycles in the caloric theory and modern thermodynamics are totally unrelated.

3.7 Applications of the first and second laws

In this chapter we shall explore some consequences of combining the first law with the concept of *entropy*. While the former involves the inexact differential $đQ$, introduction of entropy trades this inexact differential with TdS. This, of course, is not a perfect differential, but the advantage is that it has been written in terms of a perfect differential dS and a *state function* T.

The total change in heat in going from a state A to state B through a sequence of *reversible* changes, formally represented by the integral $\int_A^B đQ$, is *path dependent*. So, in order to know or specify this quantity, the entire *history* of the passage from A to B, along with all the data for all the intermediate parts, have to be specified. That's too much information, and often it may not even be possible to provide it. That's the down side of the inexact differential $đQ$, which nevertheless has a very clear and measurable physical meaning.

On the other hand, if we consider the total change of $\frac{đQ}{T}$ in going through the same sequence of reversible changes, it, represented by $\int_A^B \frac{đQ}{T}$ does not depend on the path taken. This quantity only depends on the difference of the entropy between the states A and B. That's really a miracle in a way, as just a weight factor of $\frac{1}{T}$ completely changes the situation. From a mathematical perspective, quantities like dS can be used as we use *differentials* in calculus, but quantities like $đQ$ can not. Therefore, as long as we have expressions involving only the perfect differentials, we can use all the machinery of differential calculus.

Let us start with the first law, for a system with a fixed number of moles,

$$đQ = dU + PdV \tag{3.22}$$

Since U is a state function, we can take it to be a function of any two independent variables (we are considering the simplest possible system now). These could be (V,T), (P,T) or (P,V). And for each of them, we can use the rule for partial differentiation of a function $f(x,y)$

$$df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{3.23}$$

Therefore

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \\ dU &= \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \\ dU &= \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \end{aligned} \tag{3.24}$$

Let us use each of these, one at a time, in the first law. Let us start with the first, which yields,

$$đQ = \left\{P + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{3.25}$$

As it stands this is not a very useful relation as the partial derivatives are as yet unrelated to *observable* quantities. Let us recall that *specific heat* is indeed an observable quantity and is experimentally measured as the ratio $\frac{\Delta Q}{\Delta T}$ as ΔT is made smaller and smaller, so that the ratio, in the spirit of calculus, can be approximated by a derivative. At least that would be the naive expectation; but $đQ$ is an inexact differential and this limit, if symbolised by $\frac{đQ}{dT}$ is quite meaningless, mathematically. Before coming up with an acceptable expression for specific heats, let us note that on physical grounds there ought to be many different specific heats. This is because the amount of heat required to raise the temperature of a body by a certain amount depends on other physical circumstances like whether the heat was absorbed by the system while maintaining its pressure or volume etc. In particular, less heat is required if volume is kept constant as no part of the heat goes off to doing work. We denote the specific heat at constant volume by C_V. Let us apply eqn.(3.25) to such constant volume processes; then $dV = 0$ and one gets

$$C_V = \frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \tag{3.26}$$

and eqn.(3.25) can be recast as

$$đQ = C_V\, dT + \left\{P + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV \tag{3.27}$$

This is somewhat better than before, but still the partial derivative $\left(\frac{\partial U}{\partial T}\right)_V$ is something that we have not related to any directly observable quantity. Now consider an adiabatic process in which $đQ = 0$; then we find

$$P + \left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_S \tag{3.28}$$

This way we can relate all the partial derivatives occurring in eqn.(3.25) to *observable* quantities!

The equality of the *mixed* partial derivatives $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ also gives the condition

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x \tag{3.29}$$

Applying this to eqn.(3.27) one would get

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}(P + \left(\frac{\partial U}{\partial V}\right)_T)\right)_V \tag{3.30}$$

which is a *contradiction* as $\left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$ already equals $\left(\frac{\partial C_V}{\partial V}\right)_T$ due to the fact that dU is a perfect differential. The contradiction is merely a pointer to the fact that $đQ$ is *not* a perfect differential. A closer inspection of the contradiction reveals its source to be the PdV term. In consequence, the work done PdV can not be a perfect differential either and should only be written as $đW$! Just as dS was a perfect differential though $\bar{d}Q = TdS$ was not, dV is a perfect differential but PdV is not. However, we shall soon come up with a very elegant fix for eqn.(3.30)!

Now let us turn to using the second of eqn.(3.24) in the first law to give,

$$\bar{d}Q = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT + PdV \tag{3.31}$$

As it stands it has all of dP, dT, dV while only P, T are to be treated as independent; therefore dV has to be expressed in terms of dP, dT using eqn.(3.23)

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \tag{3.32}$$

Substituting this in eqn.(3.31 gives

$$\bar{d}Q = \left\{\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right\} dP + \left\{\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right\} dT \tag{3.33}$$

Once again, the specific heat C_P is obtained by

$$C_P = \frac{\bar{d}Q}{dT}|_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{3.34}$$

The rhs can also be written as $\left(\frac{\partial(U+PV)}{\partial T}\right)_P$, introducing the notion of *enthalpy* $H = U + PV$. In terms of enthalpy, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ looks very similar in structure to $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. Using C_P, eqn.(3.33) can be written as

$$\bar{d}Q = C_P\, dT + \left\{\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right\} dP \tag{3.35}$$

Equations (3.27) and (3.35) are sometimes referred to as the *dbar Q equations*. They are somewhat undesirable because of the presence of inexact differentials. On the other hand, $\bar{d}Q$ can be written as TdS whereby both the equations will only contain perfect differentials. The resulting equations are called TdS equations (jocularly called the *tedious* equations!). By doing so more useful results can be obtained.

Let us start by recasting the first law itself in the TdS form:

$$TdS = dU + PdV \quad \rightarrow dU = TdS - PdV \tag{3.36}$$

An immediate consequence of eqn.(3.36) is

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \tag{3.37}$$

In axiomatic approaches (see chapter 6), this is in fact taken as the defining relation for temperature. The other TdS equations arising out of eqns.(3.27,3.35) are

$$\begin{aligned} TdS &= C_V\, dT + \left\{P + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV \\ TdS &= C_P\, dT + \left\{\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right\} dP \end{aligned} \tag{3.38}$$

Let us first illustrate getting a relation between partial derivatives of a different type than what we have obtained so far. From eqn.(3.36) it is easy to get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{3.39}$$

It is to be noted that we got this even though neither of the independent variables in eqn.(3.36) has been held fixed. Once again, the integrability condition for the first of eqn.(3.38) is

$$\left(\frac{\partial}{\partial V}\frac{C_V}{T}\right)_T = \left(\frac{\partial}{\partial T}\frac{P+\left(\frac{\partial U}{\partial V}\right)_T}{T}\right)_V \tag{3.40}$$

On using the integrability condition for dU, $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$ and $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, the above equation reduces to

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3.41}$$

Eqn.(3.41) is a very important equation in thermodynamics from which many interesting conclusions can be drawn. Comparing eqn.(3.39) and eqn.(3.41) one concludes

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{3.42}$$

This is one of the so called *Maxwell Relations* and a much less tedious derivation of it will be given later on. By similar manipulations one can show that

$$\left\{\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right\} = -T\left(\frac{\partial V}{\partial T}\right)_P \tag{3.43}$$

Now we use the eqns.(3.41,3.43) to recast eqn.(3.38) in the form

$$\begin{aligned} T\,dS &= C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \\ T\,dS &= C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \end{aligned} \tag{3.44}$$

An important result follows on obtaining the integrability conditions for this pair of equations:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{3.45}$$

Let us pause and reflect on what has been done; starting with the first law which had a term dU that is not directly observable, we have recast it as equations where every term is measurable in principle. Even though entropy is not directly measurable,

TdS, being the amount of heat exchanged, is certainly measurable. Though we have succeeded in writing first law in a form involving directly measurable quantities, it is desirable to further express these measurable quantities in terms of *properties* of the system. Examples of such properties are the specific heats C_V and C_P.

To do so, we introduce some additional properties. One of the first properties that one can think about is *thermal expansion*. In principle one could introduce coefficients of *linear* and *volume* expansions, but as they are related let us just discuss the coefficient of volume expansion. The idea is that if the temperature of a body is increased by δT and if as a consequence the volume increases by δV, the coefficient of volume expansion is $\frac{\delta V}{V\delta T}$ as $\delta T \to 0$. Just as in the case of specific heats, the conditions under which this expansion is measured ought to be specified. Let us just consider this coefficient under *constant pressure*.

The coefficient then, designated by α is given by $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. This is indeed one of the quantities that appears in the TdS equation involving C_P. But the partial derivative that occurs in the TdS equation with C_V is $\left(\frac{\partial P}{\partial T}\right)_V$. To relate this to properties of a system requires more work. Let us first introduce the so called *compressibility*. Imagine applying pressure to a gas, one would expect the volume of the gas to decrease. The ratio $\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)$ is clearly a measure of how effectively the gas can be compressed, i.e it is a measure of compressibility. As before, things depend on the conditions of the experiment, and the important ones are when compression is carried out *isothermally* or *adiabatically*. Therefore we have the *isothermal compressibility* κ_T and *adiabatic compressibility* κ_S given by

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{3.46}$$

A minus sign has been introduced as normally the volume decreases with increased pressure, and in such cases the compressibility is *positive*.

Now $\left(\frac{\partial P}{\partial T}\right)_V$ can be related to the expansion coefficient α and isothermal compressibility κ_T as follows: using

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -1 \tag{3.47}$$

one gets

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P^{-1}\left(\frac{\partial V}{\partial P}\right)_T^{-1} = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial V}{\partial P}\right)_T^{-1} = \frac{\alpha}{\kappa_T} \tag{3.48}$$

Hence the new form of TdS equations involving specific heats, volume expansion coefficients and compressibilities is

$$\begin{aligned} TdS &= C_V\,dT + \frac{\alpha T}{\kappa_T}dV \\ TdS &= C_P\,dT - TV\alpha\,dP \end{aligned} \tag{3.49}$$

By equating the two TdS equations we get

$$C_V\,dT + \frac{\alpha T}{\kappa_T}\,dV = C_P\,dT - TV\alpha\,dP \tag{3.50}$$

This equation involves dT,dV and dP, but only two among them are independent. So one of them must be expressed in terms of the other two. Choosing dP and dV to be independent, $dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$ and we can rewrite the above as

$$(C_P - C_V)\left\{\left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV\right\} - T\left(\frac{\partial V}{\partial T}\right)_P dP - T\left(\frac{\partial P}{\partial T}\right)_V dV = 0 \tag{3.51}$$

Since dP and dV are independent, their coefficients must both vanish and we get two equations

$$(C_P - C_V)\left(\frac{\partial T}{\partial P}\right)_V = T\left(\frac{\partial V}{\partial T}\right)_P \qquad (C_P - C_V)\left(\frac{\partial T}{\partial V}\right)_P = T\left(\frac{\partial P}{\partial T}\right)_V \tag{3.52}$$

Because $\left(\frac{\partial T}{\partial P}\right)_V^{-1} = \left(\frac{\partial P}{\partial T}\right)_V$ etc., these two equations are identical, yielding the important relation

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = \frac{TV\alpha^2}{\kappa_T} \tag{3.53}$$

In simplifying we have made repeated use of the properties of partial derivatives. We could have also considered adiabatic processes characterised by $dS = 0$. The two TdS equations would then have yielded

$$C_V = -T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_S \qquad C_P = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_S \tag{3.54}$$

The ratio of specific heats $\gamma = \frac{C_P}{C_V}$ is yet another important property of systems. We can use the previous equation and get

$$\frac{C_P}{C_V} = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_S \cdot \left(\frac{\partial P}{\partial T}\right)_V^{-1}\left(\frac{\partial V}{\partial T}\right)_S^{-1} = \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial V}{\partial P}\right)_S^{-1} = \frac{\kappa_T}{\kappa_S} \tag{3.55}$$

Therefore we have related the ratio of specific heats to the ratio of compressibilities. This relationship holds for all systems and this illustrates the power of these manipulations though they may have appeared very opaque and without focus in between. We end this discussion by combining eqn.(3.55) with eqn.(3.54) to derive individual expressions for the specific heats in terms of $\alpha, \kappa_T, \kappa_S$:

$$C_V = TV \cdot \frac{\alpha^2}{\kappa_T - \kappa_S} \cdot \frac{\kappa_S}{\kappa_T} \qquad C_P = TV \cdot \frac{\alpha^2}{\kappa_T - \kappa_S} \tag{3.56}$$

Once again, the power of thermodynamics is in giving such totally general relationships between various observables. It must however be emphasized that the observables themselves can not always be computed unless there is some additional information, like the equation of state, or some accurate data. But such general relations are extremely valuable as they may circumvent limitations posed by the difficulties of performing certain experiments. For example, it may turn out that measuring adiabatic compressibilities is difficult experimentally; then a knowledge of γ and κ_T can be used to calculate κ_S. Another very important use of such general relations even when all experiments can easily be performed is that they provide consistency checks on measurements. The last feature is indispensable in experimental science.

3.8 Third law of thermodynamics - the Nernst-Planck postulate

A very important consideration in thermodynamics concerns the meaning of the zero on the absolute scale of temperature, i.e 0 K. Though the full significance of this issue can only be unravelled through considerations of *Quantum Statistical Mechanics*, thermodynamics comes with very strong pointers that 0 K is indeed a very special temperature.

A practical question that first comes to mind is whether this temperature is physically realizable, and if so, how? A somewhat related question is whether its existence is in conformity with the first and second laws of thermodynamics. Let us begin by recounting an objection to absolute zero that would be the first reaction by many. This is based on the premise that a Carnot cycle operating between 0 K and any other T, would be a *perfect heat engine* in the sense that its efficiency $\eta = 1 - \frac{0}{T} = 1$! This would most directly contradict the Kelvin postulate and hence the second law.

Pippard, who in his book [54] has given a most comprehensive critique of the issue of absolute zero, warns against accepting this 'objection' uncritically. The point is, in order to take this objection seriously, one has to carefully examine whether a Carnot cycle with the lower reservoir at 0 K can operate at all. Recall that for the operability of the Carnot cycle, there has to be an *isothermal* change in entropy at the lower temperature as some property of the system, volume in the case of the traditional Carnot cycle, is varied. It's only this feature that allows *two distinct* adiabats to intersect the isotherm at 0 K, and make the Carnot cycle implementable. If we call properties other than T collectively as ξ, then the operability of the Carnot cycle with lower temperature at 0 K requires $\left(\frac{\partial S}{\partial \xi}\right)_{T=0} \neq 0$. Only then is absolute zero in contradiction with the second law.

Therefore, if the isothermal variation of entropy *vanishes* at absolute zero, one can not have two distinct adiabats intersecting the $T = 0$ isotherm, and no Carnot cycle can be operated, removing that particular objection to absolute zero. But evading inconsistency with second law by taking refuge under the assumption of a vanishing $\left(\frac{\partial S}{\partial \xi}\right)_{T=0}$, lands one in a different kind of difficulty. That difficulty is that when $\left(\frac{\partial S}{\partial \xi}\right)_{T=0} = 0$, *absolute zero is simply unattainable*! So there are two *logically distinct* aspects to the absolute zero issue; one being some system already existing in it, and the other being the attainability of absolute zero from an initial $T \neq 0K$.

To see that when the isothermal variation of entropy at absolute zero vanishes, no system initially at $T \neq 0$ can attain absolute zero, let us enquire into the operational meaning of this attainability. As Pippard has emphasized, of all the ways of lowering

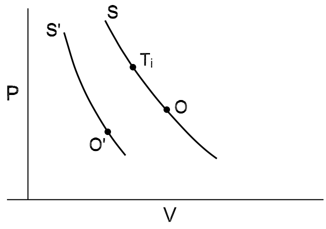

FIGURE 3.13 Third Law

temperatures, adiabatic means are the most efficient, so let us only consider them. If absolute zero is attainable *adiabatically* from some T_i, we should have an adiabat, say S, passing through both T_i and 0 K, as shown in the figure 3.13 shown in the P-V plane for the case when $\xi = V$, but generalizations are obvious. Now continuity would require the same to happen with a nearby adiabat, say, S'. Let O be the $T = 0$ point on S and O' be the 0 K point on S'. Since no two adiabats can ever intersect, the curves S,S' have no common points, and consequently, the points O,O' both corresponding to 0 K, must be *distinct*. This also means that in this example $\left(\frac{\partial S}{\partial V}\right)_T \neq 0$.

But that is precisely when the conflict with second law would arise, as argued before. To summarize, either the isothermal changes in entropy are not vanishing, allowing absolute zero to be attainable but violate the second law, OR the isothermal variations of entropy vanish, but then absolute zero is *unattainable*!

Negative Temperatures Some caveats with the above arguments ought to be pointed out. If the $T = 0$ point lies in the *interior* of an isentropic surface (shown as a line in the figures above), continuity would imply that at least some of the neighbouring points could be at *lower* temperatures; but then they have to be at *negative* temperatures! It is therefore pertinent to ask whether temperatures have to be *necessarily positive*. If temperatures can be negative on, say, the centigrade scale, why can they not be negative on the Kelvin scale? Some immediate objections to negative temperatures on the Kelvin scale may come to mind; for example, the lhs of ideal gas law is manifestly positive (though the issue of negative pressures too can be a confusing one; see chapter 12 on van der Waals fluids for some discussion), so T has to be positive. But this is not a very persuasive argument as it is eminently conceivable that at such temperatures no gas is ideal. Another objection, more serious, can be that a Carnot cycle operating between negative and positive temperatures may be contradictory with an efficiency exceeding 1; but this too can not be that straightforward and would necessitate a critical examination of whether under such conditions a Carnot cycle is at all operative. That issue is already very subtle even when the lower temperature is 0 K, as we are finding out!

In fact, in classical statistical mechanics, there exist well known systems like *spin systems*, *two dimensional point vortices* etc where the entropy as a function of internal energy reaches a *maximum*. Then from eqn.(3.37) it follows that temperature can be both positive and negative in these systems. In the vortex gas case, as elegantly shown by Onsager, the negative temperature sector is not only physical but manifests itself observationally in very novel ways [51]. But what is common to all these systems with both positive and negative temperatures is that the two sectors do not communicate to each other, and no smooth transformations connect them. Therefore in effect, one is dealing with systems where the temperature is always of one sign.

In classical thermodynamics temperatures are always understood to be positive. Pippard points out that as long as specific heat of a system (isolated) does not vanish as $T \to \infty$, the unattainability of absolute zero implies that temperatures in classical thermodynamics can be consistently taken to be positive.

So, either the $T = 0$ points lie on the *boundary*, if any, of the isentropic surface, or at the boundary of the physical region (P-V plane) above, if negative temperatures are to be avoided, in the operational sense mentioned.

Returning to the discussion on the attainability or otherwise of absolute zero, the situation turns out to be even more subtle. The conclusion that the second law would be violated when $\left(\frac{\partial S}{\partial \xi}\right)_{T=0} \neq 0$ because that would allow a Carnot cycle to be operated between 0 K and any higher temperature, itself requires greater scrutiny. The point is that, as long as $T \neq 0$, an *adiabatic* process, characterized by $\Delta Q = 0$, is also an *isentropic* process characterized by $\Delta S = 0$ as $\Delta Q = T\Delta S$. But precisely at $T = 0$ this identification is no longer necessary. Even processes that are not isentropic i.e $\Delta S \neq 0$ are still adiabatic at 0 K! Thus at the lower end of the cycle, since no heat is given out irrespective of whether the change involves isothermal changes in entropy or not, there is no *practical* way of ensuring that the cycle is operable! That an isotherm at 0 K also becomes an adiabat for these very reasons adds further confusion.

Therefore, there is no way to conclude that the second law precludes the attainability of absolute zero.

W. Nernst, the winner of the Nobel prize for chemistry in 1920, had been investigating for a long time the connection between thermodynamics and *chemical equilibria*, particularly of *different phases* of the same chemically pure substance. Such problems consitute the fascinating field of study called *thermochemistry*. Nernst initially formulated his so called *Heat Theorem* which subsequently became the *Nernst-Planck postulate*. As we shall see these issues were intricately interwoven with the developments leading to the birth of quantum theory.

As narrated by Nernst in his book *The New Heat Theorem* [50], the precursor to these developments lay in the early works of Berthelot and Thomsen (whom Nernst calls the *fathers* of thermochemistry) in 1869–70. A proper understanding of these ideas will require familiarity with the concept of *thermodynamic potentials* discussed at length in chapter 8. According to Berthelot and Thomsen (reworded in modern language), the condition for chemical equilibrium for changes that are *isobaric* and *isothermal* (i.e under constant pressure and temperature) is the stationarity of the quantity $H = U - PV$. This is called *enthalpy*. But developments in thermodynamics had shown that this is in fact not correct generally, and that the correct condition for equilibrium under these circumstances is actually the stationarity of $G = U - PV - TS$. When dealing only with *condensed* states like liquids and solids, the PV term can be dropped as there is hardly any change in it during transformations. In that case, H can be replaced by the internal energy U, and G replaced by the Helmholtz free energy F. The analysis given by Nernst in his book then follows.

Therefore the Berthelot-Thomsen principle, which was found to be a fairly good guide at low temperatures, can only be tenable if one demands $F = U$ (or more generally, $G = H$) over a *range* of temperatures. At $T = 0$, this is what is to be expected as long as $TS \to 0$ as $T \to 0$ (note that the boundedness of S in the limit need not be insisted upon — a point that will assume significance in what follows). However, the validity of this principle in the neighbourhood of $T = 0$ would *at least* require

$$\frac{d\Delta F}{dT}|_{T=0} = \frac{d\Delta U}{dT}|_{T=0} \quad \frac{d\Delta G}{dT}|_{T=0} = \frac{d\Delta H}{dT}|_{T=0} \quad \to \Delta S|_{T=0} = 0 \qquad (3.57)$$

This was the main point of a presentation Nernst had made in late 1905, and subsequently published as a paper in 1906 [49, 48]. We have already seen that this by itself *suffices* to preclude the attainability of absolute zero.

But it should be carefully noted that this condition on the *changes* in entropy during transformations does not say anything about specific heats themselves. All it says is that specific heats must be *continuous* during such phase transformations. In fact Nernst himself was careful not to say anything about specific heats by themselves.

It was in the same year, i.e 1906, that Albert Einstein, inspired by Planck's theory of charged oscillators, gave his theory of the specific heats of solids. A key feature of Einstein's work was that the specific heats vanished (exponentially) near absolute zero. Here was a theory that predicted a key consequence of the Nernst-Planck third law at least five years before it was clearly formulated in 1911!

Several qualifications need to be made even regarding the preliminary form of the third law that Nernst had enunciated in 1905. For one thing, the low temperatures that were accessible to Berthelot and Thomsen were certainly not very close to absolute zero, even by the wildest stretch of one's imagination. Therefore, Nernst was extrapolating in a big way to the vicinity of absolute zero. As we shall see while discussing *Pomeranchuk cooling* in He3, naive extrapolations of the old results for He3 would have entirely missed the essential physics of the system! Nernst was himself aware of this and he strongly advocated further experimental work at the time he made the original conjecture.

In the next five years, he and his collaborators undertook vigorous experimental work on specific heats which culminated in a series of papers by Lindeman and Nernst by 1911. The upshot of this very important body of work was the unambiguous support for the *vanishing* of specific heats near absolute zero for a wide variety of substances. Nernst openly acknowledged the influence of Einstein's 1906 paper in this context, and Einstein in return complimented Nernst in his concluding talk of the First Solvay meeting for having removed, decisively, the many theoretical confusions surrounding the topic.

Somewhere around 1910, Max Planck added the crucial finishing touch to the formulation of the third law, as understood even today. He elaborated on this in the third edition of his treatise on thermodynamics that came out in 1910. Planck's refinement lay in postulating that not just *changes* in specific heats vanished at absolute zero, but the specific heats themselves vanished at absolute zero. As a consequence, the entropy of *all* systems must approach a universal constant, independent of the state of the system. This refinement is crucial to removing the arbitrariness in entropy up to additive constants, characterstic of all thermodynamics involving as it does only entropy differentials. The importance of this for the determination of the so called *entropy constants* is dealt at great length in the last chapter of this book.

It is said that Nernst himself was not so sympathetic to this extension by Planck, seeing in it certain *ad hoc* elements. Planck readily admitted his inability to provide any *proofs* for his conjecture. In fact, Einstein emphatically stated the *indispensability* of quantum theory to an understanding of the third law.

Returning to the relevance of the original Nernst postulate, i.e $\Delta S = 0$ at $T = 0$, the following observations are in order. It must be realized that all these peculiarities apply *precisely at absolute zero*, and not to any other temperature, however close in magnitude it is to zero. Thus none of these considerations can be taken as any thermodynamic barrier to reaching a temperature *arbitrarily close* to zero. The *Nernst Postulate* in the light of this discussion can be taken to mean: *By no finite series of processes is absolute zero attainable.*

This postulate only precludes reaching absolute zero in one or finitely many steps. Now one can work backwards from this postulate, and conclude that on no isentropic surface can be there be states belonging to both 0 K and to nonzero K; because if there existed such an isentropic surface, one could have, with one adiabatic cooling step, attained 0 K, starting from $T \neq 0$. This has the consequence that all states at 0 K must lie on a *single* isentropic surface. This single isentropic surface must also be an isolated surface.

This is the *essential content* of the original Nernst postulate: *As the temperature tends to 0 K, the magnitude of entropy change in any reversible process tends to zero.* With the Planck refinement this becomes the statement that *as the temperature tends to 0 K, the entropy of all states tends to the same (constant) value.* It is this that is taken to be the form of the third law which should rightly be called the *Nernst-Planck heat theorem.*

It should be noted that with this the third law has laid to rest the confusion as to whether the $T = 0K$ isotherm is only an adiabat (which it always is) or an isotherm (which it could be, but need not be). The third law decrees that the isotherm at absolute zero is necessarily an isentrope (i.e constant entropy).

Without loss of generality, at least in thermodynamics, this constant value of the entropy at 0 K can be taken to be zero. This has the remarkable consequence that any state at 0 K can be taken as a fiducial state, and an unambiguous expression for the entropy of a state can be given as

$$S(A) = \int_0^A C_X \frac{dT}{T} \tag{3.58}$$

where X is any quantity that is held fixed like P,V etc., and the path of integration is along $X = const$. This automatically determines the so called *entropy constants* and in the last chapter of the book we discuss wide-ranging applications of these ideas. In fact the Nernst-Planck theorem makes its appearance very frequently in this book, testifying to its great importance. Many are of the opinion that in its importance, the third law does not quite match the first and second laws. It is interesting to recall Planck's own words in this regard as stated by him in the preface to the famous third edition of his treatise on thermodynamics: *Should this theorem, as at present appears likely, be found to hold good in all directions, then Thermodynamics will be enriched by a principle whose range, not only from the practical, but also from the theoretical point of view, cannot as yet be foreseen* [57]. Prophetic words, indeed.

An important addendum, before we consider some consequences of the third law, is the following: originally Nernst thought that the scope of this theorem was relevant only to *condensed systems* such as liquids and solids. This was, in his words, due to *the uncertainty in the fate of gases at such low temperatures*. But with Einstein's pioneering work on the *quantum theory of ideal monatomic gases*, it became clear (Nernst was one of the first to stress this) that the third law was applicable to gases too. In fact, Einstein's theory predicted the entropy and specific heat (only C_V is well defined for this system) of such ideal gases to vanish like $T^{3/2}$ close to absolute zero.

We cite here some of its most immediate consequences. It is clear from eqn.(3.58) that *all* specific heats like C_P, C_V etc. must vanish as $T \to 0$ (else, the statement $S \to 0$ as $T \to 0$ will not hold), and in particular $C_P - C_V \to 0$ too. This is a clear demonstration that no gas can remain ideal down to absolute zero. In a curious remark, Pippard points out that if all specific heats took nonvanishing constant values at all temperatures, the issue of reaching absolute zero would not even arise as then $S \to -\infty$! Classical statistical mechanics, through the *equipartition theorem*, in fact predicts such constant specific heats for all temperatures. It is only quantum theory that gives specific heats dependent on temperature, and that too specific heats which vanish as $T \to 0$.

Likewise, all partial derivatives like $\left(\frac{\partial S}{\partial V}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T \ldots$ must all tend to zero in this limit. Let us first consider the implications when $\left(\frac{\partial S}{\partial P}\right)_T \to 0$. By eqn.(3.44) it follows that this is equivalent to $\left(\frac{\partial V}{\partial T}\right)_P \to 0$. But that is the same as $V\alpha \to 0$ where α is the *coefficient of thermal expansion*. Consequently, $\alpha \to 0$ unless $V \to 0$.

By the application of the same eqn.(3.44) it follows that $\left(\frac{\partial S}{\partial V}\right)_T \to 0$ would imply $\left(\frac{\partial P}{\partial T}\right)_V \to 0$, i.e the *coefficient of pressure expansion* too vanishes at absolute zero. This can be further related, through eqn.(3.48), to $\frac{\alpha}{\kappa_T} \to 0$. Though α vanishes in the limit, it is not required that the *isothermal compressivity* κ_T do likewise (see problem below).

We conclude by showing the direct relevance of results like these to the practical problems of cooling to very low temperatures. It is reasonable to parametrize

$C_P(T,P)$, which, as we have seen above, vanishes at 0 K, by

$$C_P(T,P) \simeq T^b A(P) + \dots \tag{3.59}$$

where b is some *positive* number. This should be a good description close to 0 K. The resulting entropy, evaluated from eqn.(3.58) is given by $S(T,P) \simeq A(P)\frac{T^b}{b} + \dots$. By using the results above one concludes

$$\frac{V\alpha}{C_P} \to b\frac{A'(P)}{A(P)} \tag{3.60}$$

i.e it approaches a *finite* value. A quantity of importance to all cooling techniques is the so called *cooling power* defined essentially as $\dot{Q}$, the dot representing a time derivative. In the present context, this is the same as $\dot{Q} = T\left(\frac{\partial S}{\partial P}\right)_V \dot{P}$. Therefore the cooling rate becomes $\dot{Q} = V\alpha T\dot{P}$. As there is no place for time in a thermodynamic treatment, $\dot{P}$ is a non-thermodynamic quantity, determined by the actual details of the cooling apparatus. But we see that as we approach 0 K, the prefactor vanishes. This means that the amount of heat that can be extracted by a given cooling machine rapidly goes to zero, making the cooling more and more inefficient.

What one may really be interested in is not so much in $\dot{Q}$ but in $\dot{T}$, the rate at which the temperature can be lowered. This is readily obtained in this case by dividing $\dot{Q}$ by C_P. But the latter too vanishes as $T \to 0$ but at a *slower rate*. This is because of eqn.(3.60), and one in fact gets $\dot{T} = T(\frac{V\alpha}{C_P})\dot{P}$, showing that the rate of change of temperature also goes to zero linearly with T, making the approach to absolute zero only asymptotic. In chapter 14, devoted entirely to the issue of cooling to ultra low temperatures, we shall see that these features are universal. In fact, the Nernst postulate can be stated in a pragmatic language as *all cooling rates must vanish as absolute zero is approached.*

3.9 Problems

Problem 3.1 1 kg of supercooled water at 260K suddenly freezes to form ice at 0° C. Calculate the change in entropy.

Problem 3.2 Analyze the irreversibility in the Joule free expansion, as well as in the porous plug experiments. Show that a decrease of pressure while maintaining enthalpy always leads to an increase of entropy. Likewise, show that a volume increase maintaining U leads to an entropy increase.

Problem 3.3 1 kg of ice at 260 K is dropped into a thermally insulated vessel containing 2 kg of water at 300 K. Calculate the equilibrium temperature, the entropy change of ice, of water, as well as total entropy change. The specific heat of ice is $c_i = 2.22 J/gmK$, that of water $c_w = 4.19 J/gmK$, and the latent heat of fusion is 333 J/g.

Problem 3.4 The molar specific heat C_V of a gas can be approximated by 1.5 R in the temperature range of (300, 400) K, by 2.5 R in the range (400,1200)K, and finally by 3.5 R for even higher temperatures. If one mole of this gas initially at 1500 K comes in thermal contact with one mole of it at 350 K, under conditions of fixed volume, calculate the final equilibrium temperature and the change in entropy.

Problem 3.5 In helium liquefaction heat is removed from gas, possibly under pressure. If the laboratory is at 300 K and if 500 mJ of heat is removed from helium at 4 K, what is the minimum heat delivered to the room. Why is this heat the minimum possible? What is the coefficient of performance?

Problem 3.6 In a heat engine with air as its medium, the intake is at 1 MPa. It is exhausted to the atmosphere after an adiabatic expansion by a factor of 5. Find the pressure of air after the expansion and the highest possible efficiency of this engine.

Problem 3.7 The work done during the isothermal expansion at T_0 of a substance from V_1 to V_2 is $W = RT_0 \ln V_2/V_1$. If the entropy of the system is given by $S(V,T) = const.VT^{\mathrm{a}}$ where a is a constant, find the equation of state $P(V,T)$, as well as the work done during an arbitrary isothermal expansion.

Problem 3.8 Of the two ways of increasing the efficiency of a Carnot cycle, i.e a)$T_H \to T_H + \Delta T$ or b)$T_L \to T_L - \Delta T$, which is preferrable if the costs involved in both the changes are the same.

Problem 3.9 Consider two Carnot engines of equal efficiency operating between T_H and T_L. Determine the intermediate temperature T, and its significance from entropic arguments. Calculate the works performed by the two cycles as a fraction of the heat intake at Q_H.

4 Carnot Cycles - The Turing Machines of Thermodynamics

The great mathematician and computer scientist Alan Turing (1912-54) was born more than a century later than Sadi Carnot, but nevertheless the closest intellectual parallel to Carnot's reversible cycle is the so called Turing machine. Turing distilled in an imaginary 'machine' of extreme purity and simplicity the entire *essence* of *computation*. The so called *Turing Machine* was no blueprint for any actual computing machine but any computation, howsoever complex, could be analyzed on it. The impact of the Turing machine was immense, creating entirely new areas of thought like *complexity theory*, and was also instrumental in bringing *information theoretic* perspectives to computer sciences.

The Carnot cycle too was a 'heat engine' of extreme purity and simplicity. It too was no blue print for any actual engine, but captured within it the true essence of *all* heat engines ever built and to be ever built! It too had an enormous impact on the entire development of thermodynamics, greatly influencing the formulation of the second law. For these reasons we think it is apt to think of Carnot cycles as the *Turing Machines* of thermodynamics.

On a personal note too there are parallels between Sadi Carnot and Alan Turing; both these great thinkers were short lived.

The cycle as envisaged originally by Carnot, and further elaborated later by Clausius and Kelvin, was based on a mixture of *isothermal* and *adiabatic* processes. In such cycles, heat is absorbed or relinquished only during the isothermal stages, and a natural notion (at least from the point of view of heat engines) of efficiency emerges as the work performed per heat absorbed at the higher reservoir. But Carnot's considerations hold for more general possibilities as long as they constitute reversible cycles, though a rethink may be necessary as to what efficiency would mean, and whether they possess the *universality* that Carnot cycle efficiencies did. In this chapter we look at a variety of cycles, starting from the ones based on gases as originally discussed by Carnot (but in the light of the first and second laws of thermodynamics) and going on to others. The main emphasis will be on the *thermodynamic aspects* of these cycles rather than their engineering aspects.

4.1 The gas Carnot cycles

4.1.1 The ideal gas cycles

Though the ideal gas cycle is one of the most important gas cycles in thermodynamics, we have already extensively discussed it under various circumstances in the earlier chapters. Hence we shall straight away consider cycles using van der Waals gases as the working medium.

4.1.2 The van der Waals cycle

We repeat the steps now for the *perfect* van der Waals gas for which, as already noted, $(P+a/V^2)(V-b)=RT$. From earlier results, we record the expressions for the internal energy and entropy of a vdW gas

$$U(T,V)=f_1(T)-\frac{an^2}{V} \qquad S(T,V)=f_2(T)+nR\ln(V-nb) \tag{4.1}$$

where f_1, f_2 are such that $f_1'=C_V(T)$ and $f_2'=\frac{C_V(T)}{T}$. Once again we are keeping the discussion general by not requiring C_V to be a constant. The heat absorbed and work done during AB are $Q_{AB}=RT_H\ln(V_B-nb)/(V_A-nb)$ and $W_{AB}=RT_H\ln(V_B-nb)(V_A-nb)+an^2(1/V_B-1/V_A)$. Note that in the vdW case, the heat absorbed and work done are not equal during an isothermal process and the difference is due to the fact that now, unlike in the ideal gas case, the internal energy also depends on volume. During the adiabatic stages BC and DA there is obviously no heat absorbed, and the work done are given by $W_{BC}=f_1(T_H)-f_1(T_L)-an^2(1/V_B-1/V_C), W_{\{DA\}}=f_1(T_L)-f_1(T_H)-an^2(1/V_D-1/V_A)$. Note that the work done during these stages do not cancel each other, and in fact their difference exactly compensates the difference between heat and work during the isothermal stages so that at the end of the cycle one indeed has $\Delta Q=\Delta W$ as first law would demand.

From the expressions for entropy, one sees that during the adiabatic change BC, $f_2(T_H)-f_2(T_L)+nR\ln(V_B-nb)/(V_c-nb)=0$ and during DA, $f_2(T_H)-f_2(T_L)+nR\ln(V_A-nb)(V_D-nb)=0$. Using these, it is easily checked that $Q_H/T_H=Q_L/T_L$ for the vdW Carnot cycle.

Example 4.1: Exotic heat engines

In the Carnot cycle type, heat engines heat is extracted at a single high temperature reservoir and relinquished at a single low temperature reservoir. This does not have to be so. Consider an exotic reversible heat engine which extracts a known amount of heat Q_H from a single high temperature reservoir at T_H, but gives up unknown amounts of heats Q_1 and Q_2 to two lower temperature reservoirs at T_1, T_2 i.e $T_1 < T_H$ and $T_2 < T_H$. If the heat engine delivers a net amount of work W (also taken to be known), find Q_1, Q_2 as well as the efficiency of the heat engine. If this were to be replaced by a single reversible heat engine of the same efficiency, what should the temperature of its lower reservoir be?

From first law it immediately follows that $Q_H=Q_1+Q_2+W$. Since the heat engine is reversible, it also follws that $Q_H/T_H=Q_1/T_1+Q_2/T_2$. In neither of these equations does it matter that Q_1 is positive or not, and likewise for Q_2. These two equations constitute two simultaneous equations for Q_1, Q_2 whose explicit solution is easily worked out to be

$$Q_1=\frac{T_1T_2}{T_H(T_2-T_1)}\left\{Q_H-\frac{T_H}{T_2}(Q_H-W)\right\} \quad Q_2=\frac{T_1T_2}{T_H(T_1-T_2)}\left\{Q_H-\frac{T_H}{T_1}(Q_H-W)\right\} \tag{4.2}$$

The apparent singularity of these expressions when $T_1=T_2$ should not be taken seriously. In that case, the heat engine degenerates into one with a single low temperature reservoir at $T = T_1 = T_2$, and only the sum $Q_1 + Q_2 = Q_H - W$ is determinate, and not Q_1 and Q_2 separately.

The efficiency of this heat engine is of course given by $\eta = W/Q_H$ without having to know any other details. If the heat engine were to be substituted by a Carnot cycle, the low temperature reservoir would be at $T' = (Q_H - W)/Q_H \cdot T_H$.

Example 4.2: Absolute scale again

Consider one mole of a gas described by the equation $P(V-b) = R\theta$, where θ is the temperature. It should be noted that this is the common equation one gets from the van der Waals, Clausius, and Dieterici equations in the limit a $\rightarrow 0$. *Show that the internal energy U is independent of volume. Show that $C_P - C_V = R$ for this system. Assuming C_V to be a constant independent of θ, calculate the the condition for adiabatic changes expressed in terms of θ, V. By analysing a Carnot cycle based on this, show that θ coincides with the absolute scale.*

From the fundamental eqn.(3.7) it is readily seen that $\left(\frac{\partial U}{\partial V}\right)_\theta = \theta\left(\frac{\partial P}{\partial \theta}\right)_V - P = 0$. Therefore, the internal energy is a function of temperature only. If C_V is a constant, $U = C_V\,\theta$. That $C_P - C_V = R$ here also can be seen on rewriting the first law in TdS form

$$\theta dS = dU + PdV = C_V d\theta + Pd(V-b) = (C_V + R)d\theta + (V-b)dP \rightarrow C_P = C_V + R \quad (4.3)$$

One also obtains, from this same equation

$$dS = C_V\frac{d\theta}{\theta} + R\frac{dV}{V-b} \rightarrow S = C_V \ln\theta + R\ln(V-b) \quad (4.4)$$

Consequently the condition for adiabaticity is $\theta(V-b)^{\gamma-1} = const.$ where $\gamma = C_P/C_V$.

Let us take the Carnot cycle to be as depicted in fig.(3.5). The heat absorbed during an isothermal expansion from V_1 to V_2 is $Q = \int PdV = R\theta\ln(V_2-b)/(V_1-b)$. Hence the heat absorbed at the higher reservoir is $Q_H = R\theta_H\ln(V_B-b)/(V_A-b)$, while the heat relinquished at lower reservoir is $Q_L = R\theta_L\ln(V_C-b)/(V_D-b)$. The condition for adiabaticity during DA is $\theta_H(V_A-b)^{\gamma-1} = \theta_L(V_D-b)^{\gamma-1}$, while that during BC is $\theta_H(V_B-b)^{\gamma-1} = \theta_L(V_C-b)^{\gamma-1}$. Putting everything together one concludes $Q_H/Q_L = \theta_H/\theta_L$. But by universality of Carnot cycles this is also T_H/T_L. Hence the θ scale coincides with the absolute scale.

4.2 The steam Carnot cycle

Now we work out the Carnot cycle where the working substance is water and steam in *phase equilibrium*. The physics of this system is obviously more intricate than that of a single gas ideal or otherwise. The first interesting difference brought about is that isotherms here are also *isobars*! This is because the pressure in question being the vapor pressure depends only on temperature. Hence the PV diagram for the cycle looks as shown. What complicates matters here is that as the volume of the system changes, the mass of the liquid also changes. Let us consider a finite cycle,

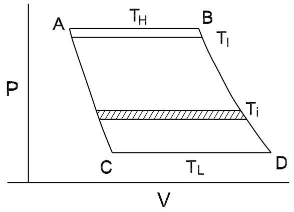

FIGURE 4.1 Steam engine

but subdivide the temperature range T_H, T_L to a large number of segments each dT in extent. Let us consider the segment whose higher temperature is T_i and its lower temperature $T_i - dT$. If $Q_H(T_i)$ is the amount of heat absorbed at T_i, it goes to convert $M_i = Q_H(T_i)/l(T_i)$ mass units of liquid to vapor, where $l(T)$ is the *latent heat per unit mass*. There are two sources of change of *total volume*; one is the volume of the steam created upon absorption of the latent heat, and the other is the *reduction* in volume of the liquid for the same reason. Though the specific volume of the liquid is much smaller than that of steam at temperatures close to the boiling point, it is not so always. In fact, close to the *critical point* the two volumes approach each other. So we shall not neglect the second effect. Then the change in volume is $(\Delta V)_i = M_i)(v_s - v_l)(T_i)$ where v is the *specific volume*, i.e volume per unit mass.

If we now consider the cycle which is of infinitesimal width along P but finite along V, the work done at the end of the cycle is $\Delta W = \Delta V\, dP$ and putting all the factors in place

$$\Delta W = dp\delta V = Q_H \frac{(v_s - v_l)}{l(T)} \frac{dP(T)}{dT} dT = Q_H \frac{dT}{T} \tag{4.5}$$

where we made use of the *Clausius-Clapeyron equation* for dP/dT. But our discussions earlier would show that the way Clapeyron and Clausius arrived at the final form of this equation was by requiring the universality of all Carnot cycles! Eqn.(4.5) simply says that the efficiency of the Carnot cycle using water-steam as its substance is the *same* as the efficiency of the gas cycles.

4.3 The Stirling engine

We now consider the so called *Stirling Engine* based on a reversible cycle that alternately uses *isochoric*, i.e constant volume, and *isothermal* processes. A related cycle is the *Ericson cycle* where instead of isochoric processes one has *isobaric*, i.e constant pressure, processes. Robert Stirling introduced this machine in 1816, nearly a decade before the publishing of Carnot's *Reflections*. It is therefore remarkable that this cycle comes so close to the expectations of Carnot, Clausius, and Kelvin! It is shown schematically in the figure 4.2, depicted as a cycle in the PV-plane.

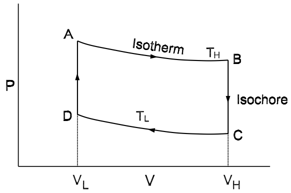

FIGURE 4.2 The Stirling Cycle

The stage AB is *isothermal*, as in the Carnot cycle, at the higher temperature T_H and heat Q_H is absorbed as before. The stage BC is, however, *isochoric*, in contrast to the Carnot cycle. Obviously, not only is work done during this cycle, heat is also relinquished as the system goes from a higher temperature T_H to a lower one at T_L under constant volume. Hence the heat relinquished is $\int_{T_H}^{T_L} C_V(V_1,T)dT$. Likewise, the heat gained by the system during the isobaric stage DA is $\int_{T_L}^{T_H} C_V(V_2,T)dT$. It is to be noticed that in general these heats are not equal. They are the same as long as C_V does not depend on volume, which is so both for ideal gases as well as vdW gases.

It is easy to check that for both ideal gases and vdW gases, the relation $Q_H/T_H = Q_L/T_L$ holds in the case of the Stirling cycle. It is *unlikely* to be so for every working substance, and in that sense, Stirling cycles do not have that universality which the Carnot cycles do. Recall that as long as one has alternating isothermal and adiabatic stages as in Carnot cycles, this relation holds universally by virtue of Clausius inequality. But before interpreting such a relation to mean that the efficiency of the Stirling cycle equals the efficiency $\eta = 1 - T_L/T_H$ of the Carnot cycle, we need to decide how the heat loss and gain during the isochoric phases are to be treated. Though they cancel (at least in the circumstances mentioned above), it is not clear that the efficiency is still to be computed as Δ/Q_H; this is because the *net* heat absorbed by the cycle is irrelevant for the purposes of computing efficiency. Also, during the stages BC and DA the temperatures are *not* uniform.

It is in fact an ingenious part of the design of Stirling engines that takes care of this issue and enables one to reason that indeed the efficiency of the Stirling cycle is $1 - T_L/T_H$. That feature, called the *regenerator* (hence the reason that Stirling engines are called *regenerative*), ensures as best as possible that the heat relinquished during BC is fully utilised during DA. This is done by making the substance physically go through the regenerator, which is nothing but a *heat exchanger,* during both BC and DA. In other words, the regenerator retains the heat *within* the system which would otherwise have been relinquished to the environment, and that too at temperatures that lie in between T_H and T_L. It is only when this regeneration is perfect that Stirling cycles can achieve the Carnot cycle efficiency.

In practical terms, even if the regeneration is not perfect, it goes to improve the overall efficiency and it is for this reason that Stirling engines are more efficient than, say, steam engines. It is a testimony to Stirling's ingenuity that his engine, discovered before Carnot, is likely to make a serious comeback in modern times. Apart from its efficiency, the Stirling engine is also distinct by its ability to make use of diverese sources of heat, not just those burning fuels. In fact in India, *Dalmia Cements* is planning a 10 MW thermal plant based on Stirling engines using solar energy.

4.4 The Otto cycle

The *Otto cycle* is named after the four stroke internal combustion engine built by Nikolaus Otto in 1876, and which forms the basis for almost all the automobile engines today. Its thermodynamic essentials are an *adiabatic compression* from volume V_H to V_L during CD, an *isochoric* process at V_L during DA that increases pressure, an *adiabatic expansion* during AB from V_L to V_H, and finally an *isochoric* process at V_H during AB restoring the system to its original state. In engineering circles DA is called the *ignition stage*, AB the *power stage* and BC the *exhaust stage*.

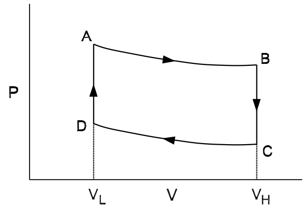

FIGURE 4.3 The Otto Cycle

To simplify the discussion let us take the working substance to be an ideal gas, and that C_V is constant. Let us denote the temperatures at ABCD by T_A, T_B, T_C, T_D respectively. Let the ratio C_P/C_V of the working substance be γ. It is clear that heat Q is absorbed during BC and Q' ejected during DA. As both these are constant volume processes, $Q = C_V(T_A - T_D)$ and $Q' = C_V(T_B - T_C)$. Hence the thermal efficiency is

$$\eta_{otto} = 1 - \frac{T_B - T_C}{T_A - T_D} \tag{4.6}$$

The adiabaticity of AB means $T_C V_H^{\gamma-1} = T_P V_L^{\gamma-1}$, and likewise the adiabaticity of CD implies $T_A V_L^{\gamma-1} = T_B V_H^{\gamma-1}$. Using these conditions, eqn.(4.6) can be simplified to

$$\eta_{otto} = 1 - (\frac{V_L}{V_H})^{\gamma-1} \tag{4.7}$$

The ratio V_H/V_L is called the *compression ratio*. The higher this ratio, the higher is the efficiency of the Otto cycle. It is to be noted that the efficiency explicitly depends on the substance through γ, and hence the Otto cycle lacks the universality of the Carnot cycle. Since the compression ratio can never be ∞, the efficiency can never equal unity, so there is no fear of violating the second law. In practice, the compression ratio can not be too high as the fuel mixture will become so hot during compression that it will preignite, seriously compromising the cycle.

4.4.1 The Diesel cycle

The Diesel cycle is considerably different from the Otto cycle, though this too has two adiabatic stages. Of the remaining two, one is an isochoric stage as in the Otto cycle, but the other is an *isobaric* stage. The schematics of the cycle on the PV-plane is shown in the figure.

The starting stage AB is an adiabatic compression from V_H to V_L, as in the Otto cycle. But the stage BC, which was isochoric at V_L in the Otto cycle, is now an *isobaric expansion* from V_L to an intermediate volume V_I. Heat Q is absorbed during this stage. The next stage CD, as in the Otto cycle, is an adiabatic expansion stage to V_H. Finally, the last stage DA is an isochoric stage, again the same as in the Otto cycle. Heat Q' is relinquished during DA. The Diesel cycle is therefore characterized by *two* compression ratios, $r_1 = V_H/V_L$ and $r_2 = V_I/V_L$.

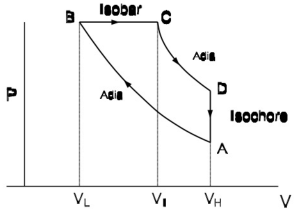

FIGURE 4.4 The Diesel cycle

Therefore, $Q = C_P(T_C - T_B)$, whereas $Q' = C_V(T_D - T_A)$. Note the occurrence of different specific heats in these expressions. Hence the thermal efficiency of the Diesel cycle is

$$\eta_{diesel} = 1 - \frac{1}{\gamma}\frac{T_D - T_A}{T_B - T_A} \tag{4.8}$$

The adiabaticity of CD gives $T_C V_I^{\gamma-1} = T_D V_H^{\gamma-1}$, while adiabaticity of BA yields $T_B V_L^{\gamma-1} = T_A V_L^{\gamma-1}$. Lastly, the constant pressure during BC means $T_B/V_L = T_C/V_I$. These can be simplified successively to get $T_B = T_A r_1^{\gamma-1}$, $T_C = T_B r_2 = T_A r_2 r_1^{\gamma-1}$, and $T_D = T_C\,(r_2/r_1)^{\gamma-1} = T_A\, r_2^{\gamma}$. Putting everything together, the efficiency of the diesel cycle in terms of the r_1, r_2 is

$$\eta_{diesel} = 1 - \frac{r_1^{1-\gamma}}{\gamma}\frac{r_2^{\gamma} - 1}{r_2 - 1} \tag{4.9}$$

Thus, even the diesel cycle is not universal.

4.5 The Brayton cycle

The Brayton cycle is in fact very close to the Otto cycle except that the two isochoric stages of the Otto cycle are replaced by two isobaric stages. Since as far as ideal gases are concerned there is a sort of symmetry between P^{-1} and V augmented with $\gamma \leftrightharpoons \gamma^{-1}$, one expects the efficiency to be of the form $1 - r_p^{\frac{1-\gamma}{\gamma}}$, where $r_p = P_H/P_L$ is the so called *pressure ratio*. We shall show by explicit evaluation that it is indeed so. The cycle consists of first an adiabatic compression stage AB from low pressure P_L to higher pressure P_H, then an isobaric stage BC at P_H, a third stage which is an adiabatic expansion along CD from P_H to P_L, and finally an isobaric compression along DA at P_L bringing the system to its original stage at P_L.

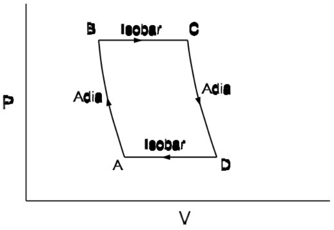

FIGURE 4.5 The Brayton Cycle

The heat Q absorbed during BC is $Q = C_P(T_C - T_B)$, and the heat relinquished during DA is $Q' = C_P(T_D - T_A)$ leading to the efficiency

$$\eta_{brayton} = 1 - \frac{T_C - T_B}{T_D - T_A} \tag{4.10}$$

Adiabaticity along AB gives $T_A^\gamma P_L^{1-\gamma} = T_B^\gamma P_H^{1-\gamma}$, and adiabaticity along CD gives $T_C^\gamma P_H^{1-\gamma} = T_D^\gamma P_L^{1-\gamma}$. Therefore, together they imply $T_B/T_A = T_C/T_D = r_p^{\frac{\gamma-1}{\gamma}}$. Hence

$$\eta_{brayton} = 1 - r_p^{\frac{1-\gamma}{\gamma}} \tag{4.11}$$

4.5.1 The magnetic Brayton cycle

So far we have constructed various cycles based on the (P,V,T) degrees of freedom. In fact, one can construct reversible cycles for power generation as well as refrigeration using other attributes. In this section we show how a Brayton-like cycle can be constructed for magnetic systems. All the necessary thermodynamics are elaborated in chapter 8 on *Magnetic Systems*.

Though a general analysis of the magnetic Brayton cycle is pretty straightforward, it is algebraically rather tedious, and the results not so transparent. For that reason, we simplify the analysis by considering a hypothetical model for which the *Curie Law* is taken to be *exact*. The two results that we shall be mainly using here are for the entropy and specific heat *at constant field*:

$$S(B,T) = S_0(T) - \frac{Va}{2}\frac{B^2}{T^2} \qquad C_B(T) = C_0(T) + \frac{Va}{2}\frac{B^2}{T^2} \tag{4.12}$$

Here a is a parameter occurring in the Curie law, $S_0(T)$ is the entropy in the absence of magnetic fields, and $C_0(T) = TS_0'$ is the zero-field specific heat.

The schematics of a *magnetic Brayton cycle* in the entropy-temperature plane (S-T) is shown in the next figure. Starting at P, the system absorbs heat while the magnetic field is held constant at B_i(*isofield transformation*) during PQ, then it is adiabatically *magnetized* along QR so that the field value is B_f , then another *isofield* transformation along RS brings it to S, where it is *adiabatically demagnetized* along SP to the original state P. It is indeed a magnetic analog of the Brayton cycle previously considered, except that the isobaric stages there have been replaced by isofield stages.

The analysis of this cycle is still rather messy mainly owing to the nature of the adiabats in the problem. Therefore, we shall only analyse an infinitesimal version of the cycle. We take the temperatures to be $T_P = T, T_Q = T + dT$, and the fields to be $B_i = B, B_f = B + dB$. These are the *four* independent parameters of the cycle. Heat $Q_1 = \frac{1}{2}(C_B(B,T) + C_B(B,T+dT))dT$ is absorbed during PQ. Given T_P, T_Q, the adiabats determine T_S, T_R, respectively. Now we use the following notation: if a point (T,B) is connected to $(T', B+dB)$ adiabatically, the shift T along the adiabat is denoted by $\delta(T)$. For example, in our case, $T_S = T' = T + \delta(T)$. The heat Q_2 given out during RS is then given by $Q_2 = \frac{1}{2}(C_B(B+dB,T') + C_B(B+dB,T'+dT'))dT'$. Explicitly

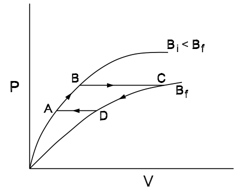

FIGURE 4.6 A Magnetic Brayton Cycle

$$
\begin{aligned}
Q_1 &= (C_0(T) + \frac{VaB^2}{2T^2})dT + \frac{1}{2}(C_0'(T) - \frac{Va^2B^2}{T^3})(dT)^2 \\
Q_2 &= (C_0(T') + \frac{VaB_f{}^2}{2T'^2})dT' + \frac{1}{2}(C_0'(T) - \frac{Va^2B_f{}^2}{T'^3})(dT')^2 \qquad (4.13)
\end{aligned}
$$

The function $\delta(T)$ has to be determined by applying adiabaticity. Applying this to the states P,S means $S(B,T) = S(B+dB, T+\delta(T))$. Writing this out explicitly

$$
S_0(T) - \frac{VaB^2}{2T^2} = S_0(T+\delta(T)) - \frac{Va(B+dB)^2}{2(T+\delta(T))^2} \qquad (4.14)
$$

It is not possible to solve for $\delta(T)$ without further approximations. It is necessary to compute $Q_2 - Q_1$ to quadratic order (compare the situation with Clapeyron's treatment of the infinitesimal Carnot cycle). Furthermore, we treat the Curie law parameter a as small, and keep terms up to quadratic order in that too (turns out the efficiency vanishes if only terms linear in a are retained!). After some algebra, the result for $\delta(T)$ can be expressed as $\delta(T) = \delta^*(T) + \bar{\delta}(T)$ where

$$\delta^*(T) = \frac{VaBdB}{TC_0(T)} \qquad \bar{\delta}(T) = -\frac{V^2a^2B^3dB}{T^3C_0(T)^2} \tag{4.15}$$

It is to be noted that while δ^* is linear in a, $\bar{\delta}$ is quadratic.

After even more algebra, the magnetic work done during the cycle, to the relevant approximation is found to be

$$Q_2 - Q_1 = dT\left\{(\delta(T)C_0)' + \frac{VaBdB}{T^2} + \frac{VaB^2}{2}(\frac{\delta(T)}{T^2})'\right\} \tag{4.16}$$

Rather remarkably

$$\delta^*(T)C_0'(T) + (\delta^*)'(T)C_0(T) + \frac{VaBdB}{T^2} = 0 \tag{4.17}$$

so the part of $Q_2 - Q_1$ linear in a vanishes! The final result for the efficiency of our infinitesimal magnetic Brayton cycle is

$$d\eta_{magbrayton} = (Va)^2B^3\left(\frac{3}{2T^4C_0^2} + \frac{5C_0'}{2C_0^3T^3}\right) \tag{4.18}$$

Clearly there is no universality to these cycles. Please see problem 4.5 for a complete theory of magnetic Brayton cycle.

4.6 Carnot cycle with photons

We finally discuss a Carnot cycle with *Photons*. Of course, in the spirit of thermodynamics, we should not be bringing any microscopics into the picture, and photons are indeed such a microscopic aspect of *electromagnetic radiation*. A more appropriate decription would be Carnot cycles with *blackbody radiation*. Blackbody radiation refers to a state of electromagnetic radiation that is in thermal equilibrium, and is consequently associated with a temperature. Once again, this Carnot cycle is of the *gedanken* type, but touches on one of the most beautiful chapters in physics ever written, bringing to the fore, more than ever, the power and elegance of thermodynamics. Before delving into the Carnot cycle, let us discuss the thermodynamics of blackbody radiation first.

4.6.1 The Thermodynamics of the radiation field

A *blackbody* is a hollow box whose walls are maintained at constant temperature. Let us consider a very small opening in the box through which radiation can easily get in, but not easily get out. Inside the cavity (hollow box) the radiation will be completely absorbed by the walls and re-emitted into the cavity. This process of absorption and remission brings the radiation into *thermal equilibrium* with the cavity, and consequently assumes the same temperature as the latter.

That radiation, one of whose familiar forms is *light*, can be in a state of thermal equilibrium is actually rather profound; it is as amazing as the possibility that light could *fall* under gravity! Of course, the latter is not just a possibility now, it is a well established consequence of *Einstein's General Relativity* theory. It is indeed true that the details of the mechanism by which radiation in a blackbody reaches equilibrium are mired in various microscopic details, which, with our oft-stated intentions, shall be kept out of purely thermodynamic descriptions. But a cursory description of them shall not be out of place here.

The nature of these microscopics is *twofold*; firstly, at a purely classical level, the electromagnetic field and its interactions with charges is completely described by *the Maxwell Equations* (not to be confused with the *Maxwell Relations* discussed elsewhere in the book). According to this, charges emit and absorb radiation, and these processes can in fact be treated on par with *chemical reactions* where one treats even radiation as a component. The other is the atomistic nature of matter, which when combined with *Quantum Theory* provides a very succesful description of the interaction between radiation and matter. This too supports the earlier picture of treating this interaction essentially along the lines of chemical reactions, with radiation itself as one of the ’chemical’ components.

But for the purposes of the thermodynamic description of radiation to be discussed now, it suffices that there is exchange of energy between radiation and matter, and that this will, depending on the circumstances, lead to a state of thermal equilibrium even for radiation. Then, in keeping with the structure of thermodynamics, all that is required are a specification of the degrees of freedom and the analog of equations of state.

From Maxwell theory it follows that radiation can be characterized by an *energy density* u, and a pressure p, and that these are related by $p = u/3$. The other feature is that the *energy density*, u, related to U by $U = Vu(T)$, depends only on *temperature*. much like the situation in ideal gases. Now, it is not possible to *derive* these laws in exactly the same way as $PV = nRT$ could not be *proved* within thermodynamics, but instead must be admitted as a characterization of ideal gases based on *empirical data*. The same attitude has to be adopted as far as these *thermodynamic equations of state* of radiation are concerned.

The rest follows from the laws of thermodynamics. Let us consider the first law in the TdS form for this system:

$$dS = \frac{1}{T}(dU + pdV) = \frac{V}{T}\frac{du}{dT}dT + \frac{4}{3}\frac{u}{T}dV \tag{4.19}$$

The exactness of the differential dS leads to the following integrability condition and consequence:

$$\left(\frac{\partial}{\partial V}\left(\frac{V}{T}\frac{du}{dT}\right)\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{4}{3}\frac{u}{T}\right)\right)_V \to \frac{du}{dT} = 4\frac{u}{T} \to u(T) = aT^4 \tag{4.20}$$

This is a remarkable conclusion indeed; that $u(T)$ is proportional to T^4 is the essential content of a law *empirically* established by J. Stefan. It was Boltzmann who gave this thermodynamic derivation of it. According to Sommerfeld, Lorentz, in a memorial address to Boltzmann, described the above thermodynamic derivation as *a veritable pearl of theoretical physics*[64]! The law is aptly called the *Stefan-Boltzmann law*, and the familiar *Stefan-Boltzmann constant* σ is related to a by $\sigma = \frac{ca}{4\pi}$ with c being the *velocity of light*.

Having obtained $u(T)$, both U and S for the blackbody radiation follow immediately:

$$U(T,V) = aVT^4 \qquad S(T,V) = \frac{4}{3}aVT^3 \tag{4.21}$$

Comparison with ideal gases It is worth comparing the blackbody thermodynamics with ideal gas thermodynamics. Firstly, the ideal gas system requires specification of *three* quantities, say, V,T,n, for specifying its states. But in the case of the blackbody, only *two* seem to be sufficient. In other words, there is no notion of a *molecular weight* for the photon gas! This is a very *deep feature* of the radiation gas, and we shall refer to it at different points of this book. A related observation [37] is that at any given temperature (and hence pressure), the volume of a photon gas can be made to vanish! To visualize this, we can imagine the hollow box being fitted with a piston; the zero volume can be achieved by pushing the piston all the way down. The entire energy contained in U to start with will then have been passed on to the reservoir, which maintains the walls at a fixed temperature. However, the entropy of the zero volume state is zero even at nonzero temperatures, and this would violate the expectations from third law that no adiabat connect $T = 0$ to $T \neq 0$, but zero volumes are sort of bizarre!

Since the pressure $p = \frac{u(T)}{3}$ is a function of T alone, every *isothermal process* of the photon gas is, at the same time, an *isobaric process* too! This is reminescent of the situation in the steam-water coexistent phase, where vapor pressure was a function of temperature alone. There too, the amount of water in the vapor phase was not a constant.

Since $S = \frac{4a}{3}VT^3$, it follows that *isentropic processes*, which are also *adiabatic*, obey $VT^3 = const$. Another form for the adiabat is $pV^{4/3} = const$. This does bear a close to resemblance to the adiabat of an ideal gas which took the form $PV^\gamma = const$ with γ taking the value 4/3. But in the case of ideal gases γ had the interpretation of being the ratio of the specific heats C_P/C_V. Does the adiabatic index of 4/3 for the photon gas have a similar meaning?

It is clear that the index 4/3 does not have the same meaning because C_P for the photon gas is a meaningless concept; this is so as during an isobaric process, temperature also gets fixed and it is meaningless to talk of specific heats then! What about C_V? This does exist, and on using its definition $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, takes the value $C_V = 4aVT^3$. Remarkably, this specific heat is in conformity with the third law, which is of course a consequence of the entropy in eqn.(4.21) satisfying the third law. The ideal gas $C_V(T)$ can be any function of T, so in this respect the ideal gas and the photon gas have compatible behaviours.

We can go on and make a few more comparisons. By reasoning similar to the above, it is easy to conclude that the concept of a *volume expansion coefficient* $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ also does not make sense for a photon gas and nor does the *isothermal compressibility* $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$.

4.6.2 Photon Carnot cycle

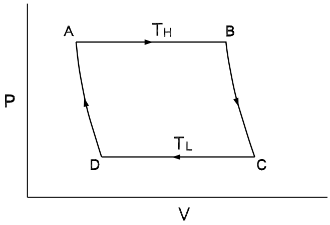

FIGURE 4.7 A Carnot Cycle With Radiation

Now we consider a Carnot cycle whose working substance is blackbody radiation. It is shown schematically in the P-V plane as shown in the diagram. Starting at the state A with volume V_A at temperature T_H, an isothermal expansion at T_H takes it to B with volume $V_B > V_A$. The heat absorbed is $Q_H = T_H(S_B - S_A) = 4a/3(V_B - V_A)T_H^4$. Then an adiabatic stage takes B with volume V_B at T_H to C with volume V_C at T_L. Therefore, $V_B T_H^3 = V_C T_L^3$. The third stage of the cycle is an isothermal compression from C with volume V_C at T_L to the state D with volume T_D also at T_L. The heat relinquished during this stage is $Q_L = 4a/3(V_C - V_D)T_L^4$. Lastly, the system returns from D to A along an adiabat and hence $V_D T_L^3 = V_A T_H^3$. The efficiency of the photon Carnot cycle is, therefore,

$$\eta_{photon} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{V_C - V_D}{V_B - V_A}(\frac{T_L}{T_H})^4 \tag{4.22}$$

But the adiabaticity conditions yield $V_A/V_D = (T_L/T_H)^3 = V_B/V_C$. Upon using these, the efficiency of eqn.(4.23) becomes

$$\eta_{photon} = 1 - \frac{T_L}{T_H} \tag{4.23}$$

which is nothing but the efficiency of an ideal Carnot cycle.

If we had allowed V_A to take zero value, the entropy at A would have been zero too. This would have been consistent only if V_D had been zero too, making V_A/V_D *indeterminate*. But then, we would not have needed to know this ratio at all as the formula for the efficiency would have been $\eta = 1 - V_C/V_B(T_L/T_H)^4$ and only the consequences of BC being an adiabat would have sufficed to evaluate it. The final result, as can easily be checked, would still have been as given by eqn.(4.23).

4.6.3 The thermodynamic gateway to quantum world

While the above considerations show how succesful thermodynamics had been in capturing some essential features of the blackbody radiation, troubles began when one attempted to go beyond the total energy density, total entropy etc., and attempt to explain the *frequency dependences* in the observed *spectrum* of blackbody radiation. The frequency distribution of the energy density was an observable feature, and initial observations seemed to indicate that the energy density of radiation when restricted to a particular frequency ν seemed to obey the so called *Wien law*, which can be roughly stated as

$$U_\nu \simeq e^{-\frac{K\nu}{T}} \tag{4.24}$$

We shall be very heuristic here, as we can not give a full and proper account of the revolutionary developments that led to quantum theory. What we wish to do, instead, is to give a flavor of how considerations based on entropy, in the hands of Planck [55, 56] and Einstein [14], played a decisive role in finding the path to quantum theory. Planck expressed the Wien law in quite a different, but equivalent form, by invoking entropic considerations. That form turns out to be

$$\frac{d^2S}{dU^2} = -\frac{K'}{U} \tag{4.25}$$

where K' is a different constant, but related to K introduced earlier. Integrating this equation once and using $\frac{dS}{dU} = \frac{1}{T}$ shows the desired equivalence to Wien's law.

But soon afterwards data started becoming available at *longer wavelengths* and here the behaviour seemed entirely different, and seemed to suggest

$$U_\nu \simeq K''T \tag{4.26}$$

What was confusing things further was that classical statistical mechanics gave eqn.(4.26) for *all* frequencies (Rayleigh-Jeans law) but experiments clearly contradicted it at high frequencies. Planck noticed that the experimental results at long wavelengths (the Rayleigh-Jeans behaviour) could be stated equivalently as

$$\frac{d^2S}{dU^2} = -\frac{K''}{U^2} \tag{4.27}$$

Planck at first sought a behaviour that would interpolate between these two limits. Instead of seeking that interpolation directly at the level of U, he sought to use entropy as a guiding principle. He proposed

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta+U)} \tag{4.28}$$

as a relation interpolating between eqn.(4.25) and eqn.(4.27). Integrating once, one gets

$$U = \frac{\beta}{(e^{-\frac{\beta}{\alpha T}} - 1)} \tag{4.29}$$

This can be identified with the famous Planck blackbody radiation formula on identifying $\alpha = -k$ and $\beta = h\nu$ where k, h are respectively the *Boltzmann* and *Planck* constants. Instead of the interpolation formula for U, one can focus on the expression for the entropy obtained upon fully integrating eqn.(4.28):

$$S = k\left[(1+\frac{U}{h\nu})\ln(1+\frac{U}{h\nu}) - \frac{U}{h\nu}\ln\frac{U}{h\nu}\right] \tag{4.30}$$

It was preciely the entropy of radiation that Einstein chose to concentrate on. In particular, he chose to look at the entropy of radiation for high frequencies, i.e in the limit when Wien's law had been found to be valid experimentally:

$$S \simeq -k\frac{U}{h\nu}\ln(\frac{U}{h\nu}) \tag{4.31}$$

Recall that U is the energy density, so expressed in terms of total energy E, Einstein recast this as

$$S = k\frac{E}{h\nu}\ln\frac{V}{V_0} \tag{4.32}$$

What was remarkable to Einstein was the close resemblance of this to the entropy of an ideal gas expressed in the form $S_{ideal} = k\frac{E}{\varepsilon}\ln\frac{V}{V_0}$, where ε is the energy per atom (molecule) of the ideal gas. Einstein drew the far reaching conclusion that insofar as its thermodynamic properties are concerned, *blackbody radiation* behaves like a *gas* of particles, later christened *photons* by Gilbert Lewis.

But this revolutionary thought process could be brought to completion only with the equally revolutionary ideas of the Indian physicist Satyendra Nath Bose, who treated the photons as *indistinguishable* and introduced a new statistics that now goes by the name of *Bose-Einstein Statistics*. The rest, as they say, is history. The subsequent impact of these ideas has been mind boggling, one of which is the discovery of a new state of matter called the *Bose-Einstein Condensate*.

Of course, one has to depart from the strict confines of thermodynamics and foray into statistical mechanics to make these connections, but the crucial role played by thermodynamics, and in particular entropy, in these epoch-making connections is undeniable.

4.7 Problems

Problem 4.1 Consider a real life heat engine operating between T_1 and T_2 with $T_1 > T_2$ that has an efficiency equalling 90% of the maximum possible. Likewise consider a real life refrigerator working between T_3 and T_4 such that $T_4 < T_3$ and which has a coefficient of performance that is also 90% of its maximum. If the work output of the heat engine drives the refrigerator, find the ratio of the heat absorbed by the heat engine to the heat relinquished by the refrigerator.

Problem 4.2 If a real life refrigerator has a coefficient of performance that is 50% of the theoretical maximum, what is the rate of entropy production per unit power consumed?

Problem 4.3 Discuss the details of a Carnot cycle with a Fermi gas (like He_3, or neutrino gas, to be more exotic) as its working substance.

Problem 4.4 Discuss how a Carnot cycle operating with a quantum ideal gas would work. Work out the cases when a) both the temperatures are above the Bose-Einstein transition temperature and b) when both temperatures are below the transition temperature. What happens when one is above, and the other below, the transition temprature?

Problem 4.5 The magnetic Brayton cycle in the text was analyzed assuming Curie law. Carry out this analysis when the magnetization is given by the classical Langevin theory.

Problem 4.6 The anomalous expansion of water at 4° C makes a Carnot cycle operating in the vicinity of this temperature, say between 3° C and 5° C, rather unusual. As both the isothermal expansion at the higher temperature and the isothermal contraction at the lower temperature absorb heat (when pressures are low enough), making it appear that heat is entirely converted into work, violating the second law. Analyse this situation and show there is no such violation.

Problem 4.7 Plot the Otto, Brayton, and Diesel cycles in the temperature-entropy (S-T) plane.

Problem 4.8 A rubber band can be envisaged as a one-dimensional system whose length L plays the role of volume, and its tension $\mathscr{T}$ that of -P. The first law for rubber bands then reads $TdS = dU - \mathscr{T}dL$. The internal energy and tension are given by $U = cL_0T$ and $\mathscr{T} = (L - L_0)$ as long as L is not too different from L_0. Construct a Carnot cycle with this rubber band as a working medium.

Problem 4.9 The compression ratio of an Otto cycle working with air is 10. The temperature and pressure at the beginning of the compression cycle are 300 K and 1 atm. If combustion adds 50 kJ/mol of heat, find the temperature and pressure at the end of each segment of the cycle, and the thermal efficiency.

Problem 4.10 Determine the compression ratio of an Otto cycle which delivers maximum work for given T_L and T_H. Why can't the work be increased forever by simply increasing T_H?

Problem 4.11 Show that the observed increase of volume in freezing water to ice would lead to a violation of the second law if at the same time the freezing point increases with pressure (normal behaviour) by constructing a Carnot cycle based on ice-water as the working substance. Are the conclusions sensitive to whether heat is described by caloric or according to first law? This line of reasoning was first pointed out by Kelvin.

5 Specific Heats: Magnificent Bridges

5.1 A brief history

It is clear that thermodynamics as understood today has two, among many, deep concepts at its very heart, namely, *heat* and *temperature*. The concept of *specific heat* is what *bridges* these two. This is in the sense that specific heats tell us how a certain amount of heat supplied to the system changes its temperature. Specific heats have played decisive roles in so many fundamental developments including that of thermodynamics itself. They played a key role in the development of *quantum theory*, and even today they continue to play a central role.

In fact, so central was the role played in the development of quantum theory that the final talk of the very first Solvay Meeting on *Radiation and Quanta*, held in 1911, was entirely devoted to specific heats. It was titled *The Present State of the Problem of Specific Heats*, and was delivered by none other than Albert Einstein, whose pioneering work on the specific heats of solids had indeed opened the flood gates! The first (1911) and the fifth (1927) (on *Electrons and Photons*) Solvay meetings are considered *legendary*; while the first highlighted the immense crisis in physics at that time, the second witnessed the essential culmination of quantum theory.

In essence, specific heats monitor the health of potential theories, and can be called the thermometers for theories. It is the *temperature and volume* dependences of specific heats that enable them to play this role. Such dependences are a major difference from the early days when specific heats were thought to be *constants* characterstic of systems. The temperature dependences, in particular, herald *new* thermodynamic aspects that hitherto lay frozen. In that sense, as more and more of such features, emerging essentially out of additional *microscopic* degrees of freedom, become important, they leave their footprints on specific heats.

Many such features of specific heats are covered in quite some detail in various parts of this book. We shall not repeat those details in this chapter. Instead, what we shall do is try and give a *bird's eye view* of the entire landscape of specific heats, to enable one to perceive all such details within a single perspective. We start by recounting some historical developments of this subject.

That adding 'heat' changes the 'temperature' of a body must have been known for a very very long time indeed. That heat can be added *without* changing the temperature of a body must indeed have come as a surprise. This discovery is credited to **Joseph Black (1728-1799)**. Black is said to have slowly melted ice and shown addition of heat still maintained the temperature of ice+water.

Early Scientific Studies One of the earliest, and scientifically systematic, works to have experimentally determined the specific heat of gases was that of **Delaroche and Berard** in 1813. This particular work stands out for many reasons. It was an essay that had won a prize competition of the famous *Institut de France*. It was considered the most precise determination of specific heats of a number of gases. Its influence went undiminished for nearly half a century.

We have already discussed the central role assumed by this experiment in Carnot's *Reflections*. Its results, according to Ingo Mueller [47], were also used by Robert Mayer in his estimation of the mechanical equivalent of heat, and by Clausius too, in his thinking on the internal heat. The incorrect values of the Delaroche and Berard specific heats had their negative impact then.

But the most serious negative impact this experiment had was on Carnot's work. This work had unambiguously claimed that the gases it had studied, very close to being ideal, had a *volume dependence* to their specific heats. As we have seen in our detailed account of Carnot's theory, the constancy of $C_P - C_V$ in the caloric theory required both C_V and C_P to have a *mild* logarithmic dependence on volume. Carnot felt that the results of Delaroche and Berard supported such a behaviour.

The Delaroche-Berard results turned out to be erroneous, and the said volume dependence of the specific heat of gases spurious. Had this grave error been detected during Carnot's lifetime, already close to two decades after the experiment, it is hard to imagine the course that development of thermodynamics would have taken. It was **Regnault**, in 1862, that showed the results of Delaroche-Berard to be spurious.

This episode not only highlights the extreme importance specific heats played in the development of a fundamental theory, it also highlights how in science there can be circumstances when completely wrong experiments hold sway for unreasonably long periods! For a fuller historical account of this see Mendoza [46].

Dulong and Petit The next extremely important development was the experimental determination of the specific heat of solids by **Pierre Louis Dulong** and **Alexis Therese Petit** in 1819. They found that the *molar specific heats* of all solids showed a *universal* value of 3R, where R is the gas constant. Of course, they had only established the constancy of the specific heats without relating the constant to the one appearing in the ideal gas laws.

But soon it was found that the Dulong-Petit law was accurate only at high enough temperatures. At intermediate and low temperatures there were significant deviations from the 3R value. Before discussing the significance of these deviations, and their remedies as pioneered by Einstein, let us continue with our historical narrative.

Another experiment of significance was that by **Charles Bernard Desormes (1771-1862)** and **Nicolas Clement (1779-1841)**, performed also in 1819. This measured the ratio of the specific heats $\gamma = C_P/C_V$ for (ideal) gases. They had established the value of $\gamma = 1.4$ for air, a value which Carnot had used extensively in his *Reflections*. But as already mentioned elsewhere, **Pierre Simon Laplace (1749-1827)** had used a similar value in his work in 1816 on the speed of sound, wherein he had corrected a major flaw in Newton's calculations.

Prominent among the early experiments on specific heats and other thermal properties is the series of very carefully planned determinations of the thermal properties of *steam* by **Henri Victor Regnault (1810-1878)**. He published them in a series of reports, the first in 1847, and the next two in 1862 and 1870 [60]. Kelvin made extensive use of whatever data of Regnault was available at the time of writing his commentary on Carnot's work. His main aim was the determination of Carnot's universal function $\mu(t)$. He could not come to any definite conclusions, nor could Clapeyron.

Thus, well before Carnot a great deal seems to have been known about the specific heats C_V, C_P for gases. These too, and hence their differences $C_P - C_V$ seemed to be *constants*. It was a triumph for Clausius's first law that it could naturally explain the constancy of this difference. In fact, the first law and the entropy axiom lead to a number of interesting relations involving specific heats, as detailed in chapter 3. These relations are general enough to accommodate both temperature and volume dependences of specific heats.

Specific heats of liquids and solids Though for gases C_P and C_V can be quite different, for liquids and solids, the difference between these two is not so great. There are many ways of understanding this; the compressibilities of liquids and solids are generally much lower than those of gases. The internal energies of liquids and solids are also, to a good approximation, only functions of temperature alone.

In this context, it is worth recalling that for the case of the blackbody radiation, C_P was ill-defined (see section 4.6). This was because of the exceptional behaviour in that case wherein pressure was a function of temperature only, and therefore no constant pressure process could result in any change of temperature. The situation is the same with saturated vapor pressures of liquids, which also depend only on temperature. So it is meaningless to talk of their C_P also.

5.2 Varieties of specific heats

While we have so far discussed C_P and C_V, it is clear that there is an infinite multitude of specific heats! This arises from the fundamental premise of thermodynamics that *heat is not a state function*. So the heat absorbed by a system in going from A at temperature T to a neighbouring state A' at temperature $T + dT$ *depends* on the path connecting the two states. C_P is the specific heat when the path in question is an isobar, i.e $P = const$, and likewise C_V is the relevant specific heat when the path is an isochore.

But any relation of the type, say, $R(V,T) = const$ also defines a path, and clearly there are infinitely many of them. So, it makes sense to define a specific heat C_R whose meaning is $\Delta Q/\Delta T$ as $\Delta \to 0$ while keeping R constant. From first law, $\text{đ}Q = C_V dT + \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\} dV$. Combining with $\left(\frac{\partial R}{\partial T}\right)_V dT + \left(\frac{\partial R}{\partial V}\right)_T dV = 0$, one gets

$$C_R(V,T) = C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_R \qquad \left(\frac{\partial V}{\partial T}\right)_R = -\left(\frac{\partial R}{\partial T}\right)_V \left(\frac{\partial R}{\partial V}\right)_T^{-1} \tag{5.1}$$

Note that the factor $\left(\frac{\partial U}{\partial V}\right)_T + P$ can not vanish generically, as, if it did, $\text{đ}Q$ would be a perfect differential. Using eqn.(3.7) this can be recast as

$$C_R(V,T) = C_V(V,T) + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_R \tag{5.2}$$

Though there is a multitude of specific heats, given C_V and C_P, or specific heats C_X, C_Y where X,Y are any two *independent* variables, any other C_R can be expressed in terms of them, as for example,

$$C_R(V,T) = C_V(V,T) + (C_P - C_V)\left(\frac{\partial V}{\partial T}\right)_R \left(\frac{\partial T}{\partial V}\right)_P \tag{5.3}$$

In addition to specific heats like these, one can have additional specific heats such as $C_{\mathscr{M}}, C_B$ in magnetic systems. They too obey a number of properties analogous to C_P, C_V, and these have been expounded in detail in the chapter on magnetic systems. There we have also discussed the properties of additional specific heats C_s, C_n that arise in the superconducting systems. These details can be found in chapter 8.

5.2.1 Negative specific heats

With such a generalized notion of specific heats, it will come as no surprise that specific heats can sometimes be *negative*. A classic case is that of the specific heat of the steam-water system in coexistence. As already emphasized, C_P is the wrong specific heat to consider. Instead, let us consider the path to be along the *coexistence curve*, which is governed by the *Clausius-Clapeyron equation*. This is dealt with at length later. Following Sommerfeld [64], if we call this specific heat C_ϕ, then it follows (see chapter 2 for details) that

$$C_\phi = C_{liq} + \frac{dL}{dT} - \frac{L}{T} \tag{5.4}$$

Here C_{liq} is the molar specific heat of water in the liquid phase and L the molar latent heat. He uses the experimentally determined values for L and $\frac{dL}{dT}$ at the boiling point (just for illustration) $T = 373K$ to estimate C_ϕ. These values are $L = 9.7$ Kcal, $\frac{dL}{dT} = -11.5 cal/deg$ leading to $C_\phi = -19 cal/deg$. So the specific heat of saturated steam along the coexistence curve is indeed negative! The physical significance of this is that when heat is added to the system, part of it goes off as latent heat and part towards performing mechanical work that in the end some of the internal energy has to be depleted. Curiously, there is a parallel to this in *black hole thermodynamics* where adding energy to the black hole actually *lowers* its *Hawking temperature*!

Example 5.1: C_V of nitrogen

If it takes 4.2 kJ of electrical heating to raise the temperature of 2 moles of nitrogen, at constant volume, by 100 K, calculate the C_V of nitrogen assuming that it behaves like an ideal gas.

Since the process is at constant volume, the change in internal energy ΔU must match the heat supplied by the electrical heater. Since nitrogen is said to behave like an ideal gas, the change in internal energy at constant volume is given by $\Delta U = nC_V\Delta T$. Therefore $C_V = \Delta U/(n\Delta T) = 21 J/K$. This is very close to the value $5R/2 = 20.8J$ which is the molar C_V of an ideal diatomic gas.

Example 5.2: C_P in superconducting transitions

If the molar entropy difference between the normal and superconducting phases depends linearly on $T - T_c$, show that there is a discontinuity in C_P at the transition temperature and that this discontinuity is proportional to T_c.

The specific heat at constant pressure is given by $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$. The entropy difference between the two phases is given to be of the form $S_s - S_n = a(T - T_c)$(this has to be so since the entropy difference vanishes at T_c), it is readily seen that at $T = T_c$, $C_P^s(T_c) - C_P^n(T_c) = aT_c$.

5.3 Specific heats and the third law

As we saw in our discussion of the (non)attainability of absolute zero, the third law requires all entropies to vanish at absolute zero, and consequently all specific heats must vanish as absolute zero is approached. The full implications of this are enormous. It means that whatever be R, C_R must vanish in this limit. The ideal gas specific heats obviously do not satisfy the third law which can be interpreted to mean that no gas can behave ideally at temperatures very close to zero. In this book we have discussed a number of specific heats that do vanish in the limit of absolute zero. In the last section of this chapter, an elaborate discussion is given of specific heats in the context of the third law.

5.3.1 Specific heats and cooling powers

The Nernst-Planck postulate or the so called third law of thermodynamics precludes the attainment of absolute zero. In practical terms, this translates to the fact that the *cooling powers* of *all* cooling devices must vanish as absolute zero is approached.

The specific heats play a somewhat subtle role here. By the same third law, all specific heats must also become vanishingly small in this limit. But a small specific heat has also the consequence that for a given loss of heat, the drop in temperature is large. This may give rise to the paradoxical thought that the third law actually facilitates faster cooling. But there is no paradox as both the cooling rates as well as specific heats are eventually governed by entropic considerations. It is instructive to see this more quantitatively. Let us restrict attention to adiabatic cooling only.

As explained later on, the essence of the adiabatic cooling method consists in the triple product identity

$$\left(\frac{\partial S}{\partial \xi}\right)_T \left(\frac{\partial \xi}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_\xi = -1 \rightarrow \left(\frac{\partial T}{\partial \xi}\right)_S = -\frac{1}{C_\xi} T \left(\frac{\partial S}{\partial \xi}\right)_T \tag{5.5}$$

Here ξ is some control parameter; in adiabatic demagnetization this is the magnetic field etc. In the context of adiabatic demagnetization, to see that even though the specific heat C_ξ vanishes as $T \to 0$, the other factors in the numerator vanish even faster, one should go beyond approximations like Curie law that are used in such discussions. One can, for example, use the *Langevin model* with some ansatz for the non-magnetic specific heat so that they are in conformity with the third law. Then one sees that in general cooling rates vanish much faster than specific heats.

5.4 Specific heats and microscopics

We have taken great care not to emphasize the atomistic aspects, with the desire to showcase the powers and the immense scope of thermodynamics, and certainly not to downplay the importance of the atomistic picture. On the other hand, it is clear that a certain minimal atomic perspective should not be totally avoided, making everything look too empirical. The behaviour of specific heats is a case in point.

At the level of thermodynamics, it suffices, for example, to know the *empirically determined* C_V; the laws of thermodynamics then go on to predict a number of relationships which too can be empirically tested. For example, even after restricting attention to ideal gases only, it is enough from thermodynamics point of view to say, for example, that C_V of some gas is 3/2 or 5/2; that one of them is *monatomic* or the other is *diatomic* from the atomic point of view, adds no more content to the thermodynamic description. But it is clearly of importance to know this atomic aspect should one wish to go further.

In fact, such constant values of C_V are clearly in contradiction of the Nernst postulate. The fix for this indeed exploits the atomic details. Since within thermodynamics there is no scope for including such details, any fix must necessarily come from going beyond the thermodynamic description, as for example from going to *Statistical Mechanics*. But it turns out that merely going to *classical Statistical Mechanics* will not suffice, and the cures lie in purely *Quantum Mechanical* Aspects!

Anyway, returning to the issue of microscopics, a balance can be struck by taking a few, but crucial results from microscopics (including possibly a statistical analysis) as *inputs* into the thermodynamic formalism. For example, bringing in notions of *electrons* and their properties into a thermodynamic discussion undoubtedly amounts to too much microscopics. But a result from the quantum statistical mechanical analysis of a gas of electrons which says, for example, that their very low temperature behaviour of specific heats is a *linear* temperature dependence, i.e $C_e \simeq T$, can simply be incorporated into thermodynamics yielding a host of useful results and insights. After that, there will never be a need to bring in the microscopics of electrons again.

Continuing in this vein, we could treat electrons as a thermodynamic 'component' whose *equations of state* are prescribed. From our discussions of the blackbody radiation, one can for example treat radiation as a component whose equations of state are $PV = U/3$ and $U = Vu(T)$. From a microscopic point of view, a statistical mechanical treatment of solids can be given in terms of the so called *lattice vibrations*. From our point of view, it suffices to give an *effective* description of them by specifying the equations of state. For example, the low temperature specific heat of such lattice vibrations turns out to be of the form $C_{lattice} \simeq a_l T^3$. Incidentally, this was also the behaviour of the low temperature specific heat of blackbody radiation(for which C_P is a meaningless concept).

The linear dependence of the electronic specific heat was the *leading order* result, valid in the immediate neighbourhood of absolute zero. At somewhat higher temperatures there are additional corrections and the behaviour is $C_e = a_e T + b_e T^3 + \ldots$. So when one considers the contributions from both the electronic and lattice vibrations, the total specific heat would have the behaviour $C = a_e T + (b_e + a_l) T^3 + \ldots$. It is to be noted that both the electronic and lattice vibration specific heats obey the third law.

In this manner, we could augment the list of possible thermodynamic components. Further examples are magnetic systems for which we can introduce the magnetic specific heats, superconducting systems with specific heats C_s, C_n for the *superconducting* and *normal* components. The specific heat C_s vanishes *exponentially* i.e $\simeq f(T)\, e^{-a/T}$ at very low temperatures, thereby satisfying the third law. Such exponential vanishing at low temperatures is also a feature of *spin* systems. For example, in magnetic systems, even without any applied magnetic fields, the tiny atomic magnets can be taken to be a thermodynamic system on their own, with their own characterstic entropy, internal energy etc..It is in fact what underlies the phenomenon responsible for *Pomeranchuk Cooling* because at very low temperatures the spin system entropy dominates, and results in the curious outcome that the solid phase of liquid He3 at these temperatures has *higher* entropy than the liquid phase.

5.5 Specific heats herald quantum theory!

As noted earlier, the Dulong-Petit law says that the molar specific heat of all solids must be 3R. This value is also what classical statistical mechanics gives. But the experimentally observed specific heats deviate from this value, and in fact the Dulong-Petit value is preferred only at high enough temperatures. Note that the Dulong-Petit value does not obey third law whereas the experimental data certainly seems consistent with the third law. A classical statistical mechanical treatment of solids, taking into account an atomistic picture of the constituents and some presumed forces between the atoms still does not fix the problem. This is where Einstein's seminal work on specific heats comes into the picture. In laying the foundations of quantum theory, this was as important as the work of Planck on the blackbody radiation and Bohr's work on the structure of atoms. Let us briefly visit Einstein's ideas.

5.5.1 Einstein and specific heats

Einstein's attention was focused on the experimental fact that the specific heat of diamond at room temperature was anomalously low when compared to the Dulong-Petit value of 6 cal/deg (see [52] for a detailed account). It is interesting to recall the history of this anomaly. The Dulong-Petit work was published in 1819 [13]. Around 1840 de la Rive and Marcet [11] found that at low temperatures specific heat of diamond was only 1.4 cal/deg, less than a fourth of the Dulong-Petit value. Regnault, to whose pioneering works on the thermal properties of steam we have already referred, reported a year later, a value around 1.8 cal/gm. De la Rive and Marcet had worked at much lower average temperatures than Regnault. This was a pointer to the fact that either the Dulong-Petit law was completely wrong, or that specific heats could have appreciable temperature dependences.

Heinrich Weber, some three decades later in 1872, undertook a careful reexamination of the diamond case by accurately determining the specific heat of diamond in the range 0-200 ° C. He found unambiguous evidence for a substantial temperature dependence of specific heats. By the observed trend at the higher temperatures, he also conjectured that the DP-law would be correct at high temperatures. This he confirmed in 1875 by going to temperatures as high as 1200 K, where he found a value of 5.5 cal/gms as against the DP value of 6. It was Weber's data that attracted Einstein's attention. Incidentally, Weber was one of Einstein's teachers and it is said that Einstein initially had done some of his doctoral work with him.

It is remarkable that these far reaching experimental discoveries had almost no theoretical impact for another 30 years! An intervening theoretical development of considerable significance was Boltzmann's programmes of *kinetic theory* and *statistical mechanics*. In 1876, he had, based on these considerations, *derived* the DP value of 3R for the specific heats of solids! The above mentioned clear experimental evidence for temperature dependence of specific heats would run counter to these theoretical developments, for which no simple fixes were available within kinetic theory.

An experimental result of immense significance to this topic was provided in 1905 by James Dewar; he reported a value for the specific heat of diamond as low as 0.05 cal/deg at the then *very low* temperatures of less than 100 K, a temperature region made possible by his own successful liquefaction of hydrogen a few years earlier (1898). Dewar also conducted specific heat experiments on diamond at high temperatures of around 2000 ° C, and concluded that at these high temperatures the experiments confirmed the Dulong-Petit value rather accurately.

A complete parallel to this situation is to be found in the case of blackbody radiation; there too, considerations based on equipartition theorem of kinetic theory would give the Rayleigh-Jeans result, which, while in good agreement with data on the low frequency spectrum, was in clear contradiction of Wien's law found to be valid at high frequencies. There too, no simple fixes to classical physics would work, and only Planck's bold ideas paved the way for further progress. While at first Planck had only obtained an *interpolation* formula for which he had relied on *thermodynamic* arguments, he later derived this interpolation formula based on his revolutionary treatment of *charged* oscillators. The upshot of that derivation was that the average energy of such oscillators had to be modified from the kT value inferred from equipartition theorem to

$$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \tag{5.6}$$

This agrees with kT for *low* frequencies, and with $h\nu e^{-\frac{h\nu}{kT}}$ behaviour of Wien's law at *high* frequencies.

In a stroke of genius, Einstein saw in this a way out of the specific heat problem! His basic argument was disarmingly simple; he said that what must hold for the Planckian oscillators must hold for the vibrating atoms of a solid too! He therefore proposed to replace the 3NkT value for the internal energy of a solid to

$$U = 3R\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \to C(T) = 3R\frac{\xi^2 e^{\xi}}{(e^{\xi} - 1)^2} \quad \xi = \frac{h\nu}{kT} \tag{5.7}$$

In making this proposal Einstein made the highly simplifying assumption that the atoms in a solid vibrate with a *single frequency* ν in all the three spatial directions.

Let us note some broad qualitative features of Einstein's proposal. For that, instead of concentrating on the frequency dependence as Planck had done in the case of the blackbody radiation, let us concentrate on the *temperature* dependence. It is clear from inspection that the behaviour in terms of temperature will be opposite to that in terms of frequency; it is the *high* temperature behaviour that will be closer to the equipartition theorem, while at *low* temperatures, the average energies and hence the specific heats will be much *lower* than the expectations of equipartion theorem. In the case of radiation, the average energy densities at high frequencies were the ones that were lower (in fact, exponentially so).

Einstein compared his result of eqn.(5.7) with Weber's data and found remarkable agreement over a wide range of temperatures, if the only parameter in his theory i.e $T_E = h\nu/k$ is taken to be 1300 K for diamond. The origin of this characteristic temperature is quantum mechanical. When this is high, as in the case of diamond, quantum effects can manifest even at room temperatures. A schematic comparison of the Weber data and Einstein prediction is shown in figure 5.1 (as it appeared in Einstein's 1906 paper [15, 78]): Thus Einstein had opened the gates of quantum theory not only for radiation but for matter too. This marked a paradigm shift in our understanding of matter, in a way completely different from the one pioneered by Niels Bohr for an understanding of atomic structure.

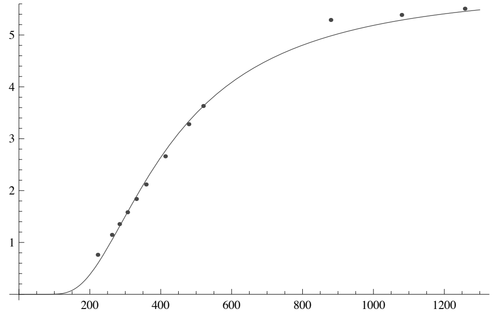

FIGURE 5.1 Comparison between Weber data and Einstein's prediction [78, 15]

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It is instructive to examine the very low temperature behaviour of specific heats in Einstein's theory:

$$C(T) \to 3R(\frac{T_E}{T})^2 e^{-\frac{T_E}{T}} \tag{5.8}$$

In other words, Einstein theory predicted a *precipitous* fall in specific heats at very low temperatures!

The modern reader may find that reasonable as that is what the *third law* or the *Nernst-Planck Postulate* would require. But this has to be viewed in the proper historical perspective. In 1906, when Einstein's paper was published, Nernst had not formulated his postulate in the sense in which third law is understood today. In 1905, based on a large body of experimental work, Nernst had only conjectured that *changes in entropy* would vanish at very low temperatures. As explained in chapter 3, this only requires changes in specific heats to vanish, and not specific heats themselves. The form of third law as recognised today only appeared in 1910 after extensive researches by Nernst had shown that in fact even the specific heats of *all* substances vanishes in the limit, and after Planck in 1910 had suggested modifying Nernst's original postulate to mean that in fact all entropies vanish in the limit.

However, on the basis of his very accurate measurements, Nernst pointed out that even Einstein's result was not in agreement with data at very low temperatures, and that while specific heat of diamond indeed vanished at very low temperatures, it did not fall as steeply as what eqn.(5.8) says; instead, he claimed a T^3 like behaviour. Again, one can see a parallel in the blackbody radiation case. There too, while the energy density of *monochromatic* radiation had the same behaviour as in eqn.(5.7), the *total* energy density, by which we mean energy density *integrated* over all frequencies has a T^4 dependence, leading to a specific heat with a T^3 behaviour for *all* temperatures (see, for example, section 4.6).

5.5.2 Debye Theory

Nernst not only noted the discrepancy between Einstein's result and the observed low temperature behaviour, he suggested the remedy too, essentially along the lines that the lattice vibrations are not monochromatic. It was Peter Debye in 1912 who completed Einstein's treatment by including other lattice vibrations. The essential point of Debye's treatment was that the atoms, by virtue of their interatomic interactions, vibrated more like *coupled oscillators*. The full problem was of such complexity that Debye approximated the entire lattice of atoms by a *continuous media* and considered all its vibrations. Shortly afterwards Max Born and von Karman undertook a detailed study of lattice vibrations taking into account the lattice structure. While the vibrations considered by Debye obeyed the so called *linear dispersion*, as in the case of the blackbody spectrum, the Born-von Karman theory had in addition the so called *optical branch* for which the dispersion relations were no longer linear.

A subtlety with frequency spectrum that arises in this context, but which is absent in the blackbody radiation case, has to do with the fact that the *total* number of modes of lattice vibrations has to be *finite* being essentially given by 3N, where N is the number of atoms. This translates to an *upper limit* to the value of the allowed frequencies. An approximate value of this is given by the so called *Debye frequency* ω_D.

While all this would considerably complicate the integration over all frequencies in general, certain simplifications are possible when dealing with the low temperature

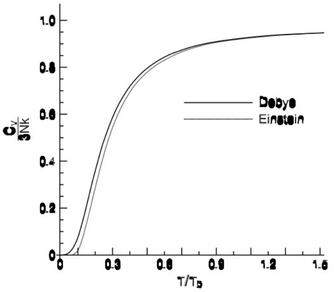

FIGURE 5.2 Comparing Einstein and Debye theories.

case. Then the optical modes can be neglected, and integration yields the T^3 law for specific heats. As already mentioned, the low temperature behaviour of the specific heat of electron gas has a linear dependence in T, and therefore the Debye theory has to be modified for *metallic* solids. We give some important, and essential, results for the Debye theory. Further discussion of the Debye theory can be found in chapter 15. Just as in the Einstein theory, in Debye theory too there is a characteristic *Debye Temperature* $\Theta_D = (\frac{6}{\pi})^{1/3} T_E$. The *low temperature* behaviour of specific heats in Debye theory is given by

$$C \approx \frac{12\pi^2}{5} R \left(\frac{T}{\Theta_D}\right)^3 \tag{5.9}$$

Likewise, the *high temperature* behaviour is given by

$$C \approx 3R \left[1 - \frac{1}{20}(\frac{\Theta_D}{T})^2 + \ldots\right] \tag{5.10}$$

So intricate are the full details of lattice vibrations that years later a controversy arose between Max Born and C.V. Raman about the lattice dynamics of Diamond (what started it all). Though Raman's views on the lattice vibrations proved somewhat incorrect, he had nevertheless correctly identified modes that in modern parlance would be said to ehibit the so called *van Hove* singularities. The reader is referred to G. Venkataramans book *Journey into Light* for a fascinating and technically complete discussion [76].

5.5.3 Specific heats of quantum ideal gases

The ideal gases too have specific heats that do not conform to the third law. Because $C_P - C_V = R$, it is impossible to make both C_P, C_V vanish near absolute zero. One way of getting around this, as already mentioned, is to note that no *real* gas would remain *ideal* at such low temperatures, something that is borne out quite well experimentally. Here *idealness* is considered in the sense of whether the atoms are interacting or not.

But it should certainly be possible, in principle, to think of a non-interacting assembly of particles. What then would be a consistent thermodynamic description of it at very low temperatures? The fact that even for solids, a consistent picture follows only if quantum behaviour is included, suggests looking for a quantum description of ideal gases. Here too, the history of ideas that eventually led to a resolution of these issues forms another of the bedrocks of quantum theory!

Recall our discussion of the blackbody radiation; Planck had sought the interpolation between the high and low frequency behaviours through considerations of *entropy*. While Planck focused on obtaining the energy density from the interpolated entropy, Einstein had focused on the entropy itself, and had made the remarkable observation that the entropy could have been thought as if radiation was like a gas of *photons*. The natural question that would have arisen is whether such a gas could be treated by the *statistical methods* that Boltzmann had used in his kinetic theory. Though Einstein's work was in 1907, the answer to this had to await yet another revolutionary development in 1924 at the hands of the Indian physicist Satyendra Nath Bose, as briefly noted in chapter 4.

Bose was able to reproduce the Planck radiation formula by treating radiation as a gas of particles. But in doing so, he had to introduce a radical departure from the counting methods of Boltzmann. This amounted to the introduction of the completely new concept of *indistinguishability* of identical particles. For example, there are six ways of distributing distinguishable particles but only *one* way of doing so if they are indistinguishable. Another feature, which was not explicitly stressed by Bose, was the lack of any condition demanding the conservation of the total number of particles. As we shall see elsewhere, this fact already manifests itself in the thermodynamics of blackbody radiation by the *vanishing Gibbs potential.*

This work of Bose made a deep impression on Einstein, who immediately saw in it a means to solve the ideal gas problem quantum mechanically. Of course, there would be important differences from the radiation case as the number of atoms of an ideal gas is indeed conserved. But what Einstein's genius recognized was that the counting rules of Bose ought to apply to the ideal gas case too. The rest was a straightforward application of Bose's methods. The outcome was a radically new thermodynamics of ideal gases! Just as Einstein had struck gold earlier with his simple but highly perceptive observation that what must hold for the Planckian oscillators must also hold for the lattice vibrations, he again struck gold by realising that Bose's rules, being of a counting nature, must apply not only to radiation quanta but also to atoms of an ideal gas! We shall not go into the detailed derivations, but simply state the crucial results.

The first surprise was a characterstic *transition temperature* T_{BE}, even for non-interacting particles, that sharply separated the thermodynamic behaviour into two regions; the numerical value of this transition temperature being given by

$$kT_{BE} \simeq (\frac{N}{V})^{2/3}\frac{\hbar^2}{m} \tag{5.11}$$

Not surprisingly, this new temperature scale is of purely quantum origin. A surprising feature is that masses have entered thermodynamics, something that we would not usually encounter in thermodynamics. Below T_{BE} the ideal gas is said to be in a state of *Bose-Einstein Condensation* (BEC). But the phrase *condensation* has to be understood with care as what is happening is no condensation of, say, the water-steam type. Let us consider the *very low* temperatures for which obviously $T < T_{BE}$ holds. The following are the chief results for thermodynamics;

$$P = \zeta(5/2)\frac{kT}{\lambda_T^3} \qquad U = \frac{3}{2}\zeta(5/2)kT\frac{V}{\lambda_T^3} \qquad C_V = \frac{15R}{4}\zeta(5/2)\frac{V}{\lambda_T^3} = AT^{3/2} \tag{5.12}$$

where $\lambda_T = \hbar\sqrt{\frac{2\pi}{mkT}}$ is the *thermal wavelength*, and $\zeta(5/2) = 1.34149$ is the *zeta function* with argument 5/2.

A rather striking result is that the pressure is independent of volume, and depends only on temperature. Therefore, isobaric processes are also isothermal. We already encountered this situation in the case of blackbody radiation also. Consequently, C_P does not make sense. At very high temperatures, however, pressure depends both on volume and temperature, and in fact the classical ideal gas law emerges.

In contrast, the pressure of a Fermi-gas (say, electron gas) at low temperatures does not depend on temperature at all! This *degeneracy pressure* plays a big role in the stability of *White Dwarfs* and *Neutron Stars* according to the seminal work by S. Chandrasekhar.

The specific heat of the quantum ideal gas is the other surprise. It has a *half-integral* dependence of $T^{3/2}$ on temperature! This is a completely new temperature dependence for specific heats than anything we have encountered so far. This behaviour is indeed consistent with the third law. For $T > T_{BE}$ the behaviour of the specific heat is entirely different, and eventually at very high temperatures it approaches the constant classical value. At $T = T_{BE}$, the specific heat is *continuous*, but with a *discontinuous slope* characterstic of a *cusp* as shown in the figure:

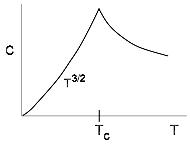

FIGURE 5.3 The cusp behaviour seen in specific heats of BEC.

Specific heats and critical phenomenon The cusp singularity in the specific heat of an ideal bose gas is only one example of the singular behaviour of specific heats near transition temperatures. In fact such singular behaviours are *generic* rather than *exceptional.* In the figure above, we display the behaviour of the specific heat at the so called λ-transition in Helium. An almost identical behaviour is seen in a totally unconnected system, i.e the behaviour of magnetic specific heats near a magnetic phase transition. This points to the great universality of the behaviour of specific heats. As discussed in several parts of the book later on, one can have a variety of situations whereby either the specific heats or some derivatives of them

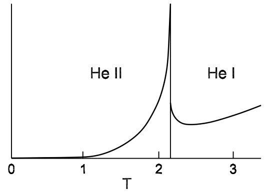

FIGURE 5.4 The λ transition.

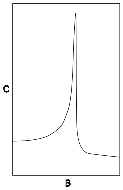

FIGURE 5.5 A magnetic transition.

become discontinuous. For example, in superconducting phase transitions, discussed at length in chapters 10 and 11, there is a finite discontinuity in the specific heat. The type of specific heat behaviour near a transition point becomes a *diagnostic* for the type of phase transition. In certain second order transitions, the specific heats may diverge as some power, i.e $C \simeq (T - T_C)^{\alpha}$, as the critical point is approached. α is one of the *critical exponents*, and what is amazing is that physically very distinct situations like the critical point in a water-steam system and the critical point in the so called *three dimensional Ising model* may possess the *same* critical exponents.

5.6 Problems

Problem 5.1 The molar specific heat of carbon at room temperature is around 6 J/mol, while that of lead at the same temperature is as high as 26.7 J/mol. Explain this on the basis of the Einstein and Debye theories.

Problem 5.2 There are two solids, one of which has a specific heat of 2.7R and the other has .15R, both at 300 K. What is the ratio of their Debye temperatures? What is the ratio of their T_E?

Problem 5.3 A mixture consists of n_1 moles of a substance with specific heat C_1 cal/deg mole, a second with C_2 etc. What is the molar specific heat of the mixture?

Problem 5.4 Derive an expression for the molar specific heat at constant enthalpy. Derive an expression for it for a vdW fluid.

Problem 5.5 Determine the conditions when $C_P > C_V$. Can you think of any counterexamples?

Problem 5.6 The Debye temperatures for Carbon and lead are 1860 K and 88 K respectively. Calculate the ratio of their specific heats at 300 K.

Problem 5.7 Consider a copper bowl of mass 100 gms which holds 300 gms of water, and both are at 300 K. A very hot copper ball of 300 gms mass is dropped into this bowl with water. It is observed that 10 gms of water is completely turned into steam, while the remaining water and the bowl reach 100 °C. Calculate the temperature of the wall if the specific heats of water and copper are, respectively, 4190 J/kg.deg and 387 J/kg.deg, and if the latent heat of vaporisation for water at 100 °C is 540 cal/gm.

Problem 5.8 It is often assumed that in measuring temperatures the effect of the thermometer may be neglected. Assess this assumption in the following case: a thermometer of mass 20 gms and a specific heat of 0.2 J/deg is at an initial temperature of 15 °C. It is dipped into 300 gms of water, and the final temperature of the water-thermometer combination is 45 °C. Find the initial temperature of water.

Problem 5.9 21.6 gms of copper is in the shape of an annulus with inner radius of 2.54 cms at 0 °C, and an aluminium ball with radius 2.54503 cms at 100 °C just passes the annulus after reaching thermal equilibrium. Find the mass of the ball if the coefficients of expansion of copper and aluminium are, respectively, $17 \cdot 10^{-6}$/deg and $23 \cdot 10^{-6}$/deg. Their molar specific heats are, respectively, 24.4 J/mol and 24.3 J/mol.

6 Structure of Thermodynamic Theories

In this chapter we shall look into somewhat formal aspects of thermodynamics. What we shall be looking at will be the general *structure* of thermodynamic theories. While such considerations may not facilitate practical applications of the theory (even the ideal gas case looks much more complicated than the usual treatments), they are very important in clarifying its logical structure. We follow Callen in the elaboration of this chapter, but unlike him, shall not stress any purely axiomatic approach.

There is a very clear parallel to be found in almost all important theories of physics. Taking the example of classical mechanics, a practical approach would be to concentrate on solving Newton's equations with appropriate initial conditions. But a more systematic understanding of Mechanics is obtained by studying it structurally.

The three laws of mechanics can be likened to the laws of thermodynamics. There too, their evolution had strong elements of empirics combined with an axiomatic approach, which, as we have seen, is true of the thermodynamic laws too. While the notions of position and velocity were amenable to direct observations, the notion of momentum was axiomatic. Likewise in thermodynamics, while pressure, volume and temperature are amenable to direct observation, notions of internal energy and entropy have to be axiomatised. In mechanics, the state of a mechanical system was fully specified by its momentum and position. In thermodynamics too there is a notion of a state, and this is the state of thermal equilibrium, and such a state of a given system is fully specified by specifying certain independent quantities like pressure, temperature etc. In mechanics, one thinks in terms of the so called *degrees of freedom* (d.o.f) which are the independent data required to specify a state.

In thermodynamics too we would like to ask what the degrees of freedom are. In mechanics, the three laws ascribed to Newton define a framework within which complete description of all mechanical systems is sought to be found. Such a description requires *system-specific information* which usually amounts to specifying masses, force laws etc. What are the corresponding system-specific details needed for a complete description of a thermodynamical system? Is there any systematics to it or is to be done case by case?

In the mechanical example, while one could have worked just with velocities, the axiomatic introduction of a momentum is indeed a great step forward conceptually. It allows the extension of the structure of mechanics even to systems where description in terms of velocities alone becomes clumsy. It is to be emphasized that at all times one could have simply worked with Newton's equation for acceleration.

A major difference between mechanics and thermodynamics is the irrelevance of the notion of time in purely equilibrium thermodynamics. Then isn't the name 'thermodynamics' which implies some sort of *dynamics* misleading? In a strict sense it is, but the notion of dynamics in thermodynamics has to be construed differently.

So the basic structural question to be answered here is *What constitutes a complete description of a thermodynamic system?* A good guess is that *equation of state* needs to be specified. But what constitute *bona-fide* equations of state? Let us take the simplest thermodynamical system, an ideal gas, as an example.

$PV = nRT$ is frequently stated as *the* ideal gas equation of state. Recall that historically this single equation was the merger of two distinct laws. *Boyle's law* which stated that at a given temperature $PV = const.$, and *Charle's law* which stated that the rhs of Boyle's law is linearly dependent on temperature (as often happens in science, the names of Mariotti in connection with Boyle's law, and of Gay-Lussac in the context of Charles's law, are frequently omitted). But does even this single combined law completely characterise a thermodynamic system? Given just that, can we compute ingredients that go into the first law like the internal energy U, the entropy S etc..? No, one can not as can be seen simply by noting that a monatomic ideal gas, a diatomic ideal gas all obey this equation. Therefore, this equation alone can not distinguish between them and hence is incapable of providing a complete description of a thermodynamic system. In fact, that equation has to be supplemented with information, say, about the specific heat C_V, or equivalently, about the internal energy U.

In the particular example of the ideal gas, that additional input is that U is a function of temperature alone, something which was experimentally established by the *Joule-Kelvin Process*. This should be, for the ideal gas, treated as yet another law, conceptually distinct from the law $PV = nRT$. If so, is this law *completely independent* of the first law? More explicitly, having its origin in experimental data, could this second law have been, *in principle*, different from the Joule-Kelvin law?

The answer turns out to be no and in fact $PV = nRT$ implies, as a consequence of the first law, that U is a function of temperature only. To see this, one uses the relation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{6.1}$$

which was already discussed in chapter 2. So it is not totally independent of $PV = nRT$ and yet it has more information than it as it is not enough for a complete thermodynamic description. The resolution is that the precise *functional* dependence of U on T is the true content of this second law, and that is truly independent of $PV = nRT$. In particular, assumption of a *constant* C_V means that $U = C_V T$.

Before going further, let us discuss another example where the corresponding equation is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{6.2}$$

This is the celebrated *van der Waals equation* to which we have dedicated an entire chapter later. Here we are using it only to exemplify the issues currently being discussed.

Now applying eqn.(6.1) to this yields

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2} \tag{6.3}$$

So in this example, the equation of state of eqn.(6.2) *completely* determines the volume dependence of U. Nevertheless, there is an unspecified function of T in U, as before. In fact, given any equation of state of the form $P = F(V,T)$, it follows from eqn.(6.1) that U is not fully determined, and that the same freedom of the type $f(T)$ persists.

This could give the impression that an equation of state specifying U is somehow subordinate to one specifying P in terms of V and T. This is not so. To see that, imagine that historically the Joule-Kelvin law, i.e $U = U(T)$, was known first for an ideal gas. The same eqn.(6.1) would now give $\left(\frac{\partial P}{\partial T}\right)_V = P$ whose solution is $P = f(V)T$, with f an *arbitrary* function of V. This is of the same form as the ideal gas law wherein $f(V) = nRV$.

For more general circumstances, given $U = U(V,T)$, then eqn.(6.1) is nothing but a *first order differential equation* for P in terms of T and where V just plays the role of a constant. Clearly the solution is not unique as changing P by a term of the type $Tf(V)$ does not alter the differential equation. Therefore, both the equations of state, happily, are on the same footing. The fact that the said arbitrarinesses are only of the type $f(T)$ in U and $Tf(V)$ in P can simply be understood from the first law itself, after use has been made of the entropy axiom:

$$TdS = dU + PdV \quad \rightarrow dS = \frac{1}{T}dU = \frac{P}{T}dV \tag{6.4}$$

It is clear that adding a $\Delta U = f_1(T)$ and a $\delta\frac{P}{T} = f_2(V)$ will not disturb S as a state function, or equivalently, of dS as a perfect differential. This is the true content of the need for *two* equations of state in these examples.

If on the other hand, we had rewritten the first law in its differential form as

$$dU = TdS - PdV \tag{6.5}$$

then, adding a $\Delta S = f_1(T)$ and a $\Delta P = f_2(V)$ would not have upset the perfect differential character of dU. Finally, specifying S as a function of U and V, or U as a function of S and V, is completely consistent *provided* T and P are suitably identified. We shall return to this later.

Following Callen, we shall call equations of the type $f(P,V,T) = 0$ as *mechanical equation of state*, as they involve purely mechanical concepts like P and V. Of course, it can not involve only such mechanical concepts and must involve temperature, which is certainly not a mechanical concept. Without that, such an equation would be irrelevant in thermodynamics. To that extent, *mechanical equation of state* is a misnomer. In contrast, Callen calls the second category of equations, of which the Joule-Kelvin law is an example, the *thermodynamic equation of state*.

It is again a good place to pause and make a comparison with the structure of classical mechanics. There, for example, there is a clear distinction between the three laws of Newton, and the law of *Gravitational attraction*, also due to Newton. The first three are to be applied to every system, while the law of gravitational attraction is to be applied only while focusing on gravitational phenomena. In this sense, the law of gravitational attraction, though being one of the laws of nature, is more like specifying the *equation of force*. Likewise the force law $f = -kx$ due to a spring.

In a completely analogous manner, the first and second laws of thermodynamics are to be applied to all systems, while $PV = nRT$ is to be applied only while determining the thermodynamics of ideal gases. Therefore, $PV = nRT$ has the same significance in thermodynamics as did Newton's law of gravitation in mechanics. They are called *equations of state*. We already saw that for a single component system we actually need two of them. For a generic thermodynamic system, how many equations of state are both necessary and sufficient? We have also not addressed, systematically, the issue of thermodynamic degrees of freedom, particularly their number.

Let us recall that the differential forms of first and second laws still do not provide a complete description of thermodynamic phenomena. This has to do with the fact that they are unable to fix the so called *entropy constants*. We found in chapter 3 that we need to postulate something additional for this. This is accomplished by *Nernst's Theorem* which is also called the *Third Law of thermodynamics* by some. So, like in mechanics, we have three laws in thermodynamics too. The empirical relevance of entropy constants is discussed in a separate chapter.

What about the *zeroth law* of thermodynamics and its mechanics counterpart? Zeroth law formalises something that is intuitively obvious and yet conceptually indispensable, that bodies in equilibrium have the same temperature. This can be taken as defining the notion of temperature itself. Most often, this law only operates from behind the scenes in the sense that one does not invoke it explicitly in any manipulations. Something remarkably similar happens in mechanics. What truly underlies the entire structural edifice of Newtonian mechanics is the concept of inertia and that of the notion of inertial frames. Yet, this too plays only from behind the scenes, though without it there are no scenes at all! So a characterization of inertial frames can be taken to be the *zeroth law of mechanics*!

Let us return to our earlier remark that specifying either S as a function of U and V, or of specifying U as a function of S and V is a completely consistent specification. But the important question is whether either of them provides a *complete* specification of thermodynamics. So far the discussion and examples have been restricted to one mole of a single component substance. Let us relax that and consider arbitrary amounts of the substance and in particular processes in which this amount is also allowed to vary. In particular, the first law takes the form

$$T\,dS = dU + P\,dV - \mu\, dn \tag{6.6}$$

where μ is the so called *chemical potential.*

6.1 Extensive and intensive variables: general

Now the very important notion of *extensive* and *intensive* variables enters. Their meaning has already been explained. The extensivity of V is in some sense obvious, and so is the intensivity of P and T. The extensivity of U and S is less obvious, and is taken as axioms in thermodynamics. On a microscopic level, these depend on such details as the *range* of inter-molecular forces, whether there are *direct many body forces* etc.

Extensivity of U, S and V means $U = nU_m, S = nS_m, V = nV_m$. Obviously, U_m, S_m, V_m are intensive. But these quantities which are *intensive by construction* should be distinguished from P, T, μ which are *intrinsically intensive*. We call variables like P,T, μ, which are intrinsically intensive as *intensive variables of first class*, while variables that are intensive by construction as *intensive variables of second class*. The reader is warned that this is a terminology that the author has introduced, and may not be found elsewhere.

Just the requirement of extensivity imposes important restrictions. Let us first look at the example of the ideal gas and consider n moles of it. From $TdS = dU + PdV$, and $U = nCRT, PV = nRT$, it follows that

$$dS = nCR\frac{dT}{T} + nR\frac{dV}{V} \quad \rightarrow S(V,T,n) = nCR\ln T + nR\ln V + S_0(n) \tag{6.7}$$

where $S_0(n)$, the *constant* of integration is a *constant* only as long as n is held fixed. But it can, at this stage, depend only on n, and can, for example, be used to *fix* the correct dimensions for the arguments of the two logs. If this entropy is *extensive* it must satisfy $S(V,T,n) = nS_m(V_m,T)$. But for one mole of the substance, eqn.(6.7) gives

$$S_m(V_m,T) = CR\ln T + R\ln V_m + s_0 \rightarrow S_m(V_m,T) = CR\ln\frac{T}{T_0} + R\ln\frac{V_m}{V_0} + R \tag{6.8}$$

where now s_0 is truly a constant, and has been used to make the arguments of the logarithms *dimensionless*. It has to be understood that T_0, V_0 are *arbitrary* constants with dimensions of T and V, respectively. The significance of retaining an explicit constant R will become clear shortly. The extensivity of volume yields $V = nV_m$ and consequently

$$S(V,T,n) = nCR\ln\frac{T}{T_0} + nR\ln\frac{V}{nV_0} + nR \tag{6.9}$$

One may wonder why one had to go through all this to get S(V,T,n) and not obtain it by directly integrating eqn.(6.6)? The catch is that to do so would require an explicit knowledge of the chemical potential μ! Since we have determined the entropy without the explicit knowledge of the chemical potential, but only invoking the extensivity of S, in effect it means that the chemical potential is in fact determined by extensivity alone. We shall soon see that it is indeed so.

Now we consider processes in which all of (V,T,n) are variable. The differential, dS, for such general processes is easily constructed:

$$dS = nCR\frac{dT}{T} + nR\frac{dV}{V} + dn\left\{CR\ln\frac{T}{T_0} + R\ln\frac{V}{nV_0}\right\} \tag{6.10}$$

from which it follows, on noting $dU = nCRdT + dnU$ that

$$TdS = dU + PdV - \mu\, dn \quad \rightarrow \mu = -U - TC_V\ln\frac{T}{T_0} - RT\ln\frac{V}{nV_0} + RT \tag{6.11}$$

The important lesson is that the requirements of extensivity of S,U and V *completely fixes* the chemical potential μ, and furthermore it is fixed to be the same as the molar Gibbs potential (note that for one mole of ideal gas $RT = PV_m$)! This is not an accidental result for the ideal gas only. The problem below will show it to be true for the van der Waals case also. Actually it is true for any system as will be shown now. Let S_m, V_m, U_m be the molar quantities at T,P. Then the first law for one mole of the substance reads:

$$TdS_m = dU_m + PdV_m \tag{6.12}$$

whereas for variable molar systems we have

$$TdS = dU + PdV - \mu\, dn \tag{6.13}$$

Consistency between eqn(6.12), eqn.(6.13), and $S = nS_m, V = nV_m, U = nU_m$ immediately gives $\mu = U_m - TS_m + PV_m$, i.e the chemical potential is equal to the molar Gibbs potential.

6.2 The Fundamental Equations

Following Callen, let us consider functional relations only among the extensive variables like (S,U,V,n..). Let us for clarity first focus on a single component system with no other attributes like magnetism etc.. Callen calls such relations exclusively among the extensive variables *The Fundamental Relations*. The reason for this nomenclature will become obvious shortly. As it turns out, any one of the fundamental equations provides a *complete* thermodynamical description!

Again a word of caution is in order; in most textbooks and even in many research or technical articles, the phrase *fundamental equations of thermodynamics* is used for the first and second laws. So it is not in that sense, but in a conceptually much deeper sense, that this phrase is used by Callen for the equations to be discussed here. Incidentally, the author has tried hard to locate the historical origins of this beautiful and very apt terminology, but has failed in the task. So it is his surmise that credit for this should go entirely to Herbert B. Callen.

For the one component system under consideration he writes down two such fundamental equations:

$$S = S(U,V,n) \tag{6.14}$$

and

$$U = U(S,V,n) \tag{6.15}$$

In the first, U is the *independent* variable while S is the *dependent* variable. The fundamental equation of eqn.(6.14) is said to be in the *entropy representation* [3]. Likewise, eqn.(6.15) in which U is the dependent variable, is called the fundamental equation in the *energy representation*.

If certain mathematical assumptions of *continuity, monotonicity, single-valuedness, and differentiability* are made about the extensive variables, the two forms of the fundamental equations will be equivalent. These assumptions are certainly very reasonable from the point of view of day-to-day experience and also from the empirics of thermodynamics. They are part of the axiomatic approaches to thermodynamics ([4]). We shall not pursue the axiomatic formulations of thermodynamics in this book.

If we scale the entire system, λ times extensivity tells us that $S \to \lambda S, U \to \lambda U$, $V \to \lambda V$, and $n \to \lambda n$. From this it follows that the fundamental equations are both *homogeneous* equations of *degree one*. More explicitly

$$S(\lambda U, \lambda V, \lambda n) = \lambda(U, V, n) \qquad U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n) \tag{6.16}$$

There are important consequences of this extensivity, one of which, i.e the equality of μ and G, has already been discussed. The other consequence, the so called *Gibbs-Duhem Relation* will be derived after we have shown how the intensive variables of the first class, T, P, μ arise from the fundamental equations. Our demonstration of the fixing of μ by extensivity also required the use of the First law. In what follows, we shall see that the first law is a consequence of the differentiability of the fundamental equations along with the identification of the intensive variables of the first class.

6.2.1 Intensive variables and the fundamental equation

The fundamental equations are relations among only the extensive variables, and are homogeneous equations of first degree. It is therefore clear that partial derivatives of the dependent variable in the fundamental equation with respect to the independent extensive variables must be homogeneous of degree *zero*, i.e they are intensive variables. Let us first consider the energy representation of eqn.(6.15). The assumptions of *differentiability* immediately yield

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \tag{6.17}$$

At this stage, two approaches for further development can be considered. The first one, which accepts the primacy of the first law, $TdS = dU + PdV - \mu dn$, would say that we must identify the partial derivatives occurring in eqn.(6.17) with the *intensive variables of the first class*, i.e (T, P, μ). More precisely,

$$\left(\frac{\partial U}{\partial S}\right)_{V,n} = T(S,V,n) \qquad \left(\frac{\partial U}{\partial V}\right)_{S,n} = -P(S,V,n) \qquad \left(\frac{\partial U}{\partial n}\right)_{S,V} = -\mu(S,V,n) \tag{6.18}$$

The other approach, axiomatic in nature, is to *define* the intensive variables (T,P,μ) by the above equation. That, on the surface of it, does not seem to have achieved anything unless these quantities as defined above can be shown to have exactly the same thermodynamic meaning that one normally attaches to them. This is indeed so, and will be explicitly demonstrated in a later section.

Similar considerations in the entropy representation lead to

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n} dV + \left(\frac{\partial S}{\partial n}\right)_{U,V} dn \tag{6.19}$$

Again, the partial derivatives are identified with suitable combinations of the first class intensive variables (T,P,μ) either by invoking the first law, or axiomatically as done in the case of the energy representation, leading to

$$\left(\frac{\partial S}{\partial U}\right)_{V,n} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,n} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial n}\right)_{U,V} = -\frac{\mu}{T} \tag{6.20}$$

In the above, the functional dependence of (T,P,μ) on (U,V,n) is understood. In both the representations, monotonicity amounts to requiring T,P to be *positive*. But as stated elsewhere, there can be systems with negative temperatures.

It is to be appreciated that in the axiomatic formulation, first law is merely a consequence of the differentiability assumption. Of course, strictly speaking this is so only after the identification of temperature, pressure, and chemical potential in the axiomatic approach has been shown to be the same as in the traditional approach. This is done later while discussing the conditions of equilibria in the axiomatic approach. It will be seen there that the second law is crucial for this.

6.2.2 The Euler relations

Let us explore the consequences of extensivity in the context of the fundamental equations. Let us first consider the example of a single component system and its fundamental equation in the energy representation as given by the second of eqn.(6.16). Differentiating that with respect to λ gives

$$\begin{aligned} U(S,V,n) &= S\left(\frac{\partial U(\lambda S,\lambda V,\lambda n)}{\partial \lambda S}\right)_{V,n} + V\left(\frac{\partial U(\lambda S,\lambda V,\lambda n)}{\partial \lambda V}\right)_{S,n} \\ &\quad + n\left(\frac{\partial U(\lambda S,\lambda V,\lambda n)}{\partial \lambda n}\right)_{S,V} \end{aligned} \tag{6.21}$$

Which, on using the definition of the intensive parameters in the energy representation, is the same as

$$U(S,V,n) = ST(\lambda S,\lambda V,\lambda n) - VP(\lambda S,\lambda V,\lambda n) + n\mu(\lambda S,\lambda V,\lambda n) \tag{6.22}$$

which becomes, on using the intensive nature of (T,P,μ),

$$U = TS - PV + \mu n \tag{6.23}$$

This is *the Euler relation* in energy representation. Its consequence, in this example, is the equality of the chemical potential μ with the *molar Gibbs potential* $\frac{G}{n}$ with $G = U - TS + PV$. We already saw this earlier. A detailed discussion of G and other *thermodynamic potentials* is given in the next chapter.

Completely analogous treatment holds for the derivation of the Euler equation in the entropy representation

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}n \qquad \rightarrow \mu = \frac{G}{n} \tag{6.24}$$

.

6.2.3 The Gibbs-Duhem relations

Let us consider the *differential form* of the Euler relations in the energy representation:

$$dU = TdS + SdT - PdV - VdP + \mu dn + nd\mu \tag{6.25}$$

On using either the first law, or the differential form of the fundamental equation in the energy representation, it is immediately seen that this leads to

$$SdT - VdP + nd\mu = 0 \qquad d\mu = -S_m dT + V_m dP \tag{6.26}$$

This is the Gibbs-Duhem relation. It implies that the intensive variable of the first class μ can not be varied independently. As already noted, μ is the molar Gibbs Potential $G_m = U_m - TS_m + PV_m$, and this form of the Gibbs-Duhem relation follows simply from first law, or again, the differential form of the fundamental relation $dU_m = TdS_m - PdV_m$. It is instructive to derive the GD relation in the entropy representation. The differential of the Euler equation eqn.(6.24) yields

$$dS = d(\frac{1}{T})U + \frac{1}{T}dU + d(\frac{P}{T})V + \frac{P}{T}dV - d(\frac{\mu}{T})n - \frac{\mu}{T}dn \tag{6.27}$$

The trick is not to expand $d(\frac{1}{T}), d(\frac{P}{T}), d(\frac{\mu}{T})$ further in terms of $dT, dP, d\mu$ as then we would just recover the GD-relation in the energy representation. The meaning of the exercise is to retain the variations of the respective intensive variables, which for the entropy representation are $\frac{1}{T}, \frac{P}{T}, \frac{\mu}{T}$. After some elementary algebra, use of the first law gives the GD-relation in the entropy representation as:

$$d(\frac{\mu}{T}) = d(\frac{1}{T})U_m + d(\frac{P}{T})V_m \tag{6.28}$$

So even in the entropy representation, the variation of the intensive parameter corresponding to n is not independent. We shall illustrate these concepts through explicit examples shortly.

6.3 True equations of state

We already saw that even in the simplest example of the ideal gas, $PV = nRT$ alone does not fix the thermodynamic description completely, and that an additional equation specifying the functional dependence of U on T was necessary. Now we shall see that from the structural point of view, $PV = nRT$ can not really be treated as a bona-fide equation of motion.

The definitions of the intensive variables of the first class, T,P and μ, of eqn.(6.18) and eqn.(6.20) are homogeneous equations of *zero degree* in terms of the respective extensive variables. To illustrate the implications, let us first consider the energy representation. Recall that a quantity Z(S,V,n) which is homogeneous of degree zero must satisfy $X(S,V,n) = X(\lambda S, \lambda V, \lambda n)$, and in particular, $X(S,V,n) = X(S/n, V/n)$(as can be seen by choosing $\lambda = 1/n$). It therefore follows that

$$T = T(S_m, V_m) \qquad P = P(S_m, V_m) \qquad \mu = \mu(S_m, V_m) \tag{6.29}$$

Let us emphasize the salient features of these equations. Firstly, the number of independent variables is *only two* though we started with *three* independent extensive variables (S,V, n). In essence, extensivity has trivialized the role of n as a degree of freedom. Dependence on this variable of all thermodynamic variables is *strictly linear*. Summarising, the number of *thermodynamic degrees of freedom* of a single component system is only two. These can be chosen, as far as the fundamental equations are concerned, to be either (S_m, V_m) for the energy representation, or, (U_m, V_m) for the entropy representation.

The second feature, which is extremely important, is that these equations express the two independent intensive variables of the first class, say, T and P, entirely in terms of two independent intensive variables of the second class (S_m, V_m) or (U_m, V_m) as the case may be. This, according to Callen, is what characterizes *true equations of state*.

It is easy to appreciate now why in the ideal gas case $PV = nRT$ or equivalently, $PV_m = RT$ would not be such a true equation of state; it involves more than one the intensive variable of the first kind, i.e it involves both T and P in the same equation. However, if a second equation of the type $U(T) = nCRT$, which is anyway needed for the complete specification of the thermodynamics of ideal gases, is provided, that can be cast as $T = \frac{U_m}{CR}$. That is of the form of a true equation of state in the sense elaborated earlier. Using that, the $PV = nRT$ equation can also be recast as a bona-fide equation of state, i.e $P = \frac{U_m}{CV_m}$.

Since these points of view are likely to be unfamiliar, let us illustrate them with yet another example, this time with the *ideal van der Waals fluid* case. The equation that is commonly cited as the *van der Waals equation of state* is

$$(P + \frac{an^2}{V^2})(V - nb) = nRT \qquad \to P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{6.30}$$

This is not a proper equation of state for reasons similar to the ones put forward in the ideal gas case. However, on supplanting with the idealness condition $T = \frac{U_m}{CR}$ which is a proper equation of state in itself, the vdW equation of eqn.(6.30) can be recast in the proper form

$$P = \frac{U_m}{C(V_m - b)} - \frac{a}{V_m^2} \tag{6.31}$$

6.4 Multicomponent systems

Let us generalize our considerations to a k-component system. Some important conceptual differences arise even when all the components are ideal gases. The first of these is the appearance of the so called *entropy of mixing*, and the second, somewhat related to the first, is that chemical potentials are no longer the same as the molar Gibbs potentials.

Let us begin by discussing the entropy of the composite system. If we denote the i-th component system entropy by $S^{(i)}$, then additivity of entropy tells us that the entropy of the total system is $S = \sum_i S^{(i)}$. Let the number of moles of the i-th component be n_i. The total number of moles in the mixture is denoted by $N =$

$\sum n_i$. Then the entropy of the i-th component is simply given by eqn.(6.9) with the possibility that the constants T_0, V_0 can be different for the different components. An equivalent way of handling this is to add a piece $n_i s_0^i$ to each $S^{(i)}$, and dropping the nR piece from the earlier expression. Also, the specific heats will be different for each component. Consequently

$$S = \sum_i n_i C_i R \ln \frac{T}{T_0} + \sum_i n_i R \ln \frac{V}{n_i V_0} + \sum_i n_i s_0^i \tag{6.32}$$

This can be rewritten as

$$S = \sum_i n_i C_i R \ln \frac{T}{T_0} + \sum_i n_i R \ln \frac{V}{N V_0} + \sum_i n_i s_0^i - R \sum_i n_i \ln \frac{n_i}{N} \tag{6.33}$$

Note that this total entropy is extensive, as each individual entropy in the sum is extensive. The last term is the famous *entropy of mixing*. Its significance can be uncovered by initially considering the components with volumes V_i such that $\frac{V_i}{n_i} = \frac{V}{N}$. Then consider mixing the components. The entropy of mixing, a *positive* quantity, is the difference between the final and initial entropies. This shows that entropy increases upon mixing and the process is therefore *irreversible*, as is intuitively clear anyway.

The internal energies (at some specified T,P) being $U^{(i)} = n_i U_m^{(i)}$, the total internal energy is $U = \sum n_i U_m^{(i)}$. Since we are considering ideal gases as components, the total pressure P is the sum of *partial pressures* as per *Dalton's law*, i.e $P = \sum_i n_i P_m^{(i)}$. Thus the total Gibbs potential G is given by

$$G = U - TS + PV = \sum_i n_i \left\{ U_m^{(i)} - T S_m^{(i)} + P_m^{(i)} \right\} + RT \sum_i n_i \ln \frac{n_i}{N} \tag{6.34}$$

Now let us consider the Euler equation in the energy representation, $U = U(S, V, \{n_i\})$ for the whole system. By repeating what was done for the single component case, it is easy to see that the Euler equation now reads

$$U = TS - PV + \sum_i \mu_i n_i \qquad G = \sum_i n_i \mu_i \tag{6.35}$$

where μ_i is the chemical potential for the i-th component. It is clear that the individual chemical potentials μ_i *need not* (we will see that they actually *can not*) equal their molar Gibbs potentials. In fact, on using eqn.(6.33) that

$$\mu_i = G_m^{(i)} + RT \ln \frac{n_i}{N} \tag{6.36}$$

The new feature is entirely due to the entropy of mixing. Though μ_i explicitly depends on n_i, it is nevertheless *intensive*.

Finally, the number of degrees of freedom for a k-component system is $k+1$, which in the energy representation can be taken to be $S/N, V/N, \{x_i\}$, where $x_i = \frac{n_i}{N}$ are the *molar fractions*, with $\sum_i x_i = 1$.

It is important, at this stage, to make a distinction between *additivity* and *extensivity*. For example, entropies of spatially separated systems, entropies of mixtures of ideal gases etc. are *additive*, even if they are not individually extensive. In fact, the Gibbs paradox, in the case of a mixture of ideal gases, arose after invoking additivity of *non-extensive* entropies.

6.5 Entropy of mixing and the Gibbs paradox

The so called *Gibbs paradox* arises on considering the possible changes in entropy as a result of mixing. It should be stated at the very beginning that an entropy that is *extensive* does not lead to any such paradox. However, such a paradox can arise from an improper treatment of the additivity of entropy. One such improper treatment, for example, is to start with the molar entropy of an ideal gas that was derived earlier in eqn.(6.8), i.e

$$S_m = CR\ln T + R\ln V_m + s_0 \tag{6.37}$$

and incorrectly generalizing to the case of n moles occupying V as

$$S = nCR\ln T + nR\ln V + ns_0 \tag{6.38}$$

While additivity of entropy has been invoked in arriving at this, extensively has not been taken into account. We shall show here that the paradox arises only on use of entropies as in this equation, and that all paradoxes disappear on using extensive entropies as in eqn.(6.9).

To appreciate what this so called paradox is about, first consider two samples of *different* ideal gases both at the same temperature and pressure T,P. The number of moles in the first sample is n_1 while that in the second is n_2. Therefore, their volumes are $V_1 = n_1RT/P$ and $V_2 = n_2RT/P$, respectively. We can imagine the two volumes to be separated by a partition dividing a container of volume $V = V_1 + V_2 = (n_1 + n_2)RT/P$. Let us consider mixing these two samples by, say, lifting the partition separating the two volumes. The final volume is V. The entropy before mixing is given by

$$S_{ini} = n_1C_1R\ln T + n_1R\ln V_1 + n_1s_0^{(1)} + n_2C_2R\ln T + n_2R\ln V_2 + n_2s_0^{(2)} \tag{6.39}$$

while the entropy after mixing is

$$S_{fin} = n_1C_1R\ln T + n_1R\ln V + n_1s_0^{(1)} + n_2C_2R\ln T + n_2R\ln V + n_2s_0^{(2)} \tag{6.40}$$

leading to the change in entropy, called *entropy of mixing*,

$$S_{mix} = S_{fin} - S_{ini} = n_1R\ln\frac{V}{V_1} + n_2R\ln\frac{V}{V_2} = -n_1R\ln\frac{n_1}{n_1+n_2} - n_2R\ln\frac{n_2}{n_1+n_2} > 0 \tag{6.41}$$

This result appears reasonable, and in conformity with experience as such mixings are in general *irreversible*. In fact, such mixing entropy is essential for the consistency of thermodynamics itself! If, for example, the salt could be separated from a saline solution (desalination) at no cost, one would end up with a perpetual machine driven by osmotic pressure (discussed in chapter 9)!

Note that this mixing entropy is only a function of the concentrations. Since nothing in the above referred to the nature of the gases, it is reasonable to conclude that the above should hold even when the two gases are the same. Since this is such an important point, let us verify by repeating the above for this case. Now the initial configuration is two samples of the same gas, at the same temperature and pressure, but with different number of moles n_1, n_2. The final configuration is the same gas, at the same P,T but with n_1+n_2 moles occupying a volume $V = V_1 + V_2$. On noting $C_1 = C_2 = C$ and $s_0^{(1)} = s_0^{(2)} = s_0$ for this case, the initial and final entropies are given by

$$\begin{aligned} S_{ini} &= (n_1+n_2)CR\ln T + n_1 R\ln V_1 + n_2 R\ln V_2 + (n_1+n_2)s_0 \\ S_{fin} &= (n_1+n_2)(CR\ln T + R\ln(V_1+V_2) + s_0) \end{aligned} \tag{6.42}$$

Indeed, we get the same expression for the entropy difference as above.

But this is patently absurd as experience tells us that mixing two samples of the same gas at the same P and T, and then repartitioning them can be performed reversibly, and hence there should be no entropy change in the mixing of ideal gases. This is one version of the Gibbs paradox. It should be emphasized that as far as classical thermodynamics is concerned, it's only the changes between thermodynamic states that are reversible.

We shall now show that on using eqn.(6.9) this paradox just disappears. Repeating the calculation for identical gases, but with the extensive entropies, it is easy to see that

$$\begin{aligned} S_{ini}^{ext} &= (n_1+n_2)CR\ln T + n_1 R\ln\frac{V_1}{n_1} + n_2 R\ln\frac{V_2}{n_2} + (n_1+n_2)s_0 \\ S_{fin}^{ext} &= (n_1+n_2)(CR\ln T + R\ln\frac{(V_1+V_2)}{(n_1+n_2)} + s_0) \end{aligned} \tag{6.43}$$

The entropy difference indeed vanishes on noting $V_1/n_1 = V_2/n_2 = (V_1+V_2)/(n_1+n_2) = RT/P$.

But does extensive entropy change the mixing entropy calculated earlier? It does not, because the difference between the two expressions for entropies consists of $-nR\ln n$, and this does not change for either of the dissimilar gases in the process of mixing. Let us explicitly carry out that calculation also to bring out some important features of this case. Eqns.(6.44,6.40) are now replaced by

$$\begin{aligned} S_{ini,het}^{ext} &= n_1 C_1 R\ln T + n_1 R\ln\frac{V_1}{n_1} + n_1 s_0^{(1)} + n_2 C_2 R\ln T + n_2 R\ln\frac{V_2}{n_2} + n_2 s_0^{(2)} \\ S_{fin,het}^{ext} &= n_1 C_1 R\ln T + n_1 R\ln\frac{V}{n_1} + n_1 s_0^{(1)} + n_2 C_2 R\ln T + n_2 R\ln\frac{V}{n_2} + n_2 s_0^{(2)} \end{aligned} \tag{6.44}$$

The difference between these two, which is the mixing entropy, indeed takes the same value as in eqn.(6.41).

In terms of pressures, the difference between mixing of similar and dissimilar gases is this: in the case of similar gases samples with (n_1, V_1, T, P) and (n_2, V_2, T, P) mix to form $(n_1 + n_2, V_1 + V_2, T, P)$ while in the case of dissimilar gases, (n_1, V_1, T, P) of first and (n_2, V_2, T, P) of the second upon mixing go over to $(n_1, V_1 + V_2, T, P_1)$ and $(n_2, V_1 + V_2, T, P_2)$ respectively where $P_1 = n_1/(n_1 + n_2)$ and $P_2 = n_2/(n_1 + n_2)$ are the *partial pressures* of the two gases in the mixture such that $P_1 + P_2 = P$.

Sometimes such mixtures are characterised loosely as being made up of $n_1 + n_2$ moles of a substance with *average molecular weight* of $M_{av} = (n_1M_1 + n_2M_2)/(n_1 + n_2)$ and average molar specific heat $C_{av} = (n_1C_1 + n_2C_2)/(n_1 + n_2)$, occupying V at (P,T). While that may work for some quantities, it fails to capture the entropy of mixing which would vanish with such a description.

The other version of the Gibbs paradox is that the entropy of mixing changes abruptly from a nonvanishing value for dissimilar gases to zero for mixing of similar gases. This is so even if the actual physical differences between the two dissimilar gases are very small, but not vanishing. For example, whether we mix O_2 and H_2 with a ratio of molecular weights of 16, or we mix uranium-235 and uranium-238 with a ratio of molecular weights of 1.013, mixing entropy for given moles of mixing is the same! This may appear paradoxical, but being a straightforward consequence of thermodynamics, there is nothing paradoxical about it!

6.5.1 Extensivity revisited

Thus we have seen that taking entropy to be extensive removes the so called Gibbs paradox while preserving the expression for the mixing entropy for dissimilar gases. In many accounts of this paradox, an impression is created that one has to go to *quantum statistical mechanics* along with notions of *indistinguishability* to 'resolve' the paradox. We see that as far as classical thermodynamics extensivity is all that is needed. Of course, extensivity can not be proved even in classical thermodynamics any more than proving the second law of thermodynamics, for example. In fact, as stated by Pauli [53], and emphasized again by Jaynes [28], the Clausius formulation was really silent on this issue of extensivity. Two factors here are that that formulation only required the extensivity of changes in entropy, i.e dS, and not of entropy itself. To this extent, the Clausius formulation was incomplete. But Jaynes goes a significant step ahead by arguing that this logical incompleteness has to be there irrespective of the theory, i.e even quantum statistical mechanics can not really prove the extensivity of entropy. It is perhaps for this reason that Callen [3] has included the extensivity of entropy as one of the *axioms* of thermodynamics obviating any issues of its proof.

Apparently Gibbs was fully aware of all these nuances in his monumental work of 1875 itself [19]. Interestingly, Jaynes opines that it was Gibbs himself who was responsible for the subsequent confusions by what he said in his other classic *Elementary Principles in Statistical Mechanics* [20]! All this notwithstanding, consequences of extensivity in thermodynamics have been spectacular, and the very role of Gibbs concept of *chemical potential*, whose equality to the Gibbs potential is one such consequences, is one tip of this massive iceberg!

Example 6.1: Mixing entropy for gases

Calculate the entropy change when two moles of H_2 gas is mixed with one mole of O_2 gas at 300 K and one bar. Compare this to the change of total entropy when both of them are isothermally doubled in volume. Treat both gases as ideal.

In this example, $n_{O_2} = 1, n_{H_2} = 2$ and $n_{O_2} + n_{H_2} = 3$. A straightforward application of eqn.(6.41) gives, for the total entropy change during mixing, $S_{mix} = R(3\ln 3 - 2\ln 2) = 0.91R = 7.57 J/K$. The change in molar entropy during isothermal expansion of an ideal gas from V_1 to V_2 is $\Delta s = R\ln(V_2/V_1)$. Hence the total entropy increase when both the gases in this example isothermally double their volumes is $3R\ln 2$ which is 17.3 J/K. This gives a comparative idea of the magnitudes of mixing entropies.

6.6 Worked out examples

6.6.1 Fundamental equations and equations of state

Let us look at some concrete examples. Obviously, the ideal gas case should be the simplest. Let us imagine that instead of the usual $PV = nRT$ and $U = nCRT$, we are given one of the fundamental equations. According to what has been described so far, a *single* fundamental equation should contain not only the equivalents of these two equations, but also the first law.

Historically, this is of course not how the ideal gas laws were discovered, but as has been emphasized before, the importance of the fundamental equation lies in the clarity it gives to the structure of thermodynamics. It is not that it provides the most user-friendly way of working out the thermodynamic properties, nor is it the most likely equation to be discovered empirically as it involves the variables U and S that are not directly observed, in contrast to P,V,T,n etc.

So for the purpose of this section, we work our way *backwards* from the usual equations of the ideal gas to one of the fundamental equations. For both the representations (energy and entropy), one essentially eliminates T in favour of U. Thus, the expression for S discussed before takes the form

$$S(U,V,n) = nCR\ln\frac{U}{nu_0} + nR\ln\frac{V}{nv_0} = nR\ln\left\{(\frac{U}{nu_0})^C\frac{V}{nv_0}\right\} \tag{6.45}$$

This is the fundamental equation in the entropy representation. Here u_0, v_0 are constants with dimensions of U,V. The corresponding equation in the energy representation can be obtained from this through inversion

$$U = nu_0(\frac{nv_0}{V})^{\frac{1}{C}} e^{\frac{S}{nCR}} \tag{6.46}$$

We work out the details in the energy representation. Let us begin by computing the intensive variables of first class:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = \frac{U}{nCR} = \frac{U_m}{CR} \qquad P = \frac{U_m}{CV_m} \tag{6.47}$$

Clearly these are the proper equations of state in the sense of Callen; they relate the intensive variables (T,P) of the first class to only the intensive variables U_m, V_m of the second class. The usual equations for ideal gases are easily recovered from them.

We see explicitly that there are only two degrees of freedom. It remains to evaluate the third first class intensive variable μ and show that it is not really independent. Evaluating the relevant partial derivative explicitly yields

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = U_m(S_m,V_m) + \frac{U_m(S_m,V_m)}{C} - \frac{S_m U_m(S_m,V_m)}{CR} = U_m + PV_m - TS_m = G_m \tag{6.48}$$

Now we discuss the somewhat more involved example of the van der Waals fluid. In that case, the internal energy U is not a function of T(in the usual treatment) alone. To keep things transparent, let us look at only the *ideal* case where

$$U = nCRT - \frac{an^2}{V} \qquad \rightarrow T = (U_m + \frac{a}{V_m})/CR \tag{6.49}$$

The equation for T is of the correct type despite the internal energy being dependent on both T and V. The entropy of the ideal vdW fluid being

$$S = nCR\ln\frac{T}{T_0} + nR\ln\frac{V-nb}{nb} = nR\ln\left\{(\frac{T}{T_0})^C\frac{V-nb}{nb}\right\} \tag{6.50}$$

Hence the fundamental equation for the ideal vdW fluid in the entropy representation is

$$S = nR\ln\left\{\frac{1}{(nu_0)^C}(U + \frac{an^2}{V})^C\frac{V-nb}{nb}\right\} \tag{6.51}$$

The fundamental equation in the entropy representation is still easily invertible. Consequently the fundamental equation in the energy representation is

$$U = nu_0\left(\frac{nb}{V-nb}\right)^{\frac{1}{C}} e^{\frac{S}{nCR}} - \frac{an^2}{V} \tag{6.52}$$

The two bona-fide equations of motion that follow are

$$T = \frac{1}{CR}\left(U_m + \frac{a}{V_m}\right) \qquad P = \frac{1}{C(V_m - b)}\left(U_m + \frac{a}{V_m}\right) - \frac{a}{V_m^2} \tag{6.53}$$

Again, equations that are commonly called the vdW equation of state can be reconstructed from these.

It is not always easy to work backwards from the standard equations to the fundamental equations. It is crucial that T be invertible in terms of U and V. An example where this does not work is in the case of the so called *Dieterici equation*. This is left as an exercise.

6.6.2 Gibbs-Duhem relations

Now we show how to solve the Gibbs-Duhem relation for a few cases. We choose to work in the entropy representation. Let us first treat the ideal gas case. In that case $\frac{1}{T} = CR\frac{1}{U_m}$ and $\frac{P}{T} = \frac{R}{V_m}$. Therefore

$$d\left(\frac{\mu}{T}\right) = U_m d\left(\frac{1}{T}\right) + V_m d\left(\frac{P}{T}\right) = CRU_m d\left(\frac{1}{U_m}\right) + RV_m d\left(\frac{1}{V_m}\right) \tag{6.54}$$

It is easy to integrate this to get

$$\frac{\mu}{T} = -CR\ln U_m - R\ln V_m + const. \tag{6.55}$$

This is the same expression for μ that we had earlier after the constant of integration is fixed suitably.

Let us now consider the ideal vdW fluid for which $U_m = CRT - \frac{a}{V_m}$ and $\frac{P}{T} = \frac{R}{V_m-b} - \frac{a}{V_m^2}\frac{CR}{U_m+\frac{a}{V_m}}$. In the true spirit of what has been said in this chapter, one should show that $\frac{\mu}{T}$ is integrable in terms of a function of U_m, V_m. This can indeed be done, but is algebraically a little messy.

Instead, we eliminate U_m in terms of T, V_m and integrate the Gibbs-Duhem relation to find an expression for $\frac{\mu}{T}$ in terms of T, V_m. Then

$$\begin{aligned} d\left(\frac{\mu}{T}\right) &= -\left(CRT - \frac{a}{V_m}\right)\frac{dT}{T^2} + V_m d\left(\frac{R}{V_m-b} - \frac{a}{TV_m^2}\right) \\ &= -CRd(\ln T) - rd(\ln(V_m-b)) + bRd((V_m-b)^{-1}) - d(\frac{2a}{V_mT}) \end{aligned} \tag{6.56}$$

The solution to this is

$$\mu = const.T - CRT\ln\frac{T}{T_0} - RT\ln\frac{V_m-b}{b} - \frac{2a}{V_m} + RT\frac{V_m}{V_m-b} \tag{6.57}$$

This is indeed the chemical potential for the vdW fluid if the constant of integration is adjusted properly.

6.7 Axiomatic intensive variables and equilibrium

We now wish to demonstrate that the first class intensive variables defined axiomatically have all the properties that have been ascribed to them through the traditional empirico-axiomatic methods. For this we need the *Second Law of Thermodynamics*. Either fully axiomatically or through the empirico-axiomatic methods of Clausius, Kelvin and others, this law can be stated as *every thermodynamic change of an isolated system is such as to either increase the entropy or keep it stationary*. Then the condition for thermal equilibrium is that *total entropy must assume its maximum value*. Stated in this manner, the fundamental equation in the entropy representation may appear to be playing a more fundamental role. This is not so, and completely equivalent conclusions can be drawn from the energy representation.

Let us first consider thermal equilibrium. Consider two systems that are allowed to exchange heat between them but the total system is isolated. Further, let the changes be such that there are no changes in the volumes of the two systems, i.e $\Delta V^{(1)} = \Delta V^{(2)} = 0$ and there is no chemical transfer so that $\Delta n^{(1)} = \Delta n^{(2)} = 0$. In such a circumstance, since total energy must be conserved one must have $\Delta U^{(1)} = -\Delta U^{(2)}$. Additivity of entropy says $S = S^{(1)} + S^{(2)}$. Then

$$dS = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V,n} dU^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V,n} dU^{(2)} = (\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}})dU \geq 0 \tag{6.58}$$

At equilibrium, stationarity of S, i.e dS=0 implies $T^{(1)} = T^{(2)}$, i.e the subsystems in thermal equilibrium must be at the same temperature. Thus the axiomatic definition of temperature is consistent with the traditional concept of temperature. Furthermore, if the two subsystems are not in equilibrium and let, for example, $T^{(1)} > T^{(2)}$, then $dS > 0$ implies $dU^{(1)} < 0$, i.e if two systems in thermal contact are not in equilibrium, then the energy (heat) flow is from the body at higher temperature to the one at lower temperature if no work is being done and there is no material transfer.

Now we can relax the conditions of no volume change so the two systems can perform work in addition to exchanging heat. By reasonings completely parallel to the pure thermal equilibrium case we can write

$$dS = (\frac{1}{T^{1)}} - \frac{1}{T^{(2)}})dU^{(1)} + (\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}})dV^{(1)} \geq 0 \tag{6.59}$$

where we have also used that the total volume of the system does not change though the individual volumes can. Now the variations $dU^{(1)}, dV^{(1)}$ are of course mutually *independent*. Therefore at equilibrium where $dS = 0$ one must separately have $T^{(1)} = T^{(2)}$ and $\frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}}$ i.e $P^{(1)} = P^{(2)}$. Hence for thermo-mechanical equilibrium both the temperature and pressure must be the same. Once again, let us consider two substances which are at the same temperature but not in equilibrium. Then, as in the earlier case, $dS = (P^{(1)} - P^{(2)})\frac{dV^{(1)}}{T} > 0$ implies that if $P^{(1)} > P^{(2)}$, $dV^{(1)} < 0$. This again fully corresponds with the traditional concept of pressure.

Lastly one can show that in addition to exchange of heat and volume, the subsystems can have chemical exchanges, then at equilibrium not only do the temperatures and pressures have to be equal, the chemical potentials have to be the same. Further, if the subsystems have the same temperature and pressure, but not the same chemical potentials, there will be a net matter flow from the subsystem with a higher chemical potential to the one with lower chemical potential.

6.7.1 Stability of equilibrium

The above conditions only ensure that the entropy is stationary at the equilibrium point. This means that the state in question can still be stable, unstable or metastable (neutral). It is of course consistent to count only stable states as (equilibrium) states, but it is useful to extend the notion of states in thermodynamics to include metastable and even unstable stationary points of entropy. Otherwise, interesting and useful configurations like supercooled liquids, superheated liquids etc. would be outside the purview of thermodynamics.

However, for the state to be stable, the entropy has to reach its maximum value. Therefore, the stationary point must actually correspond to a *maxima*. Let us consider the hypothetical case where S only depends on U. From calculus, it then follows that $\frac{d^2S}{dU^2} < 0$. If we now consider the more realistic situation of S depending on both U and V, then in addition one expects $\frac{\partial^2 S}{\partial V^2}|_{(U,n)}$ to be also negative. But that is not enough; the *matrix* formed by the second derivatives $\frac{\partial^2 S}{\partial U^2}|_{(V,n)}\frac{\partial^2 S}{\partial V^2}|_{(U,n)}$ and $\frac{\partial^2 S}{\partial U \partial V}$ must be *negative*, i.e all its eigenvalues must be negative. For this case, since the matrix is 2x2, the *determinant* must be *positive*. This leads to the additional condition

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,n}\left(\frac{\partial^2 S}{\partial V^2}\right)_{U,n} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0 \tag{6.60}$$

As they stand, these mathematical expressions for stability do not convey their physical meaning very clearly. For that, let us express the various second derivatives in terms of physically observable quantities. Let us examine this issue in the entropy representation. The reader is urged to work out the analogous results when, for example, S is taken to be a function of (V,T).

From $\left(\frac{\partial S}{\partial U}\right)_{V,n} = \frac{1}{T}$, it follows that

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,n} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{V,n} = -\frac{1}{C_V T^2} \leq 0 \tag{6.61}$$

Thus one of the stability conditions requires that the specific heat C_V be *positive*. Likewise, from $\left(\frac{\partial S}{\partial V}\right)_{U,n} = \frac{P}{T}$ it follows that

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_{U,n} = -\frac{1}{TV\kappa_{U,n}} - \frac{P}{VT^2\beta_{U,n}} \qquad \frac{\partial^2 S}{\partial U \partial V} = -\frac{1}{VT^2\beta_{U,n}} \tag{6.62}$$

In these equations $\kappa_{U,n}, \beta_{U,n}$ are the compressibility and expansion coefficient under the conditions of constant (U,n). They are not the compressibilities and expansion coefficients introduced before, but can be related to them.

In fact stability analysis can also be performed for the maxima of Helmholtz free energy F and Gibbs potential G. In terms of physical quantities, these conditions are: $\kappa_T \geq \kappa_S \geq 0, C_P \geq C_V > 0$. For more details, please see [3].

6.8 Problems

Problem 6.1 Is the fundamental equation in the U-representation, $U = ANVe^{-S/NR}$(A is a constant), consistent with all the known properties of a thermodynamic system? If not, make the simplest modification that would make it so.

Problem 6.2 Find the intensive quantities T, P and the chemical potential μ for a system whose fundamental equation in the U-representation is given by $U = A(S^2/V)\,e^{S/NR}$. Determine the fundamental equation in the S-representation.

Problem 6.3 Is the fundamental equation in the S-representation, $S = A\ln(UV/N^2B)$(A and B are constants), consistent with the third law? If not, does it mean that such an equation is never acceptable? Compare this with the ideal gas case.

Problem 6.4 For what values of α, β, γ is the fundamental equation, $S = (NU^{\alpha} + AV^{\beta})^{\gamma}$, in the S-representation, physically acceptable?

Problem 6.5 As in the previous problem, determine the consistency conditions for the constants α, β, γ occurring in the fundamental equation $S = AU^{\alpha}V^{\beta}N^{\gamma}$ where A is a positive constant. What further restrictions arise from stability, which in this context requires the pressure P to be a monotonically increasing function of the internal energy density. Apply to ideal gases and blackbody radiation.

Problem 6.6 The molar entropy s, internal energy u, and the volume v of a system are known to satisfy the U-representation fundamental equation $u = As^2 - Bv^2$. Determine the equations of state for this system and show that the chemical potential μ is negative of internal energy.

Problem 6.7 N moles of a system satisfying the fundamental equation $u = (A/v^2)\,e^{s/R}$ for the molar quantities u,v,s, is initially at T_0,P_0. Determine the final temperature if it is adiabatically compressed to half its pressure.

Problem 6.8 Show that for all systems whose adiabats are given by $PV^k = const.$, the internal energy U is given by

$$U = \frac{PV}{k-1} + Nf(\frac{PV^k}{N^k}) \tag{6.63}$$

where f is a suitable function. Apply this to a) ideal gases and b) blackbody radiation.

Problem 6.9 The equations of state of a system are given to be $u = APv$ and $Pv^2 = bT$. Are they consistent thermodynamically? If not, find a simple modification that will restore consistency.

Problem 6.10 Express the fundamental equation $S = A(NVU)^{1/3}$ in Euler form.

Problem 6.11 Given that $T = A(s^2/v)$ and $P = B(s^3/v^2)$, determine the ratio (A/B) for which the Gibbs-Duhem relation can be integrated. Find the chemical potential μ as a function of s,v.

Problem 6.12 Consider the fundamental equation

$$U = \frac{\mathscr{M}^2}{N} + Ne^{\frac{\alpha S}{N}} \tag{6.64}$$

Determine the three equations of state giving T, B_e and μ as a function of S,N and $\mathscr{M}$.

Problem 6.13 The atmospheric air when dry is essentially a mixture of oxygen and nitrogen in the molar ratio 1:4. It is required to separate air at 300 K and 1 bar into its pure components also at the same temperature and pressure. Treating all components as ideal gases, what is the minimum power required to purify 10 mol/s of air? What is the role of the enthalpy of mixing in this?

7 Thermodynamic Potentials and Maxwell Relations

7.1 Thermodynamic potentials

The notion of a *potential* plays a very important role in mechanics. Even without solving dynamical equations like for example the Newton's laws (which necessarily bring in the notion of *time*), a knowledge of even the gross features of a potential, like its maxima or minima (also called the *stationary points*), tells us about special configurations called the stable(unstable) points. The significance of the stable configurations, given by the location of the *minima* of the potential, is that if the system when isolated happens to be in one such configuration, it will continue in it forever (thereby making time irrelevant). One would say it is in a state of *static equilibrium.*

One may hope that in equilibrium thermodynamics too (where time is irrelevant) there would be analogous potentials that would be helpful in identifying equilibrium states. In the mechanical system, the *state* was characterised by position. In the full time-dependent description of a mechanical system, one would need both position and momentum to characterize a state. But when one restricts attention to static aspects, momentum plays no role. In equilibrium thermodynamics, a state is characterised by some set of *independent thermodynamic coordinates* like P,T or P,V etc. So the goal is to find *functions* of such thermodynamic coordinates whose gross features like minima will identify equilibrium states.

Apart from this physical motivation, there is also a mathematical motivation which amounts to finding *state functions* $f(x,y,..)$ of the independent thermodynamic coordinates $(x,y,...)$ such that

$$df(x,y,..) = A_1\, d\xi_1 + A_2\, d\xi_2 + \dots \tag{7.1}$$

where A_i are either coordinates or known functions, and so are ξ_i. It should be noted that any df can *always* be written as

$$df(x,y,...) = \left(\frac{\partial f}{\partial x}\right)_{y,..} dx + \left(\frac{\partial f}{\partial y}\right)_{x,..} dy + \dots \tag{7.2}$$

The important difference between eqn.(7.1) and eqn.(7.2) is that in the case of the former, the set of partial derivatives appearing in a generic expression like eqn.(7.2) are *known*. It is not always easy to achieve this, and there will be integrability conditions associated with eqn.(7.1); these are an essential part of the Maxwell relations. We shall return to further mathematical properties of the thermodynamic potentials later.

The reader may find the meaning, and even the usefulness, of these mathematical aspects rather obscure at first. They will, of course, become clearer as we go on, and more so after these concepts are repeatedly applied to concrete physical problems.

In fact, thermodynamic potentials are very powerful, and practically indispensable, tools for a finer understanding of thermodynamics.

The coordinates for a single component, *non-magnetic* material can be taken to be (T, P),(T, V) or (V, T). In multicomponent systems, various *concentrations* are also among the coordinates. In magnetic systems, *magnetization* is among the coordinates. Likewise, for the simplest of the systems, S,U are for example, functions to be considered. To get a clearer idea of what we are going to do, let us start with the simplest possible system, i.e a single component non-magnetic system with *fixed* number of moles; we shall return to an inclusion of more coordinates and functions, and how the simple considerations will generalize, later.

7.1.1 Internal energy and enthalpy

The first law can be rewritten as

$$dU = T\,dS - P\,dV \tag{7.3}$$

This is indeed of the form of eqn.(7.1). Some general features of such equations are i) they are obviously dimensionally homogeneous, ii) one of the factors on the rhs is *intensive*, while the other is *extensive*. In the internal energy example, U is extensive and so are S and V, while P and T are intensive.

The specific heat at constant volume is given as the temperature derivative of U at constant V, i.e $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. This motivates us to look for a state function whose temperature derivative at constant pressure gives C_P. It is straightforward to find it; it is the *enthalpy* $H = U + PV$, and

$$dH = d(U + PV) = T\,dS + V\,dP \tag{7.4}$$

and indeed $C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$.

7.1.2 Helmholtz free energy

In a mechanical system all the work done goes to change the energy of the system and one has the equality $\Delta W = -\Delta E$. In thermodynamics, however, we have the concept of internal energy U instead of E, and from first law we know that $\Delta W = -\Delta U + \Delta Q$. Therefore, depending on the sign and magnitude of the heat supplied to the system, the work done may equal, be greater than, or even be less than the change in the internal energy.

Now consider a system in the state A, at temperature T_A, such that it is in contact with a reservoir at a constant temperature T_{res}. The system can exchange heat with this reservoir but is not *necessarily* in equilibrium with it. If it were in equilibrium with the reservoir, the system would always be at the same temperature as the reservoir and we would be restricting ourselves to only *isothermal transformations*. Now let us envisage the system making a sequence of heat exchanges with the reservoir and finally ending in a state B.

We have the fundamental entropy inequality

$$\int_A^B \frac{đQ}{T_{res}} \leq S(B) - S(A) \tag{7.5}$$

Following Fermi [17], we again emphasize that the temperature occurring under the integral sign is *not* the system temperature, but the temperature of the reservoir. Since in our context, T_{res} is constant, we get, for the total heat Q_{AB} received by the system during the transformation from A to B

$$Q_{AB} = \int_A^B đQ \leq T_{res}\,(S(B) - S(A)) \tag{7.6}$$

Consequently we find that the work performed during the transition $A \to B$ satisfies the inequality

$$W_{AB} = U(A) - U(B) + Q_{AB} \leq U(A) - U(B) + T_{res}\,(S(B) - S(A)) \tag{7.7}$$

The rhs of this equation involves both the system and environment state functions, and is as such not a very natural quantity. However, we can choose the temperature of the system to be *the same as* T_{res} both initially and finally, but not necessarily during the transformation.

This is a very important and subtle point often glossed over. Overlooking this subtlety would give the impression that the Helmholtz free energy inequality to be derived shortly is valid only for *isothermal* transformations. With the choice above for T_A, T_B we have $T_A = T_B = T_{res} = T$(say). Then, eqn.(7.7) takes the form

$$W_{AB} = U(A) - U(B) + Q_{AB} \leq U(A) - U(B) + T\,(S(B) - S(A)) \tag{7.8}$$

This allows the definition of a new *state function*

$$F = U - TS \tag{7.9}$$

in terms of which we can write the work inequality as

$$W_{AB} \leq F(A) - F(B) = -\Delta F \tag{7.10}$$

This state function F (also denoted by A in some texts, apparently for the German word *Arbeit* for work) is called the Helmholtz free energy. It plays a fundamental role in thermodynamics as well as *Statistical Mechanics*.

The inequality says that during any transformation of a thermodynamic system such that the initial and final temperatures are the same, and the system exchanges heat with a reservoir also at the same temperature, the work performed is bounded by the negative of the change in Helmholtz free energy. The following are important remarks in this context:

- Though $T_A = T_B$, the system need not be at the same temperature throughout, i.e the transformation $A \to B$ need not be *isothermal* for the bound of eqn.(7.10) to hold.

- It certainly holds when the transformation is restricted to be isothermal. This requires the system to be in *equilibrium* with the heat reservoir throughout.
- An important physical significance of the free energy F is that its change in any change consistent with the above restrictions gives the *maximum* work that can be performed during the transformation.
- The equality holds when the transformation is *reversible* and in that case $W_{AB} = F(A) - F(B) = -\Delta F$; in this case, the Helmholtz free energy behaves like energy in mechanical systems.

Now we discuss what is essentially the most important property of F. For this, consider the system to be mechanically isolated, though continuing to be in contact with the heat reservoir. Then W_{AB} is necessarily zero and we get

$$F(B) \leq F(A) \tag{7.11}$$

This means that under the conditions stated above, a mechanically isolated system at a minimum of F must *necessarily* be in a state of equilibrium. Otherwise, any transformation has to only increase the free energy and that would contradict eqn.(7.11).

But is the converse also true? That is, if a system, subject to the above mentioned restrictions, is in a state of thermal equilibrium, does it have to be at a minimum of its free energy? This is a subtler issue. If the system is not at a minimum of F, there will certainly be states with *lower* free energies. Therefore, unless there are some barriers, specific to the system, that prevent transformations from taking the system to these lower F states, the system will not be in equilibrium. But ruling out such barriers requires additional considerations, and one can not say with all generality that the system in a higher state of F will necessarily transform to a state with lower F. But if one takes the attitude that 'unless otherwise specified' the system *will* tend towards minimising F, the minimum of F becomes both a necessary and sufficient condition for thermal equilibrium.

7.1.3 Gibbs free energy

Now we introduce the Gibbs Free Energy, also called the *thermodynamic potential at constant pressure*. The motivation for this stems from the fact that many important transformations take place under conditions of constant temperature and constant pressure. Notable among them are the *phase transformations*, which will be discussed at length in chapter 14.

So we consider a transformation that is both *isothermal* (constant temperature) and *isobaric* (constant pressure). It should be appreciated that the conditions discussed while defining the Helmholtz free energy F are such that, if the transformation is *reversible*, it is necessarily isothermal. But irreversible transformations need not be isothermal. Nevertheless, the irreversible transformations can be taken to be isothermal without any contradiction. If the volume of the system changes from $V(A)$ to $V(B)$ during the isothermal-isobaric process, the work done is $W_{AB} =$

$P(V(B)-V(A))$, and the inequality eqn.(7.10) becomes

$$P(V(B)-V(A)) \leq F(A)-F(B) \tag{7.12}$$

This immediately suggests the introduction of the state function

$$G = F + PV = U - TS + PV \tag{7.13}$$

In terms of this state function, the isothermal-isobaric transformation $A \to B$ must satisfy

$$G(B) \leq G(A) \tag{7.14}$$

Once again, we conclude from this that a system at the minimum of G will be in thermal equilibrium under conditions of constant temperature and pressure. In the same spirit as the corresponding discussion for F, we take the minimum of G as a condition for thermal equilibrium under these conditions.

Example 7.1: Potentials and intensive parameters

Show that a knowledge of the thermodynamic potentials enables the determination of T and P as suitable partial derivatives.

Let us consider the potentials per unit mass, i.e u,s,h,f and g, and let v denote the specific volume. We have the following differential identities:

$$du = Tds - Pdv \quad dh = Tds + vdP \quad df = -sdT - Pdv \quad dg = -sdT + vdP \tag{7.15}$$

Consequently, T and P can be obtained as the following partial derivatives:

$$T = \left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_P \qquad P = -\left(\frac{\partial u}{\partial v}\right)_s = -\left(\frac{\partial f}{\partial v}\right)_T \tag{7.16}$$

The Gibbs free energy is not useful in this context.

7.2 Maxwell's relations

With every equation of the type of eqn.(7.1) the following are associated:

$$\left(\frac{\partial f}{\partial \xi_1}\right)_{\xi_2} = A_1 \qquad \left(\frac{\partial f}{\partial \xi_2}\right)_{\xi_1} = A_2 \tag{7.17}$$

An integrability condition as a consequence of $\frac{\partial^2 f}{\partial \xi_1 \partial \xi_2} = \frac{\partial^2 f}{\partial \xi_2 \partial \xi_1}$ is

$$\left(\frac{\partial A_1}{\partial \xi_2}\right)_{\xi_1} = \left(\frac{\partial A_2}{\partial \xi_1}\right)_{\xi_2} \tag{7.18}$$

Let us start by applying these considerations to the first law described in eqn.(7.3) which has the same form as eqn.(7.1). The equations that follow are:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{7.19}$$

The last of these is traditionally called one of the *Maxwell Relations*, and following Pippard, we denote it by M.1. Some authors (Huang) refer to the first two also as Maxwell relations. We shall adhere to the traditional terminology. We have applied our considerations to the internal energy U, even though the word *potential* may not usually be applied to it. In a certain sense, to be made more precise shortly, one could call U a *thermodynamic prepotential.* In a completely analogous fashion, one gets the next set of relations by considering the enthalpy, H:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{7.20}$$

The Maxwell relation here will be designated M.2. Continuing in the same fashion, we obtain two more sets of equations, by considering F and G respectively:

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{7.21}$$

We call the Maxwell relation of eqn.(7.21) as M.3, and,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{7.22}$$

as M.4. The four Maxwell relations are not mutually independent. In fact they are all mathematically equivalent to any one of them. Let us show how this follows from the identities obeyed by partial derivatives. Let us consider M.4; both the lhs and rhs can equivalently be rewritten as

$$-\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial T}\right)_P = -\frac{\left(\frac{\partial V}{\partial S}\right)_P}{\left(\frac{\partial T}{\partial S}\right)_P} \tag{7.23}$$

On using $\left(\frac{\partial T}{\partial S}\right)_P^{-1} = \left(\frac{\partial S}{\partial T}\right)_P$, one sees that this is just M.2! likewise, we rewrite the lhs and rhs of M.3 as

$$-\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial T}{\partial S}\right)_V} \tag{7.24}$$

On using $\left(\frac{\partial T}{\partial S}\right)_P^{-1} = \left(\frac{\partial S}{\partial T}\right)_V$, one sees that this is just M.1! Pippard has explicitly shown the equivalence of M.1 and M.2 in his book. Thus all four Maxwell relations are equivalent to a single relation (see also the problem 7.4 at the end of this chapter).

This is hardly surprising as they are all consequences of the first law. But what is important is not whether the relations are independent in a mathematical sense or not. Though mathematically dependent, each one of them plays a different role in relating quantities that may be hard to obtain experimentally to those that can be obtained more easily. That is the true import of the different Maxwell relations.

Example 7.2: Determining enthalpy

It is often necessary to determine enthalpy as a function of T and P. Suppose there is a substance whose constant pressure specific heat $C_P(T)$ is a function of temperature alone. What consistency condition is to be satisfied by the coefficient of volume expansion α? With such a condition satisfied, find enthalpy as a function of T and P.

Let us consider enthalpy h as a function of T and P. Then a knowledge of its partial derivatives can be used to find h explicitly. This is possible as these partial derivatives can be expressed in terms of observables. Let us begin with the enthalpy differential encountered in the example above. It follows from it that

$$\left(\frac{\partial h}{\partial P}\right)_T = t\left(\frac{\partial s}{\partial P}\right)_T + \mathrm{v} \rightarrow \left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial \mathrm{v}}{\partial T}\right)_P + \mathrm{v} = \mathrm{v}(1-\mathrm{T}\alpha) \qquad (7.25)$$

where use has been made of the Maxwell relation M.3. On the other hand, one also has

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T^d P = C_P dT + \mathrm{v}(1-T\alpha)dP \qquad (7.26)$$

Let C_P in this case be $C_P(T)$. The integrability of h requires that $\mathrm{v}(1-T\alpha)$ must be a function of P alone. Denoting that function as f(P), the expression for the enthalpy is

$$h(T,P) = \int dT C_P(T) + \int dP f(P) \qquad (7.27)$$

7.2.1 How many different potentials?

We introduced four potentials U, H, F and G; the question that naturally comes to mind is whether there are more, and how we can be sure that we have found them all. We first answer this in the simple context of only two independent variables, and then answer the question in general.

Starting with dU we find that it equals $TdS - PdV$ as per the first law. The independent variables here are S,V, and the dependent variables T,P are given by the first two of eqn.(7.19). Can U be transformed into another *state function* which is now a function of P, which was a dependent variable in the case of U, and of S, which was an independent variable for U? This is an intermediate step where we have traded only one of the independent variables (in this case V) to one of the dependent variables (in this case P). Clearly, this process can be carried out one at a time till all the original independent variables have been swapped with all the original dependent variables.

The underlying mathematics is called *Legendre transform* and we shall not go into the details of this very beautiful concept, but simply illustrate how it works in our thermodynamics context (it works in a very simple and straightforward way!). It is obvious that by changing U to $U' = U + PV$, one gets $dU' = dU + PdV + VdP = TdS + VdP$. Several important features of this very elementary manipulation deserve to be stressed; firstly, U' is also a state function satisfying eqn.(7.1). The independent variables for the specification of U' are now (S,P) as againt (S,V) for U. Secondly, the sign of VdP in U' is *opposite* to that of PdV in U. We may call this elementary operation a *Legendre transform of U in the P,V variables.*

Clearly, an independent Legendre transform of U in the S,T variables is also possible leading to yet another state function, say, U^*, also obeying eqn.(7.1). The thrust of these considerations is, therefore, that new thermodynamic potentials can be obtained starting from old ones through the process of Legendre transforms. Posed this way, the question as to the number of possible thermodynamic potentials boils down to the number of possible independent Legendre transforms that can be performed.

The systematic way of answering that question is by studying the *algebra* of Legendre transforms, or put in simpler terms, by finding out how two Legendre transforms can be combined to yield a third. Let us look at U' obtained by Legendre transforming U in (P,V) variables. The structure of $dU' = TdS + VdP$ indicates that U' too can be further Legendre transformed in two independent ways, in (P,V) or in (S,T). For the sake of clarity in expressions, let us say that in (P,V) variables it is Legendre transform 1, and in (S,T) variables it is 2. Further, let us denote by A^i the Legendre transform of A by transform i, and by $A^{i,j,..}$ the result of successively transforming A by transforms i,j,..etc.

With this notation, $U^1 = U'$ and $U^2 = U^*$. Quite obviously, $(U')^1 = U^{1,1} = U, (U^*)^2 = U^{2,2} = U$, and, $U^{1,2} = U^{2,1}$. The important rule we abstract is that repeated Legendre transforms in the same pair of variables do not generate new potentials, and that the order of independent Legendre transforms is *irrelevant*. So in our simplest example, starting with U (hence our choice to call it the *prepotential*), we generate three more potentials $U^1 = U' = U + PV = H$, $U^2 = U^* = U - ST = F$, and $U^{1,2} = U^{2,1} = U + PV - ST = G$. Thus the answer to our earlier question is that U,H,F,G are all the thermodynamic potentials one can have in the simplest case.

7.2.2 Inclusion of chemical potential

We will show the generalisation when we include the concentration N and the *chemical potential* μ, which is the case of three independent variables. If the concentration of a substance is also considered as an independent variable, the first law generalizes to

$$dU = TdS - PdV + \mu dN \tag{7.28}$$

where μ is the *chemical potential*, and it plays the same role to N as what pressure plays to V. The intensive variables (T, P, μ) are given by

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \tag{7.29}$$

while the corresponding Maxwell relations, now three in number, are given by

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \quad \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{N,N} \tag{7.30}$$

Now, it is possible to perform *three* independent Legendre transforms; in (P,V) denoted by 1, in (S,T) denoted by 2, and finally, in (μ,N) denoted by 3. Using these we construct the eight potentials (including U) and their differentials

$$
\begin{aligned}
U^0 &= U \qquad dU = TdS - PdV + \mu dN &(7.31)\\
U^1 &= U + PV = H \qquad dH = TdS + VdP + \mu dN &(7.32)\\
U^2 &= U - TS = F \qquad dF = -SdT - PdV + \mu dN &(7.33)\\
U^3 &= U - \mu N = U_\mu \qquad dU_\mu = TdS - PdV - Nd\mu &(7.34)\\
U^{1,2} &= U^1 - TS = G \qquad dG = -SdT + VdP + \mu dN &(7.35)\\
U^{2,3} &= U^2 - \mu N = F_\mu \qquad dF_\mu = -SdT - PdV - Nd\mu &(7.36)\\
U^{3,1} &= U^3 + PV = H_\mu \qquad dH_\mu = TdS + VdP - Nd\mu &(7.37)\\
U^{1,2,3} &= U^{1,2} - \mu N = G_\mu \qquad dG_\mu = -SdT + VdP - Nd\mu &(7.38)
\end{aligned}
$$

where we have adopted the notation by Callan whereby $X_\mu = X - \mu N$ with X being a potential in the absence of a chemical potential.

Thus at first glance we find 8 potentials for this case, pointing to a 2^n rule for the number of thermodynamic potentials. In addition to the previous four potentials U,H,F,G we have four more U[μ],H[μ],F[μ] and G[μ]. The new potentials are nothing but the Legendre transforms of the previous potentials in the new direction.

But now there is a new subtlety that was absent when we had not included N among the independent coordinates; this has to do with the fact that the Euler relation, expressing the consequences of *extensivity*, equates $N\mu$ to the Gibbs potential (see chapter 6). This means that the 'new' potential G_μ actually vanishes! Thus there are only 7 new potentials instead of 8! There will be 21 Maxwell relations now. We shall not write them down explicitly.

Thus the general answer is that if there are n independent variables, not counting N, the total number of thermodynamic potentials, including U, is 2^n. Since each potential generates n integrability conditions, one will have $n \cdot 2^n$ Maxwell relations in that case. On the other hand, if the independent variables includes N, there are only $2^n - 1$ potentials and $n(2^n - 1)$ Maxwell relations.

7.3 Problems

Problem 7.1 The enthalpy of superheated steam at 300°C at 30 bar is roughly 3000 kJ/kg, while at 1 bar is 3080 kJ/kg. Likewise, the specific entropy at this temperature is 6.54 kJ/kgK at 30 bar and 8.22 kJ/kgK at 1 bar. What is the maximum work that 1 kg of steam can deliver as it expands from 30 bar to 1 bar?

Problem 7.2 Show that for an ideal gas, the enthalpy at constant temperature is independent of entropy. In particular, show that

$$\left(\frac{\partial H}{\partial S}\right)_T = 0 \qquad \left(\frac{\partial H}{\partial S}\right)_V = T\gamma \tag{7.39}$$

where $\gamma = C_P/C_V$.

Problem 7.3 Find the condition for the C_P of a gas to be independent of pressure.

Problem 7.4 Show that all the Maxwell relations involving only T,S,P,V are equivalent to the single *Jacobian* condition:

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \tag{7.40}$$

Problem 7.5 Derive the fundamental equations of an ideal gas in the F,G,H representations. From each of them, derive the equations of state and the chemical potential μ.

Problem 7.6 Derive the fundamental equations for the vdW fluid in the F-representation.

Problem 7.7 Find the fundamental equation for blackbody radiation in the F-representation. Derive from it the corresponding thermal and mechanical equations of state.

Problem 7.8 The fundamental equation for a system in the S-representation is given by $S = A(NU + BV^2)^{1/2}$ where A,B are constants. Find the fundamental equation in the G-representation. Determine the coefficient of volume expansion α and the isothermal compressibility κ_T.

Problem 7.9 Show, by using the fundamental equation in the S-representation for a mixture, that the Helmholtz free energy F for the system is additive, i.e $F(T,V,\{N_i\} = \sum_i F(T,V,N_i)$. Also show that no other thermodynamic potential satisfies this additivity.

Problem 7.10 For the rubber band model of problem 4.8, calculate the various thermodynamic potentials. Find the Maxwell relations for this system. Show that the tension at constant length increases with temperature if it is given that the entropy of the band decreases when it is stretched at constant temperature.

Problem 7.11 Consider the molar fundamental equation in the u-representation:

$$u = Ae^{(\mathrm{v}-\mathrm{v}_0)^2} e^{s/3R} s^{4/3} \tag{7.41}$$

a) For this system show that third law is satisfied, and in particular find the low temperature behaviour of C_V; b) show that the high temperature behaviour of C_V is in accordance with the Dulong-Petit law; c) show that the coefficient of expansion α for this system vanishes at P=0. What happens to the volume at this point?

Problem 7.12 Is it enough to know the Joule-Kelvin coefficient $\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H$ of a gas and its C_P as functions of T and P to determine the equation of state of the gas? If not, what is the minimal additional information that is required for this purpose?

8 Magnetic Systems

8.1 Introduction

A magnet is such an integral part of our world that it is natural to expect thermodynamics to play a role in its description, or more generally, in the description of *magnetic systems*. That temperature has a central role to play in magnetism is revealed by the fact that magnets lose their *magnetism* when heated. The power of thermodynamics, as we have amply demonstrated so far, is in providing a fairly detailed, and even quantitative, description of a system without invoking much of the *microscopic* characterstics of the system. For the thermodynamics of magnetic systems too we would like to achieve the same. Nevertheless, there are so many peculiarities of magnetic systems vis a vis mechanical systems that some broad understanding of the physics of magnetism is necessary to appreciate, and even correctly formulate, their thermodynamics.

Magnetic materials can be in the form of solids, liquids, as well as gases. According to their magnetic properties, to be explained shortly, they are classified as the so called *Diamagnetic, Paramagnetic and Ferromagnetic* substances. In addition one can have *anti-ferromagnetic* as well as *superconducting* substances. The latter display a number of novel magnetic phenomena. The quest for lower and lower temperatures has also opened the gates to more and more novel magnetic phenomena.

Let us begin with the simplest physical situation of magnetic phenomena in *free space*. Let us further restrict ourselves to the cases where neither the currents nor the magnetic fields produced by them vary with time. This is called *magnetostatics*. As far as thermodynamics is concerned, time plays no role anyway and it is only the magnetostatics that is of interest.

Quantitatively, the magnetic field produced by a current is given by the *Biot-Savart Law*. For example, a very long straight wire carrying a current I, measured in *amperes* (A), produces a magnetic field

$$B = \frac{\mu_0}{2\pi}\frac{I}{R} \tag{8.1}$$

at a distance R from it. The quantity μ_0 is called the *permeability of free space*. Its dimensions are *Newtons per ampere-squared* (N/A^2). Its numerical value is $4\pi \times 10^{-7} N/A^2$. The dimensions of the magnetic field are *Newtons per ampere-metre* and the SI unit is the **Tesla** (T), i.e $1T = 1N/(A.m)$. Its relation to the more commonly used unit **Gauss**, which is actually the cgs unit, is $1T = 10^4 \, gauss$. Actually the magnetic field is a vector **B**, and what this equation gives is its magnitude. The force exerted by a magnetic field **B** on a wire of length **d***l* (this is a vector as the elementary length can point in different directions) is given by

$$\mathbf{d}F = I\mathbf{d}l \times \mathbf{B} \tag{8.2}$$

For more general circumstances the magnetic fields are obtained by solving the *Maxwell's Equations*:

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J}_f \qquad \nabla \cdot \mathbf{B} = 0 \tag{8.3}$$

here $\mathbf{J}_f$ is called the current density. Its magnitude J_f is the current per unit area perpendicular to the flow. Following Griffith, we have added a subscript 'f' to the current density to indicate it is the *free* current. An example of a free current is the current that flows in a wire whose ends are connected to a battery. Soon, we will introduce another type of current. These are equivalent to the Biot-Savart law. If you are not familiar with these equations, do not worry! Just think of them as the precise mathematical form of the laws governing the magnetic fields created by currents.

We next discuss the very important notion of magnetic dipole moments (magnetic moments, for short) and magnetization. Consider a tiny loop of area Δa carrying a current i. Using the Biot-Savart law, the magnetic field produced by this current loop at distances much greater than its size can be shown to be

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi}\frac{\mathrm{i}}{r^5}[3(\Delta\mathbf{a}\cdot\mathbf{r})\mathbf{r} - r^2\Delta\mathbf{a}] \tag{8.4}$$

The area element has been represented here by a vector whose magnitude is the area, and whose direction is the direction of the normal to the area element. This is indeed the field of a dipole as can be seen by comparing this with the form of the *electric* field produced by an *electric* dipole. Therefore, eqn(8.4) tells us that an elementary current loop behaves like a *magnetic dipole moment* $\mathbf{m} = \mathrm{i}\Delta\mathbf{a}$, as far as the magnetic fields produced at large distances are concerned.

Let us now revisit the familiar bar magnet. It clearly produces a magnetic field (otherwise, it would not be called a magnet!), yet visibly there are no currents flowing anywhere. The common attitude taken then is to claim that the atomic structure of the magnet is actually a source of currents, though these currents are not visible to the naked eye because of their extraordinarily small size, and that the magnetic field of the bar magnet is due to them. But the spirit of thermodynamics is to avoid relying on such microscopic details. So what else can be one's attitude to the puzzle of the bar magnet?

The example of the elementary current loop tells us that the magnetic field can either be thought of as being produced by the current in the loop, *or* as being produced by an elementary magnetic dipole. In so far as one has information only about the magnetic field, there is no way to distinguish one of these possibilities from the other. The actual microscopic description could in principle have been in terms of elementary *magnetic charges* (magnetic monopoles) and dipoles constructed out of them. Thermodynamics should be insensitive to which of the microscopic descriptions is *actually* correct.

With such an attitude, we could ascribe the magnetic properties of a bar magnet as due to magnetic moments, without asking any questions as to the *microscopic origin* of these moments. Then the currents, as for example, in a solenoid, and magnetic moments, as a description, for example, of bar magnets, are to be treated on the same footing. This shall be our attitude in what follows. Rather than elementary magnetic dipole moments, what is relevant for thermodynamics is the concept of *magnetization*, which is nothing but the total magnetic moment per unit volume, **M**, added vectorially.

With this long, but necessary, introduction to the basics of magnetic phenomena, we turn our attention to the task of a thermodynamic description of magnetic phenomena. For that, we need to clarify both the nature of *energy* and of *work* in magnetic systems.

Firstly, as per *electrodynamics* there is an *energy density* associated with the magnetic field itself, even without the presence of any material magnetic system.This energy density of vacuum in the presence of a $\vec{B}$ field is $\frac{B^2}{2\mu_0}$ (Griffiths, Jackson). As regards work, what is relevant is the work done in changing the magnetization in a given magnetic field. This can be computed by using an elementary current carrying loop as a model for the dipole moment, and adding the work done on all the elementary dipoles to get the work done in changing magnetization. A lucid account of this can be found in Pippard. For an elementary dipole this is

$$\delta W = \delta \mathbf{m} \cdot \mathbf{B} \tag{8.5}$$

Would it then be a correct way to obtain the First law for magnetic systems by adding the magnetic energy density $\frac{B^2}{2\mu_0}$ to internal energy density u, and adding the magnetic work, $dW_m = \delta \mathbf{M} \cdot \mathbf{B}$ to the PdV term in the usual first law? Reasonable as it sounds, this recipe will actually turn out to be *wrong*! We shall explain the reasons after describing the *correct* way of formulating the first law. For that we have to turn to understanding magnetostatics in the presence of magnetic materials.

Before doing that, let us clarify the meaning of an *external magnetic field*. In this context, it is very important to remember an advice from Pippard, which is to always keep the actual *experimental arrangement* in mind while analysing any particular question. Otherwise, an excessive reliance on only the equations divorced from the experimental arrangements can lead to a plethora of confusions. By 'actual experimental arrangement' he is of course not talking about nitty-gritty details of a laboratory. Rather, his emphasis is on 'the measurable content' of an experiment.

We digress here to point out that Pippard's advice actually touches the very basic chords of science. The final arbiter in science is the experiment, so when interpretational problems arise, their resolution is really to be sought in what is measured and how. Nowhere has this line of thinking proved more powerful than in the thorny issues of Quantum Theory.

We could take a typical solenoid along with its battery which supplies the e.m.f for it as the 'experimental arrangement' in question. The current flowing in the coils of the solenoid will then be a directly observable measure of the magnetic field. Imagine placing an elementary current loop inside such a solenoid. Any attempt to change this dipole moment, either in its orientation or in its magnitude, will set up an additional e.m.f in the coils of the solenoid. Then, in order to maintain the original current, and hence the original magnetic field, the battery will have to supply additional e.m.f *opposite* to that induced by the changing dipole. This is tantamount to the battery doing work on the system. This is the operational meaning of eqn.(8.5). Thus in the thermodynamic context, by *magnetic system* we not only mean the magnetic material placed in the magnetic field, but also the solenoid along with its source of e.m.f. The field produced by the solenoid in the absence of any magnetic material placed inside it will be called the *external magnetic field* B_e.

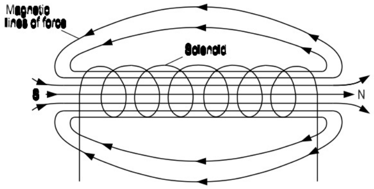

FIGURE 8.1 A solenoid.

We finally turn to an analysis of the situation when a magnetic material is placed inside the solenoid. The situation becomes quite complex and here we indicate in broad terms the resulting picture. The current in the solenoid not only produces a magnetic field everywhere, it also induces a magnetization in the magnetic body. Therefore, to describe the system under consideration, not only the magnetic field but also the magnetization, which depends both on the substance as well as its thermodynamic state, has to be specified. We shall only give the most basic equations necessary for our purposes, but the reader is strongly urged to consult Griffiths, Jackson, Callen etc.. Essentially, magnetization acts as an additional conserved (recall that we are restricting attention to static phenomena) current $\mathbf{J}_M = \nabla \times \mathbf{M}$, so that the Maxwell equation of eqn.(8.3) now becomes

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{J}_f + \nabla \times \mathbf{M}) \to \nabla \times \mathbf{H} = \mathbf{J}_f \qquad \mathbf{H} \equiv \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \tag{8.6}$$

The current $\mathbf{J}_M = \nabla \times \mathbf{M}$ is called the *magnetization current density*. It is also sometimes called the *bound current density* to distinguish it from the free current introduced earlier.

Strictly speaking, one should have solved for $\mathbf{B}$ arising from the *total* current density $\mathbf{J} = \mathbf{J}_f + \mathbf{J}_M$, subject to $\nabla \cdot \mathbf{M} = 0$. Such a $\mathbf{B}$ would have truly behaved like a magnetic field. Though the mathematical trick employed to get $\nabla \times \mathbf{H} = \mathbf{J}_f$ is a neat one in the sense that this equation is determined only by the free part of the current density, physically the meaning of $\mathbf{H}$ is far from clear. For one thing, it is not *divergence free* like a true magnetic field. Instead, $\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}$.

Even though $\mu_0 \mathbf{H}$ and $\mathbf{B}_e$ satisfy the same Ampere like equation, because their divergences obey different equations, they are in general not equal. When there are enough symmetries in the problem, like spherical symmetry etc., Ampere's equation alone is enough to determine $\mathbf{H}$ and in those situations, $\nabla \cdot \mathbf{M}$ is zero (Griffiths). In such situations $\mu_0 \mathbf{H}$ also equals the external field $\mathbf{B}_e$. The reader is encouraged to go through the detailed treatment of the bar magnet in Sommerfeld's treatise on Electrodynamics, for a better understanding of these subtleties.

Therefore in general, if an external magnetic field is applied, the magnetic field inside the system is *different* from this external field. As we have already seen, it becomes necessary to introduce *two* distinct types of fields, $\vec{B}(x)$ and $\vec{H}(x)$. Also, as noted before, the physical meaning of **H** is somewhat obscure. Even their names have not been without controversy. As we have already seen, $\vec{B}(x)$ is the more *fundamental* field; yet, $\vec{H}(x)$ is called the *magnetic field* by many. Having done that, it becomes necessary to give another name to $\vec{B}$ that will distinguish it from $\vec{H}$. To that end, $\vec{B}$ is called by some as *magnetic flux density*, and by some others as *magnetic induction*. The latter, as remarked by Griffiths, is particularly misleading as the word *induction* has already been given an altogether different meaning.

Confusion in this regard does not stop there; as elaborated by Feynman, the quantities $\mathbf{B},\mathbf{H}$ have *dimensions* that are not always the same! In a CGS system both of them have the same dimensions, but not the same *units*! The CGS unit of **B** is the *gauss* (G), while that of **H** is *oersted* (Oe). In an SI system, they don't even have the same dimensions; the dimensions of B are $N/A.m$ while those of H are A/m. According to Griffiths, Sommerfeld is supposed to have said 'the unhappy term 'magnetic field' for H should be avoided as far as possible. It seems to us to that this term has led into error none less than Maxwell himself'!

Before finally turning to addressing the issues of energy and work for magnetic systems, we discuss the important notion of *magnetic susceptibility*. The source of both the magnetic fields H, B, and the magnetization in the magnetic medium is the same and that is the current J_f. In this sense, the example of the elementary current loop is very different as its magnetic moment has an independent existence from the source of the magnetic field. Thus, in the context of the magnetic systems, a variation of the external current already induces a change in the magnetization. This can be expressed quantitatively through a functional dependence of **M** on the magnetic field(s). We shall refrain from doing this in all generality, but do so for the class of systems for which this dependence is *linear*. This is not such a great restriction, as for a large number of systems of interest, this is a very good approximation. In fact, for superconductors, it is even exact!

But here too there is a source of confusion; some authors define magnetic susceptibility through $\mathbf{M} = \chi_m \frac{\mathbf{B}}{\mu_0}$, while many others define it as $\mathbf{M} = \chi_m \mathbf{H}$. As long as the susceptibility χ_m is very small, both work reasonably well. But when susceptibilities are not small, as indeed happens in the context of superconductivity, to be discussed in later chapters, the two versions have dramatically different consequences, and the *correct* relation to use is

$$\mathbf{M} = \chi_m \mathbf{H} \tag{8.7}$$

In the table below, we list the magnetic susceptibilities of a few substances. Apart from ferromagnetic materials, susceptibilities are usually very small.

This is a good place to explain the nomenclature of magnetic substances. Before that, let us note the relation between the external field B_e (or equivalently $\mu_0 H$), and the B-field. Using the various definitions and results obtained till now, it follows that $B = (1 + \frac{\chi_m}{\mu_0})B_e$. Diamagnetic substances are those for which the susceptibility is *negative*, as can also be gathered from the table (8.1). Physically, what is happening is that the external fields induce in a diamagnetic substance currents that tend to oppose the external field, thereby *reducing* it effectively, i.e $B < B_e$. As we shall see later, superconductors are *perfect diamagnets* in the sense that $B = 0$ irrespective of B_e. In paramagnetic substances, with *positive* susceptibilities, just the opposite happens. The induced magnetization actually *enhances* the external field, i.e $B > B_e$. For ferromagnetic substances, these considerations are not really applicable because of the so called *spontaneous magnetization* because of which the magnetic system may possess magnetization even in the absence of any external fields.

TABLE 8.1

Some magnetic materials and their magnetic susceptibility χ_m.

Name	Type	Temp(K)	χ_m
Water	Dia.	300	$-9.0\cdot10^{-6}$
Bismuth	Dia.	300	$-16.7\cdot10^{-5}$
Oxygen	Para.	300	$0.2\cdot10^{-5}$
Aluminium	Para.	300	$2.2\cdot10^{-5}$
Iron	Ferro.	300	3000

From electrodynamics it follows that the magnetic energy density is given by $u = \frac{1}{2}\mathbf{B}\cdot\mathbf{H}$. In free space, upon using $\mathbf{M} = 0$, it goes back to the earlier expression $u_m = \frac{B^2}{2\mu_0}$. For materials for which $\mathbf{M}$ has a linear dependence on $\mathbf{H}$, as in eqn.(8.7), the variation of the magnetic energy takes the form

$$\delta u_m = \mathbf{H}\cdot\delta\mathbf{B} = \delta\frac{\mu_0 H^2}{2} + \mu_0\mathbf{H}\cdot\delta\mathbf{M} \tag{8.8}$$

It should be noted that the same variation could have equally well been written as

$$\delta u_m = \delta\frac{B^2}{2\mu_0} - \mathbf{M}\cdot\delta\mathbf{B} \tag{8.9}$$

We shall now argue that though both are equivalent, the former is better suited for thermodynamic applications. Irrespective of which one of them is used, it is clear that the thermodynamics of magnetic systems requires modifications to both the internal energy and the work done. If we choose eqn.(8.9), the variation of the internal energy has to be modified by $d\frac{B^2}{2\mu_0}$ and the infinitesimal work by $-\mathbf{M}\cdot d\mathbf{B}$. With the help of suitable Legendre transforms (see chapter 9 and also later sections of this chapter), we can make the work term look like $+\mathbf{B}\cdot d\mathbf{M}$.

The problem with including $\frac{B^2}{2\mu_0}$ in the internal energy is that even when the external currents in our reference solenoid are kept constant, this term can change dramatically in a phase transition. A prime example is that of the superconducting phase transition. After the system has become superconducting, the $\mathbf{B}$ inside the superconducting material becomes strictly zero (Meissner effect), whereas this is practical equal to $\mathbf{B}_e$ in the normal phase. This difficulty is only of a practical nature as in principle one can keep this term and keep track of its changes, though over whole space. For the same reason, using $\mathbf{B} \cdot d\mathbf{M}$ or the other way round can lead to singularities unless the susceptibility in the normal phase is carefully kept track of. Once again, these difficulties are not one of principle, only one of practice.

Let us contrast this with what would ensue had one chosen eqn.(8.8) instead. Then the internal energy density would have been modified by $\frac{\mu_0 H^2}{2}$. But when external currents are fixed, this does not change during phase changes and as far as phase changes in magnetic systems are concerned, it acts as a harmless constant and can be ignored without any consequences. The work likewise has many nice features too; the coefficient of $d\mathbf{H}$ never vanishes. When we apply these ideas to superconducting transitions, these points will become more transparent.

As clarified earlier, in situations with symmetry, as will be the case mostly, $\mu_0\mathbf{H}$ can be taken in value to be the external field $\mathbf{B}_e$. Therefore the energy and work terms can be equivalently written as $\frac{B_e^2}{2\mu_0}$ and $\mathbf{B}_e \cdot \mathbf{M}$ respectively. However, it should be kept in mind in general situations it is the H-field that should be used. Henceforth, the H-field and equivalently the B_e-field will be taken to be uniform. We introduce the notation $\mathbf{M} = V\mathbf{M}$ for the total magnetic moment in the volume V. Though both the magnetic induction and magnetic fields are vectors, we have chosen the component of the magnetization vector along the external field as the magnetization itself. Clearly there may be circumstances where the full vector nature of these quantities may be important, and in those cases this expression should be appropriately modified.

We can now write down the statement of first law as generalized to magnetic systems

$$dU' = TdS - PdV + \mu\, dN + B_e\, d\mathscr{M} \tag{8.10}$$

where $U' = U - \frac{B_e^2}{2\mu_0}V$. Before proceeding to build the thermodynamics of magnetic systems based on this, and the second law, we bring out a number of features that distinguish magnetic systems from mechanical systems. Comparing the magnetic work $\vec{B}_e \cdot d\vec{\mathscr{M}}$ with the mechanical work $-PdV$, one sees that there is a parallel between the component of magnetization parallel to the external field and $-V$. But there are many very important differences; in mechanical systems it made sense to talk of processes at *fixed volume*. In magnetic systems, it is very difficult to constrain magnetization. Therefore *fixed magnetization* changes are often beyond one's reach. The other important difference is that while P,V were taken to be *uniform* in space, neither the magnetic field nor magnetization is often uniform. As the source of magnetic fields are currents, even the *shape* of the magnetic body is of importance.

One sees that in addition to the usual specific heats for mechanical systems, there are now two additional specific heats C_B and $C_{\mathscr{M}}$ (modulo our remarks about constant magnetization processes). It should also be noted that $\mathscr{M}$ can be positive or negative, while its analog in mechanical systems, -V, was *always negative*.

For many magnetic systems of interest, the PdV term is often very small compared to $Bd\mathscr{M}$ term, and in such circumstances, the simplified form of the first law without the PdV term can be employed. A numerical comparison of these two terms will be made later on.

It is important to examine the issue of *extensive* and *intensive* variables in magnetic systems. The external field, B_e, is obviously *intensive* as it does not depend on the system volume. The total magnetization $\mathscr{M}$, on the other hand, is more subtle. As mentioned before, the shape of bodies becomes important for magnetic systems. If magnetization were to behave like $-V$, it should indeed be extensive. But because of the shape dependence, magnetization does not strictly grow with volume, i.e it is not strictly *extensive*. But in many substances this is a very small effect and ignoring it would make $\mathscr{M}$ extensive for all practical purposes. However, in superconducting substances this could be very important and it may not be a good approximation to treat magnetization as extensive. So a case by case scrutiny is essential and that, to some extent, is antithetical to the spirit of thermodynamics!

Returning to magnetic susceptibility χ_m, introduced in eqn.(8.7), this is the magnetic analog of compressibility in nonmagnetic systems. Compressibility was the response of volume to pressure. It is quantified by the fractional change of volume with pressure and is given by $\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_X$, where X depends on the precise conditions. It is T for isothermal changes etc. Now the analog of V is $-\mathscr{M}$, and of P is B. Therefore, in complete analogy with compressibility one can think of introducing $\frac{1}{\mathscr{M}}\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_X$. But the actual definition of magnetic susceptibility differs from this though the essential idea that it quantifies the response of magnetization to changes in B_e is still retained.

The susceptibility definition introduced in eqn.(8.7), as stressed then, is really suitable for linear systems. In general, there are actually two definitions used which should be carefully distinguished; the first is $\chi = \frac{1}{V}\frac{\mathscr{M}}{B_e}$. The second, the so called differential susceptibility, is given by $\chi'_X = \frac{1}{V}\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_X$, where X stands for the conditions that are fixed. For the large class of materials for which the magnetization is linearly dependent on the external field, χ equals χ'. But χ can be a bad definition when there can be residual magnetization even after the external field has been removed. This happens for ferromagnets. Therefore, one should use the differential susceptibility always. In what follows, we shall mean by *susceptibility* the differential one, and drop the $'$ notation.

Furthermore, if we had followed a strict analogy between $\mathscr{M}$ and $-V$ on the one hand, and between κ and χ on the other, we would have defined χ as $-\frac{1}{\mathscr{M}}\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_X$. But here too some notable differences between the two situations would make such a choice somewhat unnatural. In the non-magnetic case the negative sign was motivated by the fact that mostly volume decreases with increase of pressure; in the magnetic case, magnetization usually *increases* with increasing external field. The other important difference is that while in the nonmagnetic case V never vanishes, in the magnetic case $\mathscr{M}$ can indeed vanish. Taking all this into account, the general formula for susceptibility that has been given is the best.

Now we shall simply repeat everything we have done for the thermodynamics of nonmagnetic systems. We shall drop the -PdV and $\mu\, dN$ terms for the moment. This is more to keep things from getting too cluttered, not for any deeper reasons. Later on, when we discuss the magnetic analogs of the Maxwell relations, we shall restore such terms to show their impact. Apart from convenience, for most systems under consideration, it's also a very good approximation to neglect these terms. When we drop these terms, the only effective variables are T, B_e, and $\mathscr{M}$ (only two of which are independent). Other variables like P,V are not explicit, and in practice this means that all quantities of interest depend very weakly on them. Then, the cases of interest are when internal energy U^*(to avoid confusion, we denote the potentials by starred quantities when P,V are neglected) is a function of (T, $\mathscr{M}$) or of (T, B_e).

Let us begin with the so called *đQ relations*. In chapter 5.2, we had explicitly worked out the cases when U is a function of (V,T) and (P,T), and had left the (P,V) case as an exercise. Under the approximation of neglecting the PdV and μdN terms,

$$\begin{aligned}
đQ &= \left(\frac{\partial U^*}{\partial T}\right)_{\mathscr{M}} dT + \left\{\left(\frac{\partial U^*}{\partial \mathscr{M}}\right)_T - B_e\right\} d\mathscr{M} \\
đQ &= \left\{\left(\frac{\partial U^*}{\partial T}\right)_{B_e} - B_e\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\right\} dT + \left\{\left(\frac{\partial U^*}{\partial B_e}\right)_T - B_e\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_T\right\} dB_e
\end{aligned} \tag{8.11}$$

From this, the two magnetic specific heats $C_{\mathscr{M}}, C_B$ follow:

$$C_{\mathscr{M}} = \left(\frac{\partial U^*}{\partial T}\right)_{\mathscr{M}} \qquad C_B = \left(\frac{\partial U^*}{\partial T}\right)_{B_e} - B_e\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \tag{8.12}$$

Substituting these into eqn.(8.11), we get

$$\begin{aligned}
đQ &= C_{\mathscr{M}} dT + \left\{\left(\frac{\partial U^*}{\partial \mathscr{M}}\right)_T - B_e\right\} d\mathscr{M} \\
đQ &= C_{B_e} dT + \left\{\left(\frac{\partial U^*}{\partial B_e}\right)_T - B_e\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_T\right\} dB_e
\end{aligned} \tag{8.13}$$

Consider applying the first of these to an adiabatic process for which $đQ = 0$. Then

$$-C_{\mathscr{M}}\left(\frac{\partial T}{\partial \mathscr{M}}\right)_S = \left(\frac{\partial U^*}{\partial \mathscr{M}}\right)_T - B_e \tag{8.14}$$

As in the nonmagnetic case, C_{B_e}, which is the analog of C_P there, can be expressed as

$$C_{B_e} = \left(\frac{\partial (U^* - B_e\mathscr{M})}{\partial T}\right)_{B_e} \tag{8.15}$$

This motivates one to introduce the magnetic analog of enthalpy as $H^*_{\mathscr{M}} = U^* - B_e\mathscr{M}$, and in terms of it, $C_{B_e} = \left(\frac{\partial H^*_{\mathscr{M}}}{\partial T}\right)_{B_e}$. As we shall see when we introduce the thermodynamic potentials for magnetic systems more systematically, this nomenclature needs some care. The *TdS equations* can now be written down in complete analogy with the nonmagnetic discussion.

$$
\begin{aligned}
TdS &= dU^* - B_e d\mathscr{M} \\
TdS &= C_{\mathscr{M}} dT + \left\{ \left(\frac{\partial U^*}{\partial \mathscr{M}} \right)_T - B_e \right\} d\mathscr{M} \\
TdS &= C_{B_e} dT + \left\{ \left(\frac{\partial U^*}{\partial B_e} \right)_T - B_e \left(\frac{\partial \mathscr{M}}{\partial B_e} \right)_T \right\} dB_e
\end{aligned} \tag{8.16}
$$

As a consequence of the first equation

$$\left(\frac{\partial U^*}{\partial \mathscr{M}} \right)_T = T \left(\frac{\partial S}{\partial \mathscr{M}} \right)_T + B_e \tag{8.17}$$

The integrability condition for the second of eqn.(8.16) along with the integrability condition for dU, now expressed as a combination of dT and $d\mathscr{M}$, yields,

$$\left(\frac{\partial U^*}{\partial \mathscr{M}} \right)_T = B_e - T \left(\frac{\partial B_e}{\partial T} \right)_{\mathscr{M}} \tag{8.18}$$

This is the precise analog of eqn.(3.7) which was first encountered in chapter 3. Likewise, the integrability condition for the last of eqn.(8.16), along with the integrability condition for the magnetic enthalpy $dH^*_{\mathscr{M}}$ yields,

$$T \left(\frac{\partial \mathscr{M}}{\partial T} \right)_{B_e} = \left(\frac{\partial U^*}{\partial B_e} \right)_T - B_e \left(\frac{\partial \mathscr{M}}{\partial B_e} \right)_T \tag{8.19}$$

As before, we combine the eqns.(8.16) with the two integrability conditions to obtain the final form of the magnetic TdS equations:

$$
\begin{aligned}
TdS &= C_{\mathscr{M}} dT - T \left(\frac{\partial B_e}{\partial T} \right)_{\mathscr{M}} d\mathscr{M} \\
TdS &= C_{B_e} dT + T \left(\frac{\partial \mathscr{M}}{\partial T} \right)_{B_e} dB_e
\end{aligned} \tag{8.20}
$$

The integrability conditions for this pair of equations give:

$$\left(\frac{\partial C_{\mathscr{M}}}{\partial \mathscr{M}} \right)_T = -T \left(\frac{\partial^2 B_e}{\partial T^2} \right)_{\mathscr{M}} \qquad \left(\frac{\partial C_{B_e}}{\partial B_e} \right)_T = +T \left(\frac{\partial^2 \mathscr{M}}{\partial T^2} \right)_{B_e} \tag{8.21}$$

Combining eqn.(8.17) with eqn.(8.18) yields the magnetic analog of one of the Maxwell relations:

$$\left(\frac{\partial S}{\partial \mathscr{M}} \right)_T = - \left(\frac{\partial B_e}{\partial T} \right)_{\mathscr{M}} \tag{8.22}$$

A systematic exposition of the magnetic Maxwell relations will be given shortly.

We have already defined the magnetic susceptibility χ_X when X is held fixed;we can specify X to be T for the isothermal susceptibility χ_T, and S for the adiabatic susceptibility χ_S. We could have introduced the magnetic analog of the coefficient of thermal expansion as $\alpha_{\mathscr{M}} = \frac{1}{V}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}$. But we shall not do so to avoid a proliferation of symbols; instead we shall explicitly display the temperature derivative of $\mathscr{M}$. However, it is useful to eliminate $\left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}}$ in terms of quantities already introduced.

$$\left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}} = -\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\left(\frac{\partial B_e}{\partial \mathscr{M}}\right)_T = -\frac{1}{V\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \tag{8.23}$$

This allows us to simplify the magnetic TdS equations further:

$$\begin{aligned} TdS &= C_{\mathscr{M}}dT + \frac{T}{V\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} d\mathscr{M} \\ TdS &= C_{B_e}dT + T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} dB_e \end{aligned} \tag{8.24}$$

Equating the two TdS equations one gets

$$0 = (C_{\mathscr{M}} - C_{B_e})dT + T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\left\{\frac{1}{V\chi_T}d\mathscr{M} - dB_e\right\} \tag{8.25}$$

As in our discussion for the nonmagnetic case, we express dT in terms of $d\mathscr{M}$ and dB_e as $dT = \left(\frac{\partial T}{\partial \mathscr{M}}\right)_{B_e} d\mathscr{M} + \left(\frac{\partial T}{\partial B_e}\right)_{\mathscr{M}} dB_e$ to rewrite the above as

$$0 = (C_{\mathscr{M}} - C_{B_e})(\left(\frac{\partial T}{\partial \mathscr{M}}\right)_{B_e} d\mathscr{M} + \left(\frac{\partial T}{\partial B_e}\right)_{\mathscr{M}} dB_e) + T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\left\{\frac{1}{V\chi_T}d\mathscr{M} - dB_e\right\} \tag{8.26}$$

Equating the coefficients of the independent variations $d\mathscr{M}$, dB_e to zero we get the two equations

$$\begin{aligned} (C_{\mathscr{M}} - C_{B_e})\left(\frac{\partial T}{\partial B_e}\right)_{\mathscr{M}} &= T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \\ (C_{\mathscr{M}} - C_{B_e})\left(\frac{\partial T}{\partial \mathscr{M}}\right)_{B_e} &= -\frac{T}{V\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \end{aligned} \tag{8.27}$$

Using the definition of χ_T and the standard properties of partial derivatives, it is easy to see that the two are actually identical. But we shall use the second of these as its consequences are more transparent:

$$(C_{B_e} - C_{\mathscr{M}}) = \frac{T}{V\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}^2 \tag{8.28}$$

Again, let us apply the TdS equations eqn.(8.24) for adiabatic processes ($dS = 0$) to derive explicit expressions for $C_{\mathscr{M}}$ and C_{B_e}:

$$C_{\mathscr{M}} = -\frac{T}{V\chi_T}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_S \qquad C_{B_e} = -T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\left(\frac{\partial B_e}{\partial T}\right)_S \tag{8.29}$$

The ratio of the magnetic specific heats,$\gamma_{\mathscr{M}} = \frac{C_{\mathscr{M}}}{C_{B_e}}$ can be worked out, after some algebra, to be

$$\gamma_{\mathscr{M}} \equiv \frac{C_{\mathscr{M}}}{C_{B_e}} = \frac{\chi_S}{\chi_T} \tag{8.30}$$

Using this, and eqn(8.28), one can work out the magnetic analogs of the expressions for C_V,C_P obtained earlier.

This is a good place to bring out some fundamental differences between the magnetic and nonmagnetic cases. In the nonmagnetic case, $C_P - C_V$ is always *positive*. But an examination of eqn.(8.28) reveals that in the magnetic case the sign of $C_{B_e} - C_{\mathscr{M}}$ depends on the sign of χ_T whereas in the nonmagnetic case this depended on the sign of the *compressibility* κ_T which is always *positive*. On the other hand, the isothermal magnetic susceptibility χ_T can be positive or negative, depending on the nature of the magnetic material.

For *paramagnetic* substances, the magnetization $\mathscr{M}$ along the external field is positive whereas it is negative for *diamagnetic* substances. In other words χ_T is small and positive for paramagnetic substances, but small and negative for diamagnetic substances. Therefore $C_{B_e} > C_{\mathscr{M}}$ for paramagnetic substances while $C_{B_e} < C_{\mathscr{M}}$ for diamagnetic substances. The magnitude of the susceptibility is about 10^{-5} for diamagnetic substances and about 10^{-3} for paramagnetic substances.

Example 8.1: A diagrammatic interpretation of $C_{B_e} - C_{\mathscr{M}}$

Show that the first of the eqns.(8.27) can be given a diagrammatic meaning by drawing two nearby magnetic isotherms *at, say, T and T+dT, and taking a point on the lower isotherm to two points on the upper isotherm via $B_e = const.$ and $\mathscr{M} = const.$ processes respectively.*

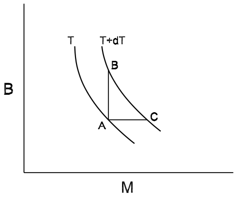

FIGURE 8.2 $C_{B_e} - C_M$

An isotherm of a nonmagnetic system such as a gas consisted of a curve of, for example, pressure P vs V at some given T. A magnetic isotherm can in general be a surface. For example, if there is pressure dependence of the magnetic phenomena, the magnetization at some temperature T can depend on both the pressure P and the external field B_e. Then a magnetic isotherm could, for example, be the two-dimensional surface $B_e = B_e(P, \mathscr{M})$. In practice, pressure dependences are small, and a magnetic isotherm would simply be a curve in the $B_e - \mathscr{M}$ plane. As emphasized in the text, then there is a precise analogy between P and B_e on the one hand, and between V and $-\mathscr{M}$ on the other.

Now consider two neighbouring magnetic isotherms, and consider the system in a state represented by the point A on the isotherm at T. Let a reversible process at constant B_e take it to the state C on the isotherm at

T+dT, and let $d\mathscr{M}$ be the resulting change in magnetization. Likewise, let a reversible process at constant $\mathscr{M}$ take it to the state B, again on the isotherm at T+dT. Consider the reversible cycle ABCA. The heat absorbed during AB is $dQ_{AB} = C_{\mathscr{M}} dT$ and the heat relinquished during CA is $dQ_{CA} = C_{B_e} dT$. To determine the heat absorbed during BC, we use eqn.(8.20) with $dT = 0$. This gives $dQ_{BC} = -T\left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}} d\mathscr{M}$.

The total heat absorbed during the cycle must match the total work, which is just the area of ABC. But that is equal to $dB_e \cdot d\mathscr{M}$, This being second order in smallness can be neglected. Thus we get

$$(C_{\mathscr{M}} - C_{B_e})dT - T\left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}} d\mathscr{M} = 0 \rightarrow C_{\mathscr{M}} - C_{B_e} = T\left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \quad (8.31)$$

In the last step we made use of the fact that $d\mathscr{M}$ during the step AC was at constant B_e. Clearly the same diagrammatic proof can be given for the nonmagnetic case of eqn.(3.52).

Example 8.2: Magnetic Joule-Kelvin process

There is a magnetic analog to the Joule-Kelvin process wherein a magnetic substance undergoes a suitable change of B_e and $\mathscr{M}$ under conditions of adiabaticity as well as constant enthalpy. At first it is not clear whether we should consider processes that keep the enthalpy H, however with magnetic contributions, of eqn.(8.49) fixed, or keep the magnetic enthalpy $H_{\mathscr{M}}$ of eqn.(8.54) fixed.

If we want to maintain the nonmagnetic result that the Joule-Thomson coeeficient vanishes for ideal gases, then one has to define the magnetic analog to be the one where it is still H that is kept fixed, and not $H_{\mathscr{M}}$. Then, since $dH = TdS + B_e d\mathscr{M}$(we are ignoring pressure terms) entropy will increase while maintaining H if $d\mathscr{M}$ is negative. As emphasized earlier, $-\mathscr{M}$ plays the role of V now. To get the magnetic Joule-Thomson coefficient, we rearrange dH as

$$\begin{aligned} dH &= TdS + B_e d\mathscr{M} = \left\{T\left(\frac{\partial S}{\partial T}\right)_{B_e} + B_e\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}\right\} dT \\ &\quad + \left\{T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} + B_e\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_T\right\} \end{aligned} \quad (8.32)$$

With dH=0, the magnetic Joule-Thomson coefficient $\mu_{\mathscr{M},JT}$ becomes

$$\mu_{\mathscr{M},JT} = \frac{T\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} + B_e\left(\frac{\partial \mathscr{M}}{\partial B_e}\right)_T}{C_{B_e} + B_e\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}} \quad (8.33)$$

It is easy to verify that this vanishes for the magnetic analogs of ideal gases, i.e systems for which $\mathscr{M}$ has the form $\mathscr{M} = f(B_e/T)$!

8.2 Thermodynamic potentials

Now we discuss the thermodynamic potentials that are relevant for magnetic systems. We will continue to ignore the -PdV and $\mu\, dN$ terms in the first law, but shall return to a treatment inclusive of them shortly. We can follow the general procedure described in chapter 9, and starting from the internal energy U^* as the *prepotential* introduce three additional thermodynamic potentials, U^*-TS, U^*-$B_e\mathscr{M}$ and U^*-TS-$B_e\mathscr{M}$. We have already encountered the second of these which we called the *magnetic enthalpy* $H^*_{\mathscr{M}}$. The first of these is the usual Helmholtz free energy F^*(remember our convention about starred potentials). We shall call the last of the three as *magnetic Gibbs potential* $G^*_{\mathscr{M}}$.

It is not very important how we name the potentials, what are important are the observable consequences stemming out of them. But it is clearly desirable to name them in such a way that in the absence of magnetism they naturally reduce to the nomenclature one would have adopted earlier. The observable consequences are certainly the Maxwell-like relations that follow, and their consequences, as also other relations between properties of systems. A very important aspect of these potentials, something we have discussed at length in the nonmagnetic context, are the various equilibrium conditions encoded in them. We shall return to those aspects later on, and we shall comment on the nomenclature issue then too.

It should be noted that even though the first two potentials, U^* and F^*, are the same ones we had earlier, they now depend on two independent variables among the three variables, namely, T, $\mathscr{M}$ and B_e. This will also be reflected in the expressions for their differentials which will be different from their corresponding differentials in the nonmagnetic context. Let us now display the four differentials in question:

$$dU^*(S,\mathscr{M}) = TdS + B_e d\mathscr{M} \tag{8.34}$$

$$dF^*(T,\mathscr{M}) = -SdT + B_e d\mathscr{M} \tag{8.35}$$

$$dH^*_{\mathscr{M}}(S,B_e) = TdS - \mathscr{M}dB_e \tag{8.36}$$

$$dG^*_{\mathscr{M}}(T,B_e) = -SdT - \mathscr{M}dB_e \tag{8.37}$$

As already noted above, the two magnetic specific heats are given by $C_{\mathscr{M}} = \left(\frac{\partial U}{\partial T}\right)_{\mathscr{M}}$ and $C_{B_e} = \left(\frac{\partial H_{\mathscr{M}}}{\partial T}\right)_{B_e}$. The consequences of eqn.(8.34) are:

$$\left(\frac{\partial U^*}{\partial S}\right)_{\mathscr{M}} = T; \quad \left(\frac{\partial U^*}{\partial \mathscr{M}}\right)_S = B_e; \quad \left(\frac{\partial T}{\partial \mathscr{M}}\right)_S = \left(\frac{\partial B_e}{\partial S}\right)_{\mathscr{M}} \tag{8.38}$$

$$\left(\frac{\partial F^*}{\partial T}\right)_{\mathscr{M}} = -S; \quad \left(\frac{\partial F^*}{\partial \mathscr{M}}\right)_T = B_e; \quad -\left(\frac{\partial S}{\partial \mathscr{M}}\right)_T = \left(\frac{\partial B_e}{\partial T}\right)_{\mathscr{M}} \tag{8.39}$$

$$\left(\frac{\partial H^*_{\mathscr{M}}}{\partial S}\right)_{B_e} = T; \quad \left(\frac{\partial H^*_{\mathscr{M}}}{\partial B_e}\right)_S = -\mathscr{M}; \quad \left(\frac{\partial T}{\partial B_e}\right)_S = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{B_e} \tag{8.40}$$

$$\left(\frac{\partial G^*_{\mathscr{M}}}{\partial T}\right)_{B_e} = -S; \quad \left(\frac{\partial G^*_{\mathscr{M}}}{\partial B_e}\right)_T = -\mathscr{M}; \quad \left(\frac{\partial S}{\partial B_e}\right)_T = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} \tag{8.41}$$

The third of the equalities in each of these equations constitutes a magnetic Maxwell relation. As in the nonmagnetic case, they are not all independent. Only one of the four is an independent relation, and the other three can be reduced to it. But, as stressed before, the important issue is not of their mathematical independence. What is important is how each one of them, possibly under different experimental circumstances, can be useful in relating some quantities to other observable quantities.

These relations once again point to some interesting differences from the nonmagnetic case. There $\left(\frac{\partial G}{\partial T}\right)_P$ was always negative but $\left(\frac{\partial G}{\partial P}\right)_T$ was always positive because volume V and entropy S are both positive. But now, the analog of V, which is $-\mathscr{M}$, can take either sign. So in the magnetic case while $\left(\frac{\partial G^*_{\mathscr{M}}}{\partial T}\right)_{B_e}$ is always negative, $\left(\frac{\partial G^*_{\mathscr{M}}}{\partial B_e}\right)_T$ can have any sign.

The last of the magnetic Maxwell relations, $\left(\frac{\partial S}{\partial B_e}\right)_T = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}$ is particularly interesting. For many magnetic systems, heating leads to loss of magnetism or to *demagnetisation*. In such situations, $\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e}$ is negative, and this particular Maxwell relation then implies that $\left(\frac{\partial S}{\partial B_e}\right)_T$ is negative too. It means, that magnetizing a sample by placing it in an external magnetic field, while maintaining its temperature, leads to a *lowering* of entropy! This will have a striking consequence for cooling objects to very low temperatures, as will be discussed later.

What is remarkable is that such conclusions follow very generally without detailed input as to the nature of the magnetic material etc., which once again speaks of the great power of thermodynamic reasoning.

8.2.1 Inclusion of PdV and μdn terms in dU

Now we discuss the thermodynamic potentials for magnetic systems *without* dropping the $-PdV$ and μdn terms in the first law. This will clarify a number of important issues besides yielding more Maxwell and other relations. The first law then takes the form

$$dU = TdS - PdV + \mu\, dn + B_e d\mathscr{M} \tag{8.42}$$

8.2.2 Magnetic Euler relations

Before working out the generalization of the thermodynamic potentials for the magnetic case, it is important to establish the Euler relation for the magnetic case, as here too, one of the potentials just vanishes as a consequence of the Euler relation. Let us consider the fundamental relation in the U-representation:

$$U = U(S,V,n,\mathscr{M}) \tag{8.43}$$

The differential form of this being

$$dU = \left(\frac{\partial U}{\partial S}\right)_{..} dS + \left(\frac{\partial U}{\partial V}\right)_{..} dV + \left(\frac{\partial U}{\partial n}\right)_{..} dn + \left(\frac{\partial U}{\partial \mathscr{M}}\right)_{..} d\mathscr{M} \tag{8.44}$$

This leads to the identification of the intensive parameters for the magnetic case as

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n,\mathscr{M}} \qquad -P = \left(\frac{\partial U}{\partial V}\right)_{S,n,\mathscr{M}} \qquad \mu = \left(\frac{\partial U}{\partial n}\right)_{S,V,\mathscr{M}} \qquad B_e = \left(\frac{\partial U}{\partial \mathscr{M}}\right)_{S,V,n} \tag{8.45}$$

The extensivity of U, as before, means $U(\lambda S, \lambda V, \lambda n, \lambda \mathscr{M}) = \lambda U(S,V,n,\mathscr{M})$. The magnetic analog of the Euler equation emerges exactly as in the nonmagnetic case:

$$n\mu = U + PV - ST - B_e\mathscr{M} \tag{8.46}$$

Thus in the magnetic case too the chemical potential equals the magnetic Gibbs potential.

8.2.3 Counting the magnetic potentials

Thus, the magnetic case, as per our counting of chapter 9, corresponds to $n = 4$, including the number of moles . Therefore, there ought to be 15 thermodynamic potentials ($2^n - 1$), and 60 Maxwell relations ($n \cdot (2^n - 1)$). All we have to do is just take over the results for the $n = 3$ case explicitly worked out there (which was by inclusion of the μdN terms for a nonmagnetic case) and suitably adapt them to the magnetic context. To avoid cluttering, we shall simply show the results for when the number of moles is held fixed as generalization to include $dn \neq 0$ is straightforward. Only in that case the potential $G_{\mathscr{M},\mu}$ exactly vanishes by virtue of the magnetic Euler relation. The 8 potentials and their differentials are given by:

$$U^0 = U \qquad dU = TdS - PdV + B_e d\mathscr{M} \tag{8.47}$$

$$U^1 = U + PV = H \qquad dH = TdS + VdP + B_e d\mathscr{M} \tag{8.48}$$

$$U^2 = U - TS = F \qquad dF = -SdT - PdV + B_e d\mathscr{M} \tag{8.49}$$

$$U^3 = U - B_e\mathscr{M} = U_{\mathscr{M}} \qquad dU_{\mathscr{M}} = TdS - PdV - \mathscr{M}dB_e \tag{8.50}$$

$$U^{1,2} = U^1 - TS = G \qquad dG = -SdT + VdP + B_e d\mathscr{M} \tag{8.51}$$

$$U^{2,3} = U^2 - B_e\mathscr{M} = F_{\mathscr{M}} \qquad dF_{\mathscr{M}} = -SdT - PdV - \mathscr{M}dB_e \tag{8.52}$$

$$U^{3,1} = U^3 + PV = H_{\mathscr{M}} \qquad dH_{\mathscr{M}} = TdS + VdP - \mathscr{M}dB_e \tag{8.53}$$

$$U^{1,2,3} = U^{1,2} - B_e\mathscr{M} = G_{\mathscr{M}} \qquad dG_{\mathscr{M}} = -SdT + VdP - \mathscr{M}dB_e \tag{8.54}$$

Now we address the issue of a consistent nomenclature for the thermodynamic potentials of magnetic systems when pressure and volume also become important. It is to be noticed from eqn.(8.47) that, when pressure and volume are ignored, pairs of potentials become the same: $H^* = U^*, G^* = F^*, H^*_{\mathscr{M}} = U^*_{\mathscr{M}}, G^*_{\mathscr{M}} = F^*_{\mathscr{M}}$. Consequently, not only is $\left(\frac{\partial H^*_{\mathscr{M}}}{\partial T}\right)_{B_e}$ equal to C_{B_e}, so is $\left(\frac{\partial U^*_{\mathscr{M}}}{\partial T}\right)_{B_e}$.

Our motivation for naming $H^*_{\mathscr{M}}$ as the *magnetic enthalpy* was that its temperature derivative at constant magnetic B_e gave C_{B_e}. So the question is, in the general case when pressure and volume are also taken into account, should we call $H_{\mathscr{M}}$ the magnetic enthalpy or call $U_{\mathscr{M}}$ that? A simple criterion to adopt is that in the *absence* of magnetism, what we call magnetic enthalpy should revert to the usual (nonmagnetic) enthalpy. Then, it is certainly more appropriate to call $H_{\mathscr{M}}$ the magnetic enthalpy. Apart from this obvious criterion, the equilibrium conditions also point towards a natural nomenclature. We shall come to this point of view later.

We will not bother to spell out all the 24 Maxwell relations explicitly. We shall explore only a couple of them, and in particular, we will investigate the difference in the relations obtainable from some potential X (amongst U, F, H, G) and its magnetic analog $X_{\mathscr{M}}$. Here too, we shall restrict the analysis to the cases $X = U, G$ only. The Maxwell relations (we only display the additional relations arising out of magnetism) coming from U and $U_{\mathscr{M}}$ are, respectively,

$$U : -\left(\frac{\partial P}{\partial \mathscr{M}}\right)_{V,S} = \left(\frac{\partial B_e}{\partial V}\right)_{\mathscr{M},S} \qquad \left(\frac{\partial T}{\partial \mathscr{M}}\right)_{S,V} = \left(\frac{\partial B_e}{\partial S}\right)_{V,\mathscr{M}} \tag{8.55}$$

$$U_{\mathscr{M}} : \left(\frac{\partial P}{\partial B_e}\right)_{V,S} = \left(\frac{\partial \mathscr{M}}{\partial V}\right)_{B_e,S} \qquad \left(\frac{\partial T}{\partial B_e}\right)_{S,V} = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{V,B_e} \tag{8.56}$$

Likewise, the relations coming from G and $G_{\mathscr{M}}$ are:

$$G : \left(\frac{\partial V}{\partial \mathscr{M}}\right)_{P,T} = \left(\frac{\partial B_e}{\partial P}\right)_{\mathscr{M},T} \qquad -\left(\frac{\partial S}{\partial \mathscr{M}}\right)_{T,P} = \left(\frac{\partial B_e}{\partial T}\right)_{P,\mathscr{M}} \tag{8.57}$$

$$G_{\mathscr{M}} : \left(\frac{\partial V}{\partial B_e}\right)_{P,T} = -\left(\frac{\partial \mathscr{M}}{\partial P}\right)_{B_e,T} \qquad \left(\frac{\partial S}{\partial B_e}\right)_{T,P} = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{P,B_e} \tag{8.58}$$

From the U and $G_{\mathscr{M}}$ Maxwell relations we get two relations both relating $\left(\frac{\partial \mathscr{M}}{\partial T}\right)$ to $\left(\frac{\partial S}{\partial B_e}\right)$; we display them together:

$$\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{S,V} = \left(\frac{\partial S}{\partial B_e}\right)_{V,\mathscr{M}} \qquad \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{P,B_e} = \left(\frac{\partial S}{\partial B_e}\right)_{P,T} \tag{8.59}$$

They show that the signs of $\left(\frac{\partial \mathscr{M}}{\partial T}\right)$ and $\left(\frac{\partial S}{\partial B_e}\right)$ are exactly correlated in two entirely different conditions. This will have very important repercussions. We shall examine these various Maxwell relations in some particular models, but they hold very generally.

8.2.4 Estimating PdV vs $B_\mathrm{e}\mathrm{d}\mathscr{M}$

Now we present an argument due to Pippard that enables one to come up with a criterion as to when the PdV terms in dU can be neglected in comparison with the $B_e d\mathscr{M}$ terms. The physical basis of this criterion is to determine conditions under which the mechanical work done is much smaller than the magnetic work. Needless to say, this depends very much on the nature of internal constraints on the system. The argument should be seen as being heuristic, and a careful check should be made as to whether all the implicit assumptions are actually fulfilled or not.

Firstly, the body is taken to be such that magnetization is linearly dependent on the external field, i.e, $\mathscr{M} = V\chi(T,P)B_e$. This in itself is not a very resrictive assumption.

A large number of magnetic systems will fulfill this for suitable ranges of external fields and (T,P). Following Pippard, let us take the pressure and temperature to be *fixed* for the comparison. Then the relevant ratio is given by

$$\mathscr{R} = \left(\frac{PdV}{B_e d\mathscr{M}}\right)_{T,P} = \frac{P}{B_e}\left(\frac{\partial B_e}{\partial P}\right)_{T,\mathscr{M}} \tag{8.60}$$

where we made use of the Maxwell relation of eqn.(41). For linearly magnetizable bodies this can be worked out to be

$$\mathscr{R} = -\frac{P}{V\chi}\left(\frac{\partial V\chi}{\partial P}\right)_T = P\kappa_T \frac{1}{\chi}\left(\frac{\partial V\chi}{\partial V}\right)_T \tag{8.61}$$

where we made use of one of the standard properties of partial derivatives, and the definition of the isothermal compressibility κ_T.

Now for an ideal gas $P\kappa_T = 1$. Therefore PdV can be neglected in comparison with $B_e d\mathscr{M}$ only when the susceptibility is such that $\frac{1}{\chi}\left(\frac{\partial V\chi}{\partial V}\right)_T << 1$. For solids on the other hand, $P\kappa_T$ is very small as long as the pressures are not too high, and the second factor is not expected to be large either, and the ratio is very small. But as cautioned before, for each circumstance these two factors should be evaluated to see if the ratio is indeed small or not.

8.2.5 Equation of state for magnetic systems

Since with every additional degree of freedom, an *equation of state* needs to specified for a complete thermodynamic description, for magnetic systems too such an equation of state is needed. In analogy with one of the equations of state for a nonmagnetic system that takes the form $P = P(V,T,N)$ (through arguments of extensivity, V and N can only occur in the ratio $\frac{V}{N} = v$), we can expect the analogous equation of state for magnetic systems to be of the form $\mathscr{M} = \mathscr{M}(B_e, P, T, N)$. The linearly magnetizable case is such an example

$$\mathscr{M} = N\chi(T,P)B_e \tag{8.62}$$

Of particular importance is the so called Curie Law

$$\chi(T,P) = \frac{a}{T} \tag{8.63}$$

where a is a constant. Curie law is seen to hold with reasonable accuracy for paramagnetic substances when the temperatures are high, and applied fields small. Further, for paramagnetic material, the constant a is *positive*, and this is crucial for cooling by *Adiabatic Demagnetization*.

An additional input, like a magnetic equation of state, can be combined with the Maxwell relations to get a number of very interesting results, as we shall show now. Using the second of the Maxwell relations in eqn.(8.58),

$$\left(\frac{\partial S}{\partial B_e}\right)_T = B_e V \frac{d\chi}{dT} = -\frac{aV}{T^2} B_e \tag{8.64}$$

This is easily integrated to give the important relation that tells the B_e-dependence of entropy at constant temperature:

$$S(B_e,T) = S(0,T) - \frac{1}{2}\frac{aVB_e^2}{T^2} \tag{8.65}$$

Because the constant a is positive, we see that entropy indeed decreases with increasing B_e, as already remarked before. There we had correlated the decreasing entropy with B_e with decreasing magnetization with temperature. The Curie law for paramagnetic materials indeed implies that $\left(\frac{\partial \mathscr{M}}{\partial T}\right) = -\frac{aVB_e}{T^2}$ is negative. The above relation immediately points to the fact that Curie law can not be valid at all temperatures as $S(B_e,T)$ does not tend to zero as T tends to zero.

Now we wish to use eqn.(8.65) as a model relation to test various equations we have obtained in this chapter. Towards that end we write down all the Maxwell relations that involve $S,T,B_e,V,\mathscr{M}$ only. In eqn.(8.59) we have already displayed two such relations.

$$\left(\frac{\partial S}{\partial B_e}\right)_{V,T} = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{V,B_e} \tag{8.66}$$

$$\left(\frac{\partial S}{\partial B_e}\right)_{V,\mathscr{M}} = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{V,S} \tag{8.67}$$

$$-\left(\frac{\partial S}{\partial \mathscr{M}}\right)_{V,T} = \left(\frac{\partial B_e}{\partial T}\right)_{V,\mathscr{M}} \tag{8.68}$$

$$-\left(\frac{\partial S}{\partial \mathscr{M}}\right)_{V,B_e} = \left(\frac{\partial B_e}{\partial T}\right)_{V,S} \tag{8.69}$$

In the process one will learn various subtleties that come up in evaluating the thermodynamic partial derivatives. A striking example of such a partial derivative is $\left(\frac{\partial B_e}{\partial T}\right)$. At first sight, such a partial derivative may appear to be zero trivially, as the external field need not be temperature dependent. But it is to be noted that such partial derivatives have to be evaluated under constraints; for example, in one case, the volume and $\mathscr{M}$ have to be kept fixed while this partial derivative is evaluated. The Curie law would then say that B_e must be changed *linearly*, and that's how the external field acquires a temperature dependence.

Let us first consider the partial derivative relation eqn.(8.66), as that is the most straightforward to evaluate given eqn.(8.65) and eqn.(8.63):

$$\left(\frac{\partial S}{\partial B_e}\right)_{V,T} = -\frac{aVB_e}{T^2};\ \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{V,B_e} = -\frac{aVB_e}{T^2} \tag{8.70}$$

Now we turn to eqn.(8.67). The lhs requires evaluating a derivative of S keeping $\mathscr{M}$ fixed. Therefore we eliminate B_e in favour of $\mathscr{M}$ in eqn.(8.65): $S(\mathscr{M},T) = S(0,T) - \frac{\mathscr{M}^2}{2Va}$. At first sight it may appear that $\left(\frac{\partial S}{\partial B_e}\right)$ now vanishes as there is no longer any *explicit* B_e-dependence in $S(\mathscr{M},T)$. But keeping $\mathscr{M}$ fixed, at say $\mathscr{M}_0$, requires

$T = \frac{Va}{\mathscr{M}_0} B_e$ and therefore the partial derivative $\left(\frac{\partial T}{\partial B_e}\right)_{V,\mathscr{M}} = \frac{Va}{\mathscr{M}_0}$! This is the kind of care that needs to be exercised in evaluating the partial derivatives. Therefore,

$$\left(\frac{\partial S}{\partial B_e}\right)_{V,\mathscr{M}_0} = \left(\frac{\partial S(0,T)}{\partial T}\right)_{V,\mathscr{M}_0} \cdot \left(\frac{\partial T}{\partial B_e}\right)_{V,\mathscr{M}_0} = S(0,T)' \frac{Va}{\mathscr{M}_0} \tag{8.71}$$

On the other hand, the evaluation of the rhs of eqn.(8.67) requires calculating partial derivatives while keeping the entropy fixed, at say S_0, so that $S_0 = S(0,T) - \frac{\mathscr{M}^2}{2Va}$ and as a consequence

$$0 = \left(\frac{\partial S(0,T)}{\partial T}\right)_{V,S} - \frac{\mathscr{M}}{Va}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{V,S} \quad \rightarrow \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{V,S} = S(0,T)' \frac{Va}{\mathscr{M}} \tag{8.72}$$

thereby verifying eqn.(8.67).

Verifying eqn.(8.68) is straightforward, if one uses the partial derivatives already evaluated:

$$-\left(\frac{\partial S}{\partial \mathscr{M}}\right)_{V,T} = \frac{\mathscr{M}}{Va} \qquad \left(\frac{\partial B_e}{\partial T}\right)_{V,\mathscr{M}} = \frac{\mathscr{M}}{Va} \tag{8.73}$$

We finally come to eqn.(8.69) which is doubly subtle! To evaluate its lhs we use eqn.(8.65) as it is, since we need to take a derivative at fixed B_e. But then T is implicitly dependent on $\mathscr{M}$. Therefore, in the first step

$$-\left(\frac{\partial S}{\partial \mathscr{M}}\right)_{V,B_e} = -S(0,T)'\left(\frac{\partial T}{\partial \mathscr{M}}\right)_{V,B_e} + \frac{aVB_e^2}{T^3}\left(\frac{\partial T}{\partial \mathscr{M}}\right)_{V,B_e} \tag{8.74}$$

$$= S(0,T)' \frac{T}{\mathscr{M}} + \frac{\mathscr{M}}{Va} \tag{8.75}$$

The rhs of eqn.(8.69) has to be evaluated at fixed entropy. Therefore, differentiating the (constant) entropy wrt T, one gets

$$0 = S(0,T)' + \frac{aVB_e^2}{T^3} - \frac{aVB_e}{T^2}\left(\frac{\partial B_e}{\partial T}\right)_{V,S} \quad \rightarrow \left(\frac{\partial B_e}{\partial T}\right)_{V,S} = S(0,T)' \frac{T}{\mathscr{M}} + \frac{\mathscr{M}}{Va} \tag{8.76}$$

thereby verifying the desired relation.

We conclude this section by verifying the various relations among the magnetic specific heats by using eqn.(8.65). Let us first consider C_{B_e} which is given by $T\left(\frac{\partial S}{\partial T}\right)_{B_e}$. Therefore

$$T\left(\frac{\partial S}{\partial T}\right)_{B_e} = C_{B_e} = TS(0,T)' + \frac{aVB_e^2}{T^2} = C_0(T) + \frac{aVB_e^2}{T^2} \tag{8.77}$$

Here $C_0(T)$ denotes the specific heat in the absence of any external field. On using the expression for $S(\mathscr{M},T)$, one finds

$$T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{M}} = C_{\mathscr{M}} = C_0(T) \tag{8.78}$$

Therefore, the Curie law gives, for the difference $C_{B_e} - C_{\mathscr{M}}$,

$$C_{B_e} - C_{\mathscr{M}} = \frac{aVB_e^2}{T^2} \tag{8.79}$$

which agrees with eqn(8.28), on using Curie law.

As another check on the model let us compute $\left(\frac{\partial C_{B_e}}{\partial B_e}\right)$ and $\left(\frac{\partial C_{\mathscr{M}}}{\partial \mathscr{M}}\right)$. Explicit evaluation yields

$$\left(\frac{\partial C_{B_e}}{\partial B_e}\right) = \frac{2aVB_e}{T^2} = T\left(\frac{\partial^2}{\partial T^2}\mathscr{M}\right)_{B_e} \tag{8.80}$$

$$\left(\frac{\partial C_{\mathscr{M}}}{\partial \mathscr{M}}\right) = 0 = -T\left(\frac{\partial^2}{\partial T^2}B_e\right)_{\mathscr{M}} \tag{8.81}$$

In obtaining the second equation we used the fact that B_e is *linear* in T when $\mathscr{M}$ is held fixed. This is in accord with eqn.(8.21).

8.2.6 Equilibrium conditions

Now we briefly discuss the connection between the magnetic thermodynamic potentials and the criterion for equilibrium for magnetic systems. As far as the Helmholtz free energy is concerned, the condition (see chapter 7) that it must be a *minimum* at thermal equilibrium was obtained by simply considering the work done. The nature of the work itself, namely, whether it is mechanical or magnetic or whatever, was not important for those considerations. Therefore the condition that the Helmholtz free energy must be a minimum at thermal equilibrium will continue to be valid for magnetic systems too. We can repeat the steps there to find out the conditions for equilibrium when not only temperature and pressure, but also the external field B_e is held fixed. As in chapter 7, let us consider a process taking the system from state A to state B under these conditions. Not only will the volume of the system change from $V(A)$ to $V(B)$, now the magnetization will also change from $\mathscr{M}_A$ to $\mathscr{M}_B$. The work done W_{AB} is however now given by $W_{AB} = P(V(B) - V(A)) - B_e(\mathscr{M}(B) - \mathscr{M}(A))$ (remember the sign convention for work done). Therefore, the inequality of chapter 9 now changes to

$$P(V(B) - V(A)) - B_e(\mathscr{M}(B) - \mathscr{M}(A)) \leq F(A) - F(B) \tag{8.82}$$

In a way completely analogous to the nonmagnetic case, this suggests the introduction of the *magnetic Gibbs potential* $G_{\mathscr{M}}$ in terms of which *any* transformation $A \to B$ under conditions of constant temperature, pressure, *and* external magnetic field B_e must satisy

$$G_{\mathscr{M}}(B) \leq G_{\mathscr{M}}(A) \tag{8.83}$$

and consequently, at equilibrium $G_{\mathscr{M}}$ must take its minimum. We had already introduced such a potential during our discussion of the magnetic analog of thermodynamic potentials. The perspective there was more mathematical. This section complements that discussion by providing the physical significance of $G_{\mathscr{M}}$.

Entirely analogous reasonings can be given for the introduction of the *magnetic enthalpy* $H_{\mathscr{M}}$, also defined previously. It should however be noted that the two additional magnetic potentials introduced there, namely, $U_{\mathscr{M}}$ and $F_{\mathscr{M}}$ are not to be interpreted likewise. It is still the conventional Helmholtz free energy F, and not its magnetic analog $F_{\mathscr{M}} = F - B_e\mathscr{M}$, that has to be a minimum at equilibrium.

8.3 Problems

Problem 8.1 Consider the following fundamental equation for a magnetic system in the U-representation:

$$U = NAe^{[S/NR+\mathscr{M}^2/2N^2a]} \tag{8.84}$$

Find the equations of state $T(S,\mathscr{M},N), B_e(S,\mathscr{M},N)$ and the chemical potential $\mu(S,\mathscr{M},N)$. Show that the Euler relation is satisfied by them.

Problem 8.2 Find the fundamental equation in the entropy representation for the above problem, and find the chemical potential by integrating the appropriate Gibbs-Duhem relation.

Problem 8.3 Calculate the magnetic specific heats C_B and $C_{\mathscr{M}}$ for the above mentioned system.

Problem 8.4 Calculate the isothermal and adiabatic molar susceptibilities for this system, and show that the isothermal susceptibility obeys the Curie law.

Problem 8.5 Calculate the internal energy for a magnetic system governed by the Langevin function

$$\frac{\mathscr{M}}{\mathscr{M}_\infty} = \coth\alpha - \frac{1}{\alpha} \qquad \alpha = \frac{\mu_0\mathscr{M}_\infty H}{RT} \tag{8.85}$$

Why are such systems called the magnetic analogues of ideal gases?

Problem 8.6 Calculate the magnetic specific heats for the magnetic system discussed in the previous problem. Find their low and high temperature behaviours.

Problem 8.7 Calculate the work done in an isothermal increase of magnetization for a system governed by the Langevin function. Discuss the result in the limit when Curie's law holds.

Problem 8.8 Find the relation between $\mathscr{M}$ and H for an adiabatic transformation of a magnetic system obeying Curie's law if the ratio $C_B/C_{\mathscr{M}}$ can be treated as a constant. Is the latter a good assumption? Discuss when it breaks down.

Problem 8.9 Show that the work done by a magnetic system under arbitrary variations of T and B_e can be calculated from the knowledge of $V, B_e, \left(\frac{\partial\mathscr{M}}{\partial T}\right)_{V,B_e}$ and the isothermal susceptibility.

Problem 8.10 Show that when the external field B_e (and pressure if there is any pressure dependence) is held fixed, the heat absorbed or relinquished by a magnetic system equals the change in magnetic enthalpy.

Problem 8.11 For a paramagnetic system obeying Curie law show that an isothermal magnetization leads to a lowering of entropy. Justify this on grounds that entropy is a measure of disorder.

Problem 8.12 Derive the magnetic analogs of the Gibbs-Duhem relations both in the U and S representations.

9 Dilute Solutions

9.1 General considerations

Now we develop the thermodynamic treatment of dilute solutions. Quite generally we can think of a number of substances called *solutes* dissolved in a liquid called the *solvent*. Let $N_1, N_2, \ldots, N_g$ be the number of moles of the solutes $A_1, A_2, \ldots, A_g$ and let N_0 be the number of moles of the solvent. A solution will be called *Dilute* when

$$N_i < N_0 \tag{9.1}$$

In terms of an atomist description, diluteness means the number of molecules per unit volume of each of the solutes is much smaller than that of the solvent.

Now let u be the internal energy of a fraction of the solution containing 1 mole of the solvent. Clearly, this fraction will contain $\frac{N_i}{N_0}$ moles of the solute A_i. This internal energy will obviously depend on the thermodynamic variables T, p. The pressure being an intensive variable, p will also be the pressure of the entire solution. The internal energy can also depend on the amount of solutes present, and possibly on other parameters not relevant for this discussion. Thus u can have the functional form

$$u = u(T, p, \frac{N_1}{N_0}, \frac{N_2}{N_0}, \ldots) \tag{9.2}$$

Since internal energy is an extensive variable, the internal energy of the entire solution will be

$$U = N_0\, u(T, p, \frac{N_1}{N_0}, \ldots) \tag{9.3}$$

As the quantities $\frac{N_i}{N_0}$ are very small because of the diluteness of the solution, we can expand u or equivalently, U, as a power series in $\frac{N_i}{N_0}$. For a very dilute solution, it would be a good approximation to retain only the first term of this expansion:

$$u = u_0(T, p) + \sum_{i=1}^{g} \frac{N_i}{N_0} u_i(T, p) + \ldots \tag{9.4}$$

At this stage the quantities u_i are merely the coefficients in the expansion, without having any obvious physical interpretation. The total internal energy can be elegantly recast as

$$U = \sum_{i=0}^{g} N_i\, u_i(T, p) \tag{9.5}$$

The total volume can likewise be expressed as

$$V = \sum_{i=0}^{g} N_i\, v_i(T, p) \tag{9.6}$$

Once again, v_0 has the physical interpretation as the volume occupied by one mole of the pure solvent. Again, the quantities $v_i(T,p)$ do not have any obvious physical meaning at this stage. Let us consider varying T,p but keep all the N_i fixed. For small changes in T,p, the change in entropy of the solution is given by

$$\begin{aligned} dS &= \frac{1}{T}(dU+pdV) \\ &= \sum_{i=0}^{g} \frac{N_i}{T}(du_i+pdv_i) \end{aligned} \tag{9.7}$$

For eqn.(9.7) to be consistent, each one of $\frac{1}{T}(du_i+pdv_i)$ must also be a perfect differential. That is, there must exist state functions $s_i(T,p)$ such that

$$ds_i(T,p) = \frac{1}{T}\,(du_i+pdv_i) \tag{9.8}$$

Though s_i have dimensions of entropy, there is again no obvious physical interpretation for them. Integrating the above (partial) differential equation, one gets

$$S = \sum_{i=0}^{g} N_i s_i(T,p) + C(N_0,N_1,\ldots) \tag{9.9}$$

In the above equation, $C(N_0,N_1,\ldots)$ is *independent* of (T,p). This fact will be crucial in determining C from general principles. Determination of $s_i(T,p)$ is not so easy.

In order to determine C, let us consider the physical situation when T is very large and p small enough that the entire solution is in a gaseous phase. One can then picture the system as consisting of several gaseous components with partial pressures $p_i = \frac{N_i}{\sum N_i}p$. Since p is small, all the p_i will also be small. Finally, since T is large and p_i small, we can well approximate the behaviour of each component by ideal gas law. In particular, the entropy per mole of each component is given by

$$\bar{s}_i(T,p_i) = C_P^i \ln T - R\ln p_i + a_i + R\ln R \tag{9.10}$$

In this equation a_i are the so called *entropy constants*, which thermodynamics is unable to fix. C_P^i are the respective specific heats at constant pressure. Refer to the chapter on *Entropy Constants* for all the deep subtleties relating to a_i. Thus the total entropy of the system at high temperatures and low pressures is given by

$$\begin{aligned} S &= \sum_{i=0}^{g} N_i(C_P^i \ln T - R\ln p_i + a_i + R\ln R) \\ S &= \sum_{i=0}^{g} N_i(C_P^i \ln T - R\ln p + a_i + R\ln R) - R\sum_{i=0}^{g} N_i \ln \frac{N_i}{\sum_i N_i} \end{aligned} \tag{9.11}$$

Comparing eqn.(9.11) with eqn.(9.9), one finds, at high T and low p

$$s_i(T,p) = C_P^i \ln T - R\ln p + a_i + R\ln R \tag{9.12}$$

and

$$C = -R\sum_{i=0}^{g} N_i \ln \frac{N_i}{\sum_i N_i} \tag{9.13}$$

The important point is that this C is valid even if T is not high and p is not low, because C does not depend on these variables! However, $s_i(T,p)$ found above is only valid at high temperatures and low pressures, and it can not be used for the circumstances in which the solution is in liquid form. Also, note the important difference between $\overline{s}_i$ and s_i. For a dilute solution, the expression for C can be approximated thus

$$\begin{aligned} C &= -R\sum_{i=0}^{g} N_i \ln \frac{N_i}{\sum_{i=0}^{g} N_i} \\ &= -R\sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} + R\sum_{i=1}^{g} N_i \end{aligned} \tag{9.14}$$

The expression for the total entropy S can be recast as

$$S = \sum_{i=0}^{g} N_i \sigma_i(T,p) - R\sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \tag{9.15}$$

where $\sigma_0(T,p) = s_0(T,p)$ and $\sigma_i(T,p) = s_i(T,p) + R$.

What is truly remarkable about this expression for the total entropy is that the mixing term is of *identical form* as for ideal gases! On the other hand, we are dealing with liquids here which are far more complicated than gases, ideal or otherwise! In fact, for liquids we often do not even know the equations of state. For these reasons, this result took some time to gain acceptance. This means the *Gibbs paradox* has its analogs for dilute solutions also. A corollary of this form of mixing entropy is Raoult's law for partial pressures, to be discussed shortly.

Likewise, the Helmholtz free energy for the dilute solution can also be written down

$$\begin{aligned} F &= U - TS \\ &= \sum_{i=0}^{g} N_i(u_i(T,p) - T\sigma_i(T,p)) + RT\sigma_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \\ &= \sum_{i=0}^{g} N_i f_i(T,p) + RT\sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \end{aligned} \tag{9.16}$$

In all these formulae, careful attention must be paid to the range of the summations, as in some of them it goes over 0 to g, which includes the solvent, while in others it goes over only 1 to g, including only the solutes.

So far we have not given any physical meanings to $v_i(T,p), u_i(T,p), s_i(T,p)$, $\sigma_i(T,p)$ and $f_i(T,p) = u_i(T,p) - T\sigma_i(T,p)$. In spite of that, some further simplifications are possible for the liquid state of the solution. Firstly, v_0 is the volume occupied by one mole of the solvent, which is a liquid. Liquids have the property that they are practically incompressible. In other words, their volume hardly depends on the pressure p. However, their volume can have noticeable temperature dependence. In fact it is this temperature dependence of volume that is responsible for the functioning of thermometers with liquids as their working material. Hence to a very good approximation $v_0(T,p)$ can be taken as a function of T alone and write $v_0(T)$. Now the solvent, being a liquid, also shares this property of near compressibility for arbitrary concentrations of solutes. In other words $V = \sum_{i=0}^{g} N_i v_i(T,p)$, is also, for all practical purposes, only a function of T alone. For this to be true for arbitrary N_i, the $v_i(T,p)$ for every solute must also be a function of T only, for all practical purposes.Thus we can set $v_i(T,p) = v_i(T)$ in all the above equations. That leaves the question of whether $u_i(T,p)$ are also functions of T only.

Here one has to rely on the empirical evidence that, for example, compressing a liquid isothermally hardly changes its internal energy. Again, as this is true for both the solvent and solutions with arbitrary concentrations of solutes, one can conclude that $u_i(T,p)$ are also functions of T only, i.e, $u_i(T,p) = u_i(T)$. As a consequence of both u_i and v_i being independent of pressure, the quantities $s_i(T,p)$ are also functions of T only, and so are $\sigma_i(T,p)$ and $f_i(T,p)$. We can summarise these conclusions as

$$\begin{aligned} S &= \sum_{i=0}^{g} N_i \sigma_i(T) - R \sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \\ F &= \sum_{i=0}^{g} N_i f_i(T) + RT \sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \end{aligned} \tag{9.17}$$

with $f_i(T) = u_i(T) - T\sigma_i(T)$. Finally, the Gibbs free energy for dilute solutions is given by

$$G = \sum_{i=0}^{g} N_i (f_i(T) + p v_i(T)) + RT \sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \tag{9.18}$$

The reader may wonder what useful things have been gained by this general analysis of dilute solutions as the functions v_i, u_i, σ_i are still undetermined. This will be addressed in the next sections where it will be shown that knowledge of C alone is enough to determine various processes of interest like Osmotic Pressure, Boiling Point of solutions and Freezing Point of solutions.

9.2 Mixing revisited

In our treatment of extensivity in multicomponent systems in section 6.5 we saw how, in the case of ideal gases, the notion of an entropy of mixing arises. We also saw that this entropy of mixing was *positive* when dissimilar gases were mixed, pointing to the irreversibility of the process. A remarkably simple formula was obtained for this entropy in eqn.(6.41). It depended only on the number of moles of the gases being mixed. Implicit expressions for other potentials were also obtained there.

It is worth emphasizing at this point that the mixing term of eqn.(9.14), which also appears in eqn.(9.18) for the Gibbs potential, does not always represent the Gibbs potential of mixing.

Remarkably, the expression for the mixing entropy of dilute solutions obtained in eqn.(9.15) has *exactly* the same form even though one is no longer dealing with ideal gases! In fact, that was obtained even without knowing the explicit form of the liquid entropies. In fact, this circumstance is even more general. Even in the case of mixing of liquids, the mixing entropy takes the same form for a large class of so called *ideal liquids*. Of course, there are many liquids for which the mixing entropy does not take this simple form only in terms of concentrations. They are called *nonideal*. One phenomenologically replaces the concentrations by so called *activity*, but we shall not pursue them here. When the solution is dilute, activities just become concentrations. We shall see in the worked example below that even for polymer solutions, the entropy of mixing takes the ideal form.

From the expression for the Gibbs potential eqn.(9.18), it can easily be derived that the *enthalpy of mixing* vanishes. This is true for the ideal gas mixing too. In general, for ideal liquids this holds, i.e $\Delta H_M = 0$. For nonideal liquids the enthalpy of mixing is in general nonvanishing. In the case of Polymers, even though the mixing entropy takes the ideal form, mixing entropy does not. The Flory-Huggins theory (see the example below) can be used to calculate it.

Given both the entropy of mixing and the enthalpy of mixing, the Gibbs potential for mixing can be computed. It can, of course, be calculated directly too. When the Gibbs potential for mixing, $\Delta G_M < 0$, the mixing can occur *spontaneously*. Thus in the case of ideal gas or ideal liquid mixing, ΔG_M is indeed negative as ΔH_M vanishes and ΔS_M is positive. Hence in these cases ΔG_M is negative at *all* temperatures. On the other hand, in cases where ΔH_M is positive, for temperatures below $T < (\Delta H_m/\Delta S_m)$ the mixing is not favoured and becomes spontaneous only for temperatures greater than that. For example, dissociation of water into H_2 and O_2 becomes spontaneous only for temperatures greater than about 5500 K (of course, this is an example of dissociation) because only then the entropy change dominates over the enthalpy change.

Example 9.1: Mixing entropy for liquids

Consider the common pastime of mixing alcohol (ethyl) with water. Let us mix 90 gms of H_2O at $40\,^\circ\mathrm{C}$ *with 46 gms of ethyl alcohol at* $30\,^\circ\mathrm{C}$*, by first bringing them into a thermal contact only and then allowing them to mix. Calculate the total entropy change if the molecular weights of water and alcohol are, respectively, 18 and 46, while their specific heats are 4.0 J/gm and 2.0 J/gm. Separate the entropy change to a part coming from mixing the two at different temperatures, and a mixing entropy arising out of mixing them at the same temperature.*

In this example we have deliberately included a part where the liquids are first brought into thermal equilibrium through a thermal contact, i.e a wall that allows only exchange of heat, so that the magnitude of the mixing entropy can be contrasted with the entropy increase during thermalization, also an irreversible process. The equilibrium temperature T_e is calculated straightforwardly to be $90\cdot 4\cdot(40-T_e) = 46\cdot 2\cdot(T_e-30)$ leading to

$T_e = 37.9646\,^\circ\mathrm{C} = 311.1146K$. The entropy lost by water is $90 \cdot 4R\ln(T_e/313.15)$ while that gained by alcohol is $46 \cdot 2R\ln(T_e/303.15$. The net gain in entropy during thermalization is therefore 0.0383 R=0.318 J/K.

The entropy of mixing is on the other hand $-5R\ln(5/6) - R\ln(1/6) = 2.703R = 22.475J/K$. Thus we see that entropy increase due to mixing far exceeds the entropy gain due to thermalization. Both are positive, pointing to the irreversibility of both processes.

Example 9.2: Mixing entropy for polymers in Flory-Huggins(FH) theory

This example is to show how the ideal mixing entropy, first shown for ideal gases and then for dilute solutions, can work in much broader circumstances. The aim is to look at mixing entropy in the FH theory for polymer solutions, and show how it too has the form of ideal mixing entropy, though in suitable variables.

Polymers are gigantic molecules with very large molecular weights. Therefore, even if the molar concentration of a polymer in solution is very small, the weight fraction can be quite large. The polymer can be thought of as a large chain living in the volume of the solvent. The FH theory provides a statistical mechanical description of this. In the spirit of a thermodynamical description, we shall not concern ourselves too much with either the microscopics of a polymer or the statistical mechanical details. The basic process of dissolving a solid polymer in a solvent can be thought of as a two step process in the first of which the ordered solid is changed to a disordered, flexible polymer chain, and the subsequent mixing of this random chain with the solvent.

The FH theory can be used to calculate the entropy changes during both these steps. We shall focus only on the mixing entropy. An important parameter is $\mathrm{r} = V_2/V_1$, where V_2 is the molar volume of the polymer and V_1 that of the solvent. Recall that for ideal gases $\mathrm{r} = 1$. If N_2 is the number of molecules of the ploymer in the solution and N_1 that of the solvent, the Flory-Huggins theory gives, for the mixing entropy,

$$\Delta S_M = -k\left(N_1 \ln \frac{N_1}{N_1 + \mathrm{r}N_2} + N_2 \ln \frac{N_2}{N_1 + \mathrm{r}N_2}\right) \tag{9.19}$$

In the FH theory this emerges on purely combinatorial grounds. This expression is unsuitable for a thermodynamic description as it is expressed in terms of microscopic parameters, and it contains k, the Boltzman constant, which is unknown to thermodynamics. First we convert N_1, N_2 to molar fractions $n_1 = N_1/N_A, n_2 = N_2/N_A$ where N_A is the Avogadro number, also unknown to thermodynamics. Now we can trade off the unknown k to the gas constant R according to $R = N_A \cdot k$. Introducing the volume fractions $\phi_2 = n_2V_2/(n_1V_1 + n_2V_2)$ and $\phi_1 = n_1V_1/(n_1V_1 + n_2V_2)$ of the polymer and the solvent respectively, the above expression for the mixing entropy can be expressed entirely in terms of macroscopic quantities as

$$\Delta S_M = -R\,(n_1 \ln \phi_1 + n_2 \ln \phi_2) \tag{9.20}$$

This is analogous to the mixing entropy expressions obtained earlier, and unlike them, depends both on molar fractions and volume fractions. The appearance of volume fractions is not peculiar to polymer solutions. It happens, for example, when an ideal gas is mixed with a van der Waals gas (see problem 12.6).

9.3 Osmotic pressure

Consider a liquid solvent, say water, separated from a solution, containing various solutes in the same solvent, by a semi-permeable membrane which is permeable to the solvent but not to the solutes. So for example, if we consider such a membrane separating water on one side and a salt solution on the other, water can move in both directions but the salt will always remain on the same side. As the solvent moves from one side to another, the concentration of the solution increases or decreases as the case may be. In terms of the moles of solute and solvent in the solution introduced above, N_0 is a variable, but N_i is not.

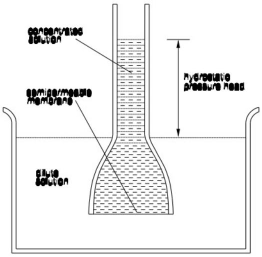

FIGURE 9.1 Osmotic Pressure

In the accompanying figure representing a standard setup for demonstrating Osmotic Pressure, it is seen that the meniscus of the solution is at a greater height than that of the solvent. First of all, the fact that the meniscuses are at different levels is indicating that there is a pressure difference between the solvent and solution. It should be appreciated that this pressure difference is solely due to the arrangement that the membrane is permeable to the solvent but not to the solutes. If one had used a symmetrical membrane instead, one that would have been permeable to both the solvent and the solutes, there would have been no pressure difference and the heights of the meniscuses would have been the same. The fact that in the actual experimental setup, the meniscus of the solution is at a greater height means that the pressure in the solution is higher than that of the solvent.

One should avoid the erroneous reasoning that a greater pressure on one side (in this case the side of the solvent), is pushing the meniscus of the other side (in this case the side of the solution).That would get things completely wrong. Instead, what is happening in the particular setup is that the pressure of the solvent is matching the atmospheric pressure, while the pressure in the solution is such as to match the atmospheric pressure plus the weight of a column of the solution of height equalling the difference in heights of the meniscuses. Hence the pressure difference is

$$\Delta p = \rho g h \tag{9.21}$$

where ρ is the density of the solution, h the difference in the meniscus levels and g the acceleration due to gravity. Since the solution is dilute, to a very good approximation, the density of the solution is the same as the density of the solvent. Henceforth, ρ will be taken to be the density of the solvent.

Let us consider a vessel with two chambers separated by a semi-permeable membrane which can be moved to left or right, and whose outer walls are permeable to the flow of heat in both directions. The whole setup is in thermal equilibrium with a heat reservoir, at temperature T. The left chamber contains the solution described by the parameters $T, p_{soln}, N_0, N_1, \ldots, N_g$ while the right chamber contains N_0' moles of the pure solvent at T, p_{solv}. Let us imagine moving the membrane to the right by a very small (infinitesimal) amount ΔV. The volume occupied by the solution increases by ΔV while the volume occupied by the pure solvent decreases by the same amount. Recall from the earlier chapters that the Helmholtz free energy differentials are given by

$$dF = -SdT - PdV \tag{9.22}$$

Since the present setup is at constant temperature (isothermal), $dT = 0$ and hence $dF = -PdV$. The change in free energy of the solution is therefore $\Delta F_{soln} = -p_{soln}\Delta V$, while the change in free energy of the pure solvent is $\Delta F_{solv} = p_{solv}\Delta V$. Thus the total change in free energy is given by

$$\Delta F_{tot} = \Delta F_{soln} + \Delta F_{solv} = -(p_{soln} - p_{solv})\Delta V = -p_{osm}\Delta V \tag{9.23}$$

where we have used the fact that the difference in the pressures of the solution and solvent, at equilibrium, is by definition, the *Osmotic Pressure*, p_{osm}.

In the process of moving the membrane to the right, certain moles of the solvent would have moved to the left. Since the volume of solvent that has crossed from right to left is ΔV, and the volume of the solvent per mole is $v_0(T)$, the number of moles of the solvent that has crossed to the left is given by $\Delta N_0 = \frac{\Delta V}{v_0}$. This can also be arrived at from the solution side, as follows: the volume of the solution is given by

$$V = N_0 v_0(T) + N_1 v_1(T) + \ldots + N_g v_g \tag{9.24}$$

At this stage, the importance of the result we established earlier viz. that all the $v_i(T)$ are functions of temperature alone, comes into play. Since our setup is isothermal, there is no change in any of the v_i during the process of moving the membrane to the right. And due to the fact that the membrane is impermeable to the solutes, none of the N_i also change during the process. Therefore, $\Delta V = \Delta N_0 \, v_0$, as before.

Hence the change in total free energy is $\Delta F_{tot} = -p_{osm} v_0 \Delta N_0$. We can compare this to a direct evaluation of ΔF_{tot} based on eqn.(9.17). The free energy of the pure solvent is $F_{solv} = N_0' f_0$, while the free energy of the solution is $F_{soln} = N_0 f_0(T) + \sum_{i=1}^{g} N_i f_i(T) + RT \sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0}$. Thus the total free energy of the solvent and solution is

$$F_{tot} = (N_0 + N_0')f_0(T) + \sum_{i=1}^{g} N_i f_i(T) + RT \sum_{i=1}^{g} N_i \ln \frac{N_i}{N_0} \tag{9.25}$$

The change in total free energy during the process is therefore

$$\Delta F_{tot} = -RT \frac{\Delta N_0}{N_0} \sum_{i=1}^{g} N_i \tag{9.26}$$

Thus, even though one does not know the various $f_i(T)$ in the total free energy, their knowledge is irrelevant for knowing the change in total free energy! It is important to appreciate how this comes about. The coefficient of the unknown $f_0(T)$ is $N_0 + N_0'$ which is the total number of moles of solvent on both sides. Even though there is transfer of the solvent from one side to another, this total quantity obviously does not change. $f_0(T)$ does not change during the process as it happens at the same temperature. Due to the semi-permeable nature of the membrane, none of the N_i changes during the process and again $f_i(T)$ does not change because of the isothermal nature of the process. Therefore, the only thing that changes during the process is the coefficient of the RT term which is solely due to the C term in eqn.(9.14). Comparing the expression for ΔF_{tot} obtained in two different ways, one gets

$$-p_{osm} v_0 \Delta N_0 = -RT \frac{\Delta N_0}{N_0} \sum_{i=1}^{g} N_i \tag{9.27}$$

leading to the remarkably simple expression for the Osmotic Pressure

$$p_{osm} = \frac{RT}{N_0 v_0} \sum_{i=1}^{g} N_i = \frac{RT}{V} \sum_{i=1}^{g} N_i \tag{9.28}$$

In summary, the Osmotic Pressure of a dilute solution is equal to the pressure exerted by an ideal gas at the same temperature and volume as the solution, and containing a number of moles equal to the total number of moles of the solutes dissolved in the solution. Van't Hoff was the first one to establish this property of Osmosis.

This is a very remarkable result indeed. The solutes are actually in a liquid medium and one would expect the interactions between solutes and solvents to result in strong deviations from ideal gas behaviour. The treatment given above is not expected to hold if there are chemical reactions between solutes, or between solutes and the solvent. Another remarkable feature is that Osmotic Pressure depends only on the number of moles of solutes dissolved, and not on their molar weight. Thus two solutes, widely different in their molar weights, will still produce the same Osmotic Pressure if the same number of moles of them is dissolved in a given volume of the solvent. This leads to some curious (and also important) consequences for strong electrolytes like salt (NaCl). In this case the molecule of salt dissociates into Sodium and Chlorine ions, and for the purposes of computing the Osmotic Pressure, we have to treat sodium and chlorine independently as solutes, yielding nearly double the Osmotic Pressure from what one would have obtained by treating NaCl as a single solute!

Example 9.3: Cost of desalination

The entropy change in mixing salt and water to form a saline solution being positive means a saline solution will not spontaneously separate into salt and pure water. Some minimal amount of work must be performed to achieve this. Consider a simple desalination setup which consists of a cylindrical tube fitted at one end with a membrane permeable only to water. Fill this with sea water approximated to have only NaCl. Apply a pressure to force pure water through the membrane. Calculate the following: a) The minimum pressure needed for this desalination to work at 300 K, b) minimum work done to get 1 liter of pure water at this temperature, and c) the cost of electricity for desalination at Rs. 10 per kWh, assuming an efficiency of 20%. Compare the energy budget if one were to boil the water and recondense.

For any process to be the most efficient possible, it has to be achieved as a reversible process. Without the application of any external pressure, pure water would enter the cylinder to dilute the sea water with a pressure equal to the osmotic pressure. Therefore, the minimum pressure needed is the osmotic pressure. The osmotic pressure, from eqn.(9.28), depends on temperature, volume of solvent and number of moles of solvent.

Sea water, under the assumption that all salts in it are NaCl, contains roughly 33gms of salt per liter. The molecular weight of NaCl is 58.5 gm/mole, so $N_1 = 33/58 \simeq 0.56$. But the fact that salt is fully ionised into Na^+ and Cl^- ions the correct number to be $N_1 = 1.2$. The osmotic pressure works out to be about 27 bar, i.e 27 Kg/sqcm. The external pressure must be at least this much.

If the cross sectional area of the cylinder is A sqcm, the force on the membrane is 27 A Kg. To produce one liter of fresh water, the piston has to move 10 meters! Consequently the work needed is 270 Kg-m or 2700 J. This is roughly 2700/4200 kcal, i.e 0.66 kcal per liter of fresh water. In terms of kWh, note that one kWh=3600 kJ. Consequently the work needed is $0.75 \cdot 10^{-3}$ kWh/liter if the efficiency was 100%. Since the latter is only 20%, the figure goes up to $3.75 \cdot 10^{-3}$ kWh/liter. This is a tiny energy indeed. But in reality there are various other costs involved.

Let us now compare the energetics of desalination through boiling and subsequent condensation of the vapor to form fresh water. Taking the specific heat of water at 4 J/gm, it would take $73 \cdot 1000 \cdot 4 = 70 kcal$ to heat from 300 K to the boiling point of water and then a whopping $540 \cdot 1000 = 540 kcal$ to vaporize it. Of course a good part of this nearly 610 kcals can be recovered, but this method can hardly match the reverse osmosis method.

9.4 Vapor pressure and boiling point of solutions

Above the surface of a liquid there is always a vapor which for a volatile liquid will have the same composition as the liquid itself. If the liquid is a solution whose solutes are non-volatile, i.e even at moderately high temperature they don't go into the gaseous phase, what is the relationship between the vapor pressure of the solution and the vapor pressure of the solvent? Intuitively one may feel that since the solutes can not contribute to the vapor pressure, the vapor pressure of solutions will be lower than the vapor pressure of solvents. The real situation is indeed so, but as we shall see later it is not straightforward to convert this intuitive feeling into a sound argument, even at a qualitative level.

To show that the vapor pressure of solutions has to be less than the vapor pressure of solvents, consider a setup as shown in the next figure. The solvent extending from A to B is separated from the solution extending from B to C by a semi-permeable membrane at B. The fact that the Osmotic Pressure of the solution is higher than the solvent means the length of the column BC is greater than the length of the column AB. If we choose a point D such that the length of the column BD equals that of AB, and furthermore if $CD = h$, the Osmotic Pressure is given by $\rho g h$ where ρ is the density of the pure solvent. It should actually be the density of the solution, but for the dilute solutions being considered, these two densities are very nearly the same. This approximation was made earlier too.

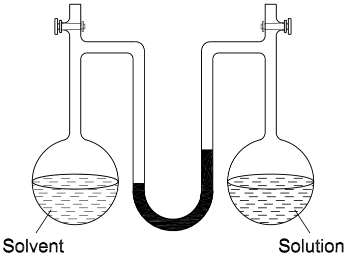

FIGURE 9.2 Vapor pressures

Since the solutes are taken to be non-volatile, the entire region AC is filled with saturated vapor of the solvent only. Just above the point C, the saturated vapor of the solvent is in equilibrium with the solution while just above A the saturated solvent vapor is in equilibrium with the solvent. The pressure at A is higher than the pressure at C and the difference in these pressures is given by

$$p_A - p_C = \rho_{vap} g h = \Delta p \tag{9.29}$$

where ρ_{vap} is the density of the saturated vapor, which, over small regions, is a function of temperature only. One must recall that saturated vapor pressure depends only on temperature and does not depend on volume at all. It should be emphasized that the whole setup is at constant temperature. Thus $p_C < p_A$ which also means that the vapor pressure of the solutions is lower than the vapor pressure of the solvent.

The magnitude of this vapor pressure lowering can be calculated easily.

$$\frac{\Delta p}{p_{osm}} = \frac{\rho_{vap}}{\rho} \quad \rightarrow \quad \Delta p = p_{osm} \frac{v_0}{v_0^{vap}} \tag{9.30}$$

where v_0^{vap} is the volume per mole of the solvent vapor. This should not be confused with v_0 which is the volume per mole of the pure solvent in the liquid state. Using the earlier result for p_{osm} given in eqn.(9.28), one gets

$$\Delta p = \frac{RT}{N_0 v_0'} \sum_{i=1}^{g} N_i \tag{9.31}$$

This is the famous Raoult's law.

Boiling point of a liquid, that is, the temperature at which the liquid boils, is given by that temperature at which the vapor pressure equals the atmospheric pressure. Once again it is worth remembering that the vapor pressure of a liquid only depends on temperature and not its volume, as would be the case for an ideal gas. Therefore, lowering of the vapor pressure of a solution in comparison to the vapor pressure of the pure solvent means that the solution boils at a higher temperature than the pure solvent. One of the standard ways of calculating this upward shift in the boiling point is to use the Clapeyron equation, which tells us how the vapor pressure of a liquid varies with temperature. As we have not derived this equation yet, and will be doing so when we discuss liquid-gas phase transitions later, we turn to a direct method advocated by Fermi [17] which addresses both the lowering of the vapor pressure and raising of the boiling point in solutions.

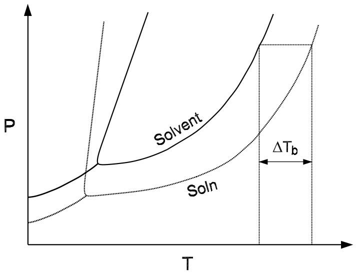

FIGURE 9.3 Boiling point shift

For this we return to the expression for the Gibbs free energy for a solution that we derived in eqn.(9.18). To keep the equations simpler, let us consider the case where there is only one solute present in the solution. Generalizing the results to more than one solute is completely straightforward. So we consider a dilute solution of N_0 moles of the solvent and N_1 moles of the solute, in equilibrium with the vapor of the solvent. Diluteness of the solution means $N_1 << N_0$. The Gibbs free energy of the solution is

$$G_{soln} = N_0 g_0(T,p) + N_1 g_1(T,p) + RTN_1 \ln \frac{N_1}{N_0} \tag{9.32}$$

where

$$g_0(T,p) = u_0(T) - T\sigma_(T) + pv_0(T) \qquad g_1(T,p) = u_1(T) - T\sigma(T) + pv_1(T) \tag{9.33}$$

Now let $g_{vap}(T,p)$ be the Gibbs free energy of one mole of the saturated vapor of the solvent. If the saturated vapor consists of N_{vap} moles of the solvent, one has

$$G_{vap} = N_{vap} g_{vap}(T,p) \tag{9.34}$$

Recalling our earlier discussion of conditions of thermal equilibrium at constant pressure, the condition for thermal equilibrium between the solution and the saturated vapor is that the total Gibbs free energy of the solution and solvent must be a minimum. In the present context the only variables are N_0 and N_{vap}, but their sum $N_0 + N_{vap}$ is constant. The total Gibbs free energy is given by

$$G_{tot} = N_0 g_0(T,p) + N_1 g_1(T,p) + RT N_1 \ln \frac{N_1}{N_0} + N_{vap} g_{vap}(T,p) \tag{9.35}$$

Notice that if the Gibbs free energies per mole of the vapor and the pure solvent were the same for all T, p, the total Gibbs free energy would have no minimum at all, except at the unphysical point $N_0 = \infty$. Of course, the Gibbs free energies per mole of the vapor and solvent are different! To find out the equilibrium condition, let us compute the change in the total Gibbs free energy when the number of moles of the solvent *in the solution* is changed by dN_0. Since the total amount of solvent in the vapor and the solution can not change, $dN_{vap} = -dN_0$ and

$$\begin{aligned} dG_{tot} &= dN_0 \frac{\partial G_{tot}}{\partial N_0} + dN_{vap} \frac{\partial G_{tot}}{\partial N_{vap}} \\ &= dN_0 \{\frac{\partial G_{tot}}{\partial N_0} - \frac{\partial G_{tot}}{\partial N_{vap}}\} \end{aligned} \tag{9.36}$$

It should be recalled that $\frac{\partial G}{\partial N}$ is nothing but the *chemical potential*. Hence the above equation is saying that at equilibrium, the chemical potentials of the solvent in the two phases must be the same. This leads to the very simple equilibrium condition:

$$\frac{\partial G_{tot}}{\partial N_0} = \frac{\partial G_{tot}}{\partial N_{vap}} \qquad \rightarrow \qquad g_0(T,p) - RT\frac{N_1}{N_0} = g_{vap}(T,p) \tag{9.37}$$

To make the equations look more transparent, let us denote the saturated vapor pressure of the pure solvent by $p_0(T)$. The condition for equilibrium between pure solvent and its vapor can be deduced from eqn.(9.37) by setting $N_1 = 0$, that is,

$$g^{(0)}_{vapor}(T,p_0) = g_0(T,p) \tag{9.38}$$

Now, after N_1 moles of the solute is dissolved in N_0 moles of the solvent, the vapor pressure changes from $p_0(T)$. Let the new vapor pressure be $p_0(T) + \Delta p$. For dilute solutions $N_1 << N_0$ we expect Δp to be small compared to p_0 and we can expand both g_0 and g_{vap} around $p = p_0$ to get

$$\begin{aligned} g_0(T,p_0+\Delta p) &= g_0(T,p_0) + \frac{\partial g_0(T,p_0)}{\partial p_0} \cdot \Delta p \\ g_{vap}(T,p_0+\Delta p) &= g_{vap}(T,p_0) + \frac{\partial g_{vap}(T,p_0)}{\partial p_0} \end{aligned} \tag{9.39}$$

Using eqn.(9.39) and eqn.(9.38) in eqn.(9.37), one gets

$$RT\frac{N_1}{N_0} = \{\frac{\partial g_0}{\partial p_0} - \frac{\partial g_{vap}}{\partial p_0}\}\Delta p \tag{9.40}$$

Now let us recall eqn.7.22 from chapter 7 i.e $\frac{\partial G}{\partial P} = V$. Since g_0 is the Gibbs free energy *per mole* of the solvent, g_{vap} that of the vapor, we conclude that $\frac{\partial g_0}{\partial p_0}$ is the volume per mole of the solvent v_0, and $\frac{\partial g_{vap}}{\partial p_0}$ the volume per mole of the vapor in equilibrium with the solution, which we called v_0' earlier. Since v_0 for the liquid is much much smaller than v_0' for the vapor, eqn.(9.40) gives

$$\Delta p = -RT\,\frac{N_1}{N_0\,v_0'} \tag{9.41}$$

which can be seen to be the same as our earlier expression, for the case of a single solute, for the lowering of the vapor pressure given by eqn.(9.31). The sign in eqn.(9.41) corresponds to a lowering of the vapor pressure, and it comes automatically from the treatment based on Gibbs free energy.

Now the same set of equations can be used to get a quantitative expression for the *elevation* of the boiling point of solutions. In literature you may find reference to two types of boiling points, *normal* and *standard.* The normal boiling point is the temperature at which liquids under *one atmospheric pressure* at sea level boil, whereas the standard boiling point is the temperature at which liquids boil under a pressure of 1 KPa. The atmospheric pressure at sea level can vary a little bit from place to place but is roughly 1.05 KPa.

Let the boiling point of the pure solvent at a pressure p_A (we have used the subscript A to denote atmospheric pressure, but if one is interested in the standard boiling point, p_A should be set equal to 1 KPa) be T_0^B, while the boiling point of the solution at the same pressure be $T_0^B + \Delta T_B$. For the pure solvent, we get, from eqn.(9.38)

$$g_0(T_0^B, p_A) = g_{vap}(T_0^B, p_A) \tag{9.42}$$

while for the solution we get, from eqn.(9.37)

$$g_0(T_0^B + \Delta T^B, p_A) - g_{vap}(T_0^B + \Delta T^B, p_A) = R(T_0^B + \Delta T_B)\,\frac{N_1}{N_0} \tag{9.43}$$

We expect the elevation of the boiling point ΔT_B to be proportional to N_1. This is so, as ΔT_B by definition is zero for the pure solvent. As we are dealing only with dilute solutions, for which $N_1 << N_0$, it is a very good approximation to write the right hand side of eqn.(9.43) as $RT_0^B\,\frac{N_1}{N_0}$. The left hand side can be expanded around $T = T_0^B$ just as we expanded around the pressure p_0 earlier . Then we can rewrite this equation as

$$\{(\frac{\partial g_0}{\partial T})_{T_0^B} - (\frac{\partial g_{vap}}{\partial T})_{T_0^B}\}\,\Delta T^B = RT_0^B\,\frac{N_1}{N_0} \tag{9.44}$$

To further simplify this we note that $(\frac{\partial G}{\partial T})_P = -S$, the negative of entropy. We apply this to the solvent and vapor Gibbs free energies, and on using eqn.(9.17) we get

$$\{\sigma_{vap}(T_0^B, p_A) - \sigma_0(T_0^B, p_A)\}\,\Delta T^B = RT_0^B\,\frac{N_1}{N_0} \tag{9.45}$$

We can evaluate the difference in specific entropies occurring in this equation by noting that a supply of *latent heat of vaporization* at (T_0^B, p_A) takes the liquid to a fully vapor state. For an infinitesimal supply of heat $đQ$, the entropy, by definition, changes by TdS. Normally the total heat change depends on the path taken in thermodynamic space. But in this particular case, the absorption of heat takes place at a definite temperature and pressure, that is, at a point in the thermodynamic space. Therefore it is legitimate to express the total heat absorbed, ΔQ, as $T\Delta S$. Therefore, $\sigma_{vap} - \sigma_0$ of eqn.(9.45) is nothing but $\frac{L_{vap}}{T_0^B}$ where L_{vap} is the latent heat of vaporization per mole of the solvent. Putting everything together we arrive at the very important result for the elevation of boiling point of solutions

$$\Delta T^B = \frac{RT_B^2}{L_{vap}} \frac{N_1}{N_0} \tag{9.46}$$

Example 9.4: Boiling point elevation in solutions

Consider a so-called normal solution of salt in water, i.e one mole of NaCl is dissolved in 1 liter of water. Estimate the shift in boiling point.

The number of moles of the solute is $N_1 = 1$ while the number of moles of the solvent is $N_0 = 1000/18$, as the molecular weight of water is 18. The latent heat of vaporization per mole is $540 \cdot 18 = 9.720$ kcal. Using eqn.(9.46) with a factor 2 as NaCl ionises and taking R= 1.986 cal, $T_B = 373.15K$ one gets $\Delta T_B \simeq 1K$. If on the other hand one had dissolved, say, CH_3OH, such a factor of 2 would not be there.

9.5 Freezing point of dilute solutions

In this section we shall discuss how the freezing points of liquids are affected when solutes are dissolved in them. Freezing point, in complete analogy with boiling points, is the point in the (P,T) diagram at which a solid and liquid coexist. Clearly, the temperature at which a liquid freezes, or equivalently the solid melts, depends on the external pressure. As in the case of boiling points, one can introduce normal and standard freezing points.

Once again, we need the condition for phase equilibrium between solid and liquid. The important point is that eqns.(9.37,9.38) expressing the equilibrium conditions for liquid-gas phase equilibrium have their precise analogs for liquid-solid phase equilibrium also. Let us start by writing these equations corresponding to liquid-solid phase equlibria:

$$g_{solid}(T_0^F, p_A) = g_0(T_0^F, p_A) \tag{9.47}$$

This states the equilibrium condition for the coexistence of the pure solvent as a liquid, and its solid phase at the freezing temperatute T_0^F and atmospheric pressure p_A. When N_1 moles of the solute are dissolved in N_0 moles of solvent to form a dilute system, the freezing point will shift to $T_0^F + \Delta T^F$, giving

$$g_0(T_0^F+\Delta T^F,p_A)-RT_0^F\frac{N_1}{N_0}=g_{solid}(T_0^F+\Delta T^F,p_A) \tag{9.48}$$

Use has already been made of the fact that ΔT^F is in itself proportional to N_1 in simplifying the second term above. Expanding eqn.(9.48) around T_0^F, one can recast it as

$$RT_0^F\frac{N_1}{N_0}=\{(\frac{\partial g_0}{\partial T})_{T_0^F}-(\frac{\partial g_{solid}}{\partial T})_{T_0^F}\}\,\Delta T^F \tag{9.49}$$

Following reasoning similar to the one adopted in the case of the boiling point, this condition is equivalent to

$$\{\sigma_{solid}(T_0^F,p_A)-\sigma_0(T_0^F,p_A)\}\,\Delta T^F=RT_0^F\frac{N_1}{N_0} \tag{9.50}$$

But now $\sigma_{solid}-\sigma_0=-\frac{L_{freez}}{T_0^F}$. Hence, one gets for the shift of the freezing point of the solution the expression

$$\Delta T^F=-\frac{RT_F^2}{L_{freez}}\frac{N_1}{N_0} \tag{9.51}$$

The freezing point of the solution actually becomes lower than that of the pure solvent, unlike the boiling point of the solution which is higher than that of the pure solvent.

Example 9.5: Salt-ice freezing mixtures

Calculate the lowering of the freezing point of water when one mole of NaCl is dissolved in 1000 liters of water (the so called normal solution) treating the solution as dilute. With the so called freezing mixture of NaCl and water, it is observed that the maximum lowering of freezing point is by about 21 K. Calculate the number of moles of salt that need to be dissolved in 1000 liters of water for this.

Using $N_1=1$, $N_2=1000/18$,$T_F=273.15$,$L_f=80cal/gm$, $R=1.986$ cal, and with an additional factor of 2 to take into account the near completion ionisation of NaCl, eqn.(9.51) gives $\Delta T_F=-1.85K$. If we calculate the amount of salt needed to depress the freezing point by the maximum value of -21 K, dilute solution theory gives $N_1\simeq 6$, or about 350 gms. This is roughly the observed concentration of salt in the freezing mixture. This is close to the maximum solubility of salt in water at these temperatures. Thus for saline solutions dilute solution theory works all the way.

9.6 Problems

Problem 9.1 Show that the chemical potential of the solvent in a solution decreases linearly with concentration, while the chemical potential of the solute in the solution increases logarithmically with concentration. Find the concentration of a saturated solution, i.e a solution for which the chemical potential of the solute in the solution equals the chemical potential for the pure solute. Explain why the solution is saturated then.

Problem 9.2 Find the maximum work that can be done in the formation of a solution, and from it the maximum work that can be done in forming a saturated solution.

Problem 9.3 Find the minimum work that must be done to raise the concentration of a solution from c_1 to $c_2 > c_1$ by removing the appropriate amount of the solvent. Is there any significance of this to the desalination problem?

Problem 9.4 Show that for ideal mixing, the enthalpy of mixing, internal energy of mixing, as well as volume of mixing vanish.

Problem 9.5 Find the equilibrium condition for a solution in an external gravitational field. Assuming that solutions are incompressible, derive an expression for the variation of concentration in a gravitational field.

Problem 9.6 If a solution of sugar ($C_6H_{12}O_6$) and another of calcium chloride ($CaCl$), both in water, have the same volume and same osmotic pressure, at the same T, in what ratio by weight are they dissolved?

Problem 9.7 Calculate the osmotic pressure and the variation in boiling and freezing points of a normal salt solution in water.

Problem 9.8 At what temperature will the osmotic pressure of a normal solution of Nacl be 100 atmospheres?

Problem 9.9 Explain why a living cell containing water and many ions, equivalent to a saline solution of 0.15 moles per liter, will burst when inserted in fresh water. This is also the reason why sea water fish will die when moved to fresh water. Estimate the osmotic pressure responsible for this by taking the temperature to be 300 K.

Problem 9.10 10 gms of an unknown electrolyte, but known to dissociate into three ions in water, is seen to shift the boiling point of water by 1 K when dissolved in one liter of water. What is the molecular weight of the unknown substance?

Problem 9.11 Calculate the osmotic pressure when 10 gms of a protein with molecular weight of 100,000 is dissolved in a liter of water at 300 K.

Problem 9.12 In what ratio by weight should hemoglobin, with molecular weight 64,000, and NaCl be dissolved in water to produce the same osmotic pressure? Does the answer depend on the temperature of the solution?

10 Phases and Their Equilibria

We are all familiar with the sight of ice floating on water. In fact, even on a warm day, we can toss an ice cube into a glass of water. What happens subsequently is that ice starts melting and will take quite some time before completely melting into water. In the interim, both ice and water are existing together. Can this be called a state of phase-coexistence? Strictly speaking not, because this is not an *equilibrium* situation. It is not a state of equilibrium because as time goes on the amount of ice left changes.

Our next question is whether we can arrange for a truly equilibrium coexistence of ice and water? It can indeed be arranged as follows: let us take a certain amount of water cooled to $0\,^\circ\mathrm{C}$. If we maintain this temperature and 1 atmosphere of external pressure, water will continue in the same state and is hence a *stable* phase. Now let us toss some amount of ice into this water. Ice, if maintained at $0\,^\circ\mathrm{C}$ is also a stable phase in the sense that no matter how much time elapses, it will remain ice. Now this combination of ice and water both maintained at 1 atmosphere and $0\,^\circ\mathrm{C}$ is also stable, and this is an equilibrium state of the coexistence of two phases, namely, ice and water. As this example makes it clear, we need to fix both the temperature and pressure at pre-prescribed values.

In this chapter we shall investigate phase co-existence or phase equilibria as generally as we can. In the example considered above there was only one chemically distinct component, that is, H_2O, but our general discussion can handle many different constituents in phase equilibrium. The following discussion is due to Gibbs. To start with, we make a distinction between number of components and the number of phases in coexistence. In the water-ice example, the number of components is one, and the number of coexisting phases is two. We shall see later that H_2O can exist simultaneously in solid, liquid, and gas phases at a very special combination of temperature and pressure called the *Triple Point*. Strictly speaking, one should consider H_2O as having two components, namely, Hydrogen and Oxygen. But at low enough temperatures and high enough pressures, it is legitimate to consider it as a single component system. The precise criterion is that rates of production, and the rates of dissociation of the chemical H_2O must be very small. In fact, we can extend this discussion to make a distinction between atomic Hydrogen H and molecular Hydrogen H_2. If we do so, then we should think of this system as having even more components. Clearly there is no strict end to this process of counting, and depending on the circumstances we may have to count electrons, protons, neutrons etc. and maybe even quarks and strings!

10.1 The Gibbs phase rule

Quite generally, let us consider a system of n independent components capable of coexisting in F phases. So far most of our discussions have involved quantities expressed in *moles* only. The actual *masses* of constituents never entered the picture.

Now we are going to make a departure from this and express amounts in their respective masses. Of course the two are completely equivalent as knowing the molecular weights means we can express one in terms of the other. But obviously care must be exercised in carefully remembering the convention used in context.

Let m_{ik} be the mass of the component labelled by k in the phase labelled by i. Here too it is very important to remember the convention, that is, the first label in m_{ik} refers to the phase and the second to the component. Since the number of phases can in general be different from the number of components, m_{ik}, viewed as a matrix is in general rectangular. As a phase need not always have all the components, and a component need not be present in all phases, some of the m_{ik} can be zero.

$$\begin{array}{cccc} m_{11} & m_{21} & \ldots & m_{f1} \\ m_{12} & m_{22} & \ldots & m_{f2} \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ m_{1n} & m_{2n} & \ldots & m_{fn} \end{array}$$

The first column in this matrix $(m_{11}, m_{12}, \ldots, m_{1n})$ carries information about the masses of the n components in the phase labelled by ’1’. The first column, $m_{11}, m_{21}, \ldots, m_{f1}$ carries information about the mass of the component labelled by ’1’ in the f phases. Likewise for other rows and columns of this matrix.

From our discussion of the elementary examples, it is clear that phase equilibria take place at fixed temperature and pressure. Thus the conditions for equilibrium are best understood in terms of the Gibbs free energy for the total system. This total Gibbs free energy must take its minimum value at equilibrium. The total Gibbs free energy is given by

$$G = G_1 + G_2 + \ldots + G_f \tag{10.1}$$

where

$$G_i = G_i(T, P, m_{i1}, m_{i2}, \ldots, m_{in}) \tag{10.2}$$

It should be carefully noted that G_i is the Gibbs free energy of the phase labelled by i in which the masses of the various components are given by the n quantities $m_{i1}, m_{i2}, \ldots, m_{in}$.

Let us first consider phase equilibrium only between a pair of phases, say the ones labelled by i and j. Before equilibrium is achieved there will be transfer of various components between the two phases. When equilibrium is reached this transfer of components ceases. This should happen when the total Gibbs free energy of these two phases, $G_{tot} = G_i + G_j$ reaches a minimum. Let us further simplify the situation by restricting the transfer to component k only. Imagine the amount of this component in the i-phase to be increased by δm; then the amount of this component in the j-phase must decrease by the same amount. Hence

$$\delta m_{ik} = -\delta m_{jk} = \delta m \tag{10.3}$$

If the Gibbs free energy is a minimum, the variation δG_{tot} of the total Gibbs free energy must vanish at the equilibrium point:

$$\delta G_{tot} = 0 = \frac{\partial G_i}{\partial m_{ik}} \cdot \delta m - \frac{\partial G_j}{\partial m_{jk}} \cdot \delta m \qquad \rightarrow \qquad \frac{\partial G_i}{\partial m_{ik}} = \frac{\partial G_j}{\partial m_{jk}} \tag{10.4}$$

It should be emphasized that eqn.(10.4) is only a *necessary* condition for phase equilibrium between the phases i and j. For the phase coexistence to be stable, Gibbs free energy must be a minimum and this requires

$$\frac{\partial^2 G_{tot}}{(\partial \delta m)^2} < 0 \tag{10.5}$$

Stability of phases is a very important and fascinating topic in thermodynamics. We will discuss some essential aspects of this later on.

Now we can remove the restriction of only two phases and a single component; that was introduced only to make the presentation less cluttered and does not really restrict the general validity of this analysis. The removal of these restrictions is straightforward and one gets, in place of eqn.(10.5),

$$\begin{aligned} \frac{\partial G_1}{\partial m_{11}} &= \frac{\partial G_2}{\partial m_{21}} = ... = \frac{\partial G_f}{\partial m_{f1}} \\ \frac{\partial G_1}{\partial m_{12}} &= \frac{\partial G_2}{\partial m_{22}} = \ldots = \frac{\partial G_f}{\partial m_{f2}} \\ \ldots &= \ldots = \ldots = \ldots \\ \frac{\partial G_1}{\partial m_{1n}} &= \frac{\partial G_2}{\partial m_{2n}} = \ldots = \frac{\partial G_f}{\partial m_{fn}} \end{aligned} \tag{10.6}$$

In each row we have $(f-1)$ equalities, and therefore all in all we have $n(f-1)$ equations. Suppose we have phase equilibrium among f phases involving n components, and we double all the masses m_{ik}; we are clearly not going to get another type of phase equilibrium. What we will get instead is the same equilibrium with twice the total mass in each phase. In another words, 5 gms of ice is not a different phase from 10 gms of ice. Therefore we conclude

$$G_i(\lambda_i m_{i1}, \lambda_i m_{i2}, \ldots, \lambda_i m_{in}) = \lambda_i G_i(m_{i1}, m_{i2}, \ldots, m_{in}) \tag{10.7}$$

In other words, G_i are *homogeneous* of first degree in the mass variables. Equivalently, G_i can only depend on the ratios of the masses, and not on all the masses. Specifically, each G_i can depend only on the $(n-1)$ independent mass ratios constructed out of n masses occurring in eqn.(10.7). It should be appreciated that each phase can have different values for λ_i. We had, to begin with, nf masses; but the number of independent ratios is $(n-1)$ for each phase, or $(n-1) \cdot f$ altogether. If we now count the thermodynamic variables (T,p) as the other independent variables, the total number of independent variables is $(n-1) \cdot f + 2$. On the other hand, we counted $n \cdot (f-1)$ independent equations. These equations are *constraints* among what we thought to be the independent variables. Therefore the true number of independent variables, or *degrees of freedom* are

$$v = (n-1)\cdot f + 2 - f\cdot(n-1) = 2 + n - f \tag{10.8}$$

This is the famous **Gibbs Phase Rule**. Let us apply this to a few simple examples.

10.2 Phases of water

Consider water in ranges of temperatures and pressures in which it remains a liquid. The system is characterized by its temperature T, pressure P and the mass of water. This is an example of a chemically defined (H_2O) homogeneous, in the sense of being in a single phase, liquid. Let us apply the phase rule to it. In this case $f = 1, n = 1$. Therefore, the number of degrees of freedom is $v = 2$. These are (T, P). As already explained, the masses of components are not degrees of freedom, but only ratios of masses. Clearly, whether we have 10gms of water or 1Kg of it, we still have the same phase!

Now let us consider two phases of water in coexistence, say water and ice or water and its vapor. The number of components is still $n = 1$ but the number of phases is $f = 2$ so the number of degrees of freedom is now $v = 1$. Compared to the previous example, the number of degrees of freedom has come down. Counting the amount of water and the amount of its vapor along with temperature and pressure would give four variables. As per the discussion of the phase rule, in *each phase*, only the ratios of masses are to be counted. Therefore, in this example, neither the amount of water nor the amount of vapor would be among the degrees of freedom. Of course, there is the ratio of the mass of water to mass of vapor; but this ratio is constructed out of masses taken from different phases, and hence is not counted.

Therefore the single degree of freedom to describe the coexistence of two phases of the same component, in this case water, can be chosen to be either the pressure or temperature. The one gets determined in terms of the other. In other words, in the (P, T) plane, the coexistence points lie on a curve. As one crosses this curve in the T, P plane, one goes from one phase to another.

We introduce some useful terminology here. Suppose two phases, say A and B, are in coexistence. This is described by, say, a curve in the P-T plane. One could of course have chosen any two independent thermodynamic variables to describe this coexistence. As we cross the coexistence curve from lower to higher temperatures, one says that we go from a *low-temperature stable* phase to a *high-temperature stable* phase. Likewise, for pressure. We shall illustrate this with specific examples later on.

That the number of degrees of freedom goes down with increasing number of phases is physically clear. It requires many more physical conditions to be satisfied at the same time. Thus the negative sign that comes with f in the phase rule. By the same reasoning, it becomes easier to have more phases in coexistence if the number of components gets larger. Indeed n comes with a positive sign in the phase rule.

There is one point worth elaborating about the coexistence between a liquid and its vapor. As we have just seen, either the temperature or the pressure suffices to fix the phase coexistence. Let us take it to be temperature. Then the pressure, which is also the vapor pressure in this case, is automatically fixed! That is, vapor pressure is a function of temperature only. But for a gas, pressure is usually determined by both its temperature and volume.

Why then does not the volume of vapor play a role in fixing its pressure? As the volume over a liquid surface is increased, say by raising a piston, more of the liquid evaporates to form saturated vapor. Thus unlike the example of a gas where the equation of state is expressed for a given amount of gas, in the case of the vapor the amount keeps increasing with volume in such a way that the pressure is kept fixed at the value that is the vapor pressure of the liquid at the given temperature.

Now let us ask if all the three familiarly known phases of water, namely, ice, liquid water, and water vapor can coexist. From our discussion a little while ago, we expect the coexistence of any two given phases to be described by a curve in the T, P plane. Thus, the water-vapor coexistence will be described by one curve, and the ice-water coexistence by another curve. If these curves intersect, at the intersection point we will have all the three phases in coexistence. Clearly, such an intersection point will have unique values of temperature and pressure. In the context of water, it means there are no degrees of freedom left at all! This is indeed what the phase rule also says as $v = 0$ for this case of $n = 1$ and $f = 3$. Such points are called *Triple Points.* The triple point for water occurs at $T = .0075\,^\circ\mathrm{C}, P = .006KPa$.

Having determined the triple point as an intersection of the ice-water and water-vapor coexistence curves, there is no freedom left for the ice-vapor curve but to pass through this triple point! In the following figure we show a typical phase diagram for a one component system capable of being in three phases. The solid-liquid coexistence curve shown as a dotted line is for the water-ice case. There is something anomalous about this *freezing curve*. Before explaining that, let us explain a simple rule that determines the way these phase boundaries are pointing in the T, P plane, or in other words, their 'slope.' If we look at the water-vapor curve, or a generic liquid-gas coexistence curve, we see that its slope in the P, T-plane is *positive*. Correlated with this is the usual situation that the density of gases is much lower than the density of liquids. The solid-gas coexistence in the above figure also shows the same thing: gases are less dense than solids and the solid-gas coexistence line has positive slope.

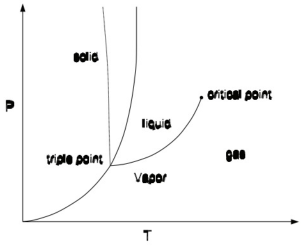

FIGURE 10.1 Phase diagram of H_2O.

Finally let us look at the solid-liquid coexistence curve. By and large liquids are less dense than solids and if the slope of the coexistence curve is dictated by it as in the above two cases, then the freezing curves should also have positive slope. But the water-ice freezing curve has negative slope. This means that at higher pressures, the melting point of ice is lowered, and the system (H_2O) can remain a liquid at lower temperatures than it did when the pressure was lower. It is claimed that skiing is facilitated by this, but we will discuss that issue elsewhere, but it is experimentally true that the melting point of ice is indeed lowered at higher pressure. But there is something else about water that is unusual too! Below 4°C, water expands upon cooling! So in fact ice is *lighter* than water reversing the usual situation that solids are *denser* than liquids! Therefore our 'rule' still works, and since the sign of relative densities is reversed, so must the slope of the freezing curve!

Example 10.1: Ice melting on a very very cold day

How does snow melt during a bitter winter when temperatures are much below 0°C*?* It certainly does not melt by first becoming water. To understand what happens, refer to the phase diagram of water as shown in Fig.(10.1). At temperatures much below the normal melting point of ice, the solid phase coexists only with the vapor phase. Therefore any loss of snow (ice) must be accompanied by gain in vapor. This process of direct passage from a solid to gas is called sublimation. Another example is the burning of Camphor. So the answer is that snow disappears in very cold weather due to sublimation.

In chapter 11 we shall derive the *Clapeyron Equation*, more aptly the *Clausius-Clapeyron Equation*, which will explain why this rule works, and even predict the slope. This is a very important equation in Thermodynamics with the help of which we can understand many things. This equation will tell us that freezing curves can have the anomalous slope even when all densities are normally behaving! We will see that this is what happens in He_3 where too the freezing curve has negative slope.

A curious feature can be pointed out about systems with *anomalous* freezing curves, i.e systems like water: first consider a 'normal' system. Draw a vertical line a little to the right of the triple point. This is a constant temperature curve. As we move from bottom to top, we move from lower pressures to higher pressures. In a normal system, we would start from a gas phase and move on to a liquid phase and then to a solid phase. This fits with our intuitive expectations of what increased pressure should do to a system. On the other hand, in the case of water, drawing the vertical line to the *left* of the triple point, one finds that with increasing pressure one goes from gas to solid first, and then from solid to liquid!!

In terms of the terminology of stable phases introduced before, we can summarize the stability aspects of the phase diagram of Fig. 1 as follows: for solid-gas coexistence, the gas phase is always the high-temperature stable phase. For the liquid-gas coexistence too, the gas is high-temperature stable. In both these cases, the vapor is also the low-pressure stable phase. The situation is more varied for the solid-liquid coexistence because there are two types of freezing curves. For both of them, the liquid is still the high-temperature stable phase. But for water, the high-pressure stable phase is the liquid, while for normal freezing curves, it is the solid phase that is stable at higher temperatures.

In addition to the triple point, there is another special point in the phase diagram of Fig. 1, called the *Critical Point*. It is the point at which the liquid-gas coexistence curve terminates, in this particular example. As one can see, beyond this point there is no phase boundary between the liquid and vapor phases. There is no physical way to distinguish them, and they must be considered to be the same phase. Among other things, the latent heat vanishes at the critical point. Such a special point was also encountered while we were discussing the van der Waals system. A full understanding of the physics of the critical points, also called *Critical Phenomena* can be considered to be one of the greatest achievements of physics. While the full machinery of *Statistical Mechanics* is needed for this, one can go a long way in understanding them only on the basis of thermodynamic principles. This will be done in the chapter on critical phenomena.

10.3 Salt water phase diagram

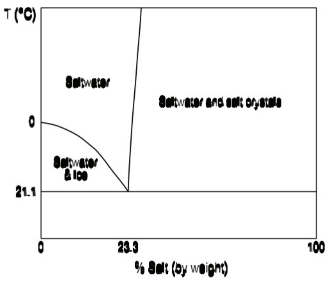

FIGURE 10.2 Salt water phases.

We end this chapter by discussing a different type of phase diagram, one where states of the water and salt are plotted in a temperature vs concentration graph. Obviously, the pressure has to be kept fixed, and we take it to be 1 atmosphere so that the freezing point of the pure solvent, namely water, is at 0 °C. The phase diagram is shown below. The temperature range is such that the gaseous phase is not relevant. For example, for the pure solvent, whose states are represented along the vertical axis, only the liquid and solid phases are relevant as long the temperature is below the boiling point of water at 100 °C. Now let us move very slightly to the right along the horizontal axis and start from the upper left hand corner of the diagram. This corresponds to high temperatures (but below 100 °C). Now we have a very dilute salt solution. Let us try to understand what happens to this dilute saline solution as we cool it. From our discussion of the freezing point of solutions, we expect this solution to freeze, not at 0 °C, but at a slightly lower temperature. Let us say that the concentration is such that this new freezing point is at $-.01\,^\circ$C. Therefore one may expect ice mixed with salt crystals below this lowered freezing point. But what happens is a little more complicated.

As ice forms, it floats on salt water of a somewhat higher concentration. Ice floats even on pure water as it is lighter. As salt water is denser than pure water, ice floats even more easily on salt water.

The rest of the salt solution is a little more concentrated because the amount of salt has remained the same but the amount of water has decreased, having formed some ice. Now this slightly more concentrated salt water, again in line with our earlier discussion, freezes not at $-.01\,^\circ$C, but at an even lower temperature. Therefore the state of the system is a mixture of ice and *salt water*. Of course, this process does not continue indefinitely and at approximately $-21.1\,^\circ$C all the water solidifies into ice and one is left with a phase of ice mixed with salt crystals (not salt water). A way to understand this is to realize that the concentration of salt in water can not be increased beyond a certain *saturation* concentration.

This can also be understood from the same phase diagram. To see this, stay at the upper left hand corner, corresponding to a dilute salt solution at high temperature, but now move horizontally taking us to higher concentrations at the same temperature. Initially one has salt water at this temperature, but eventually, after reaching concentrations somewhat in excess of 23.3%, one gets salt water and salt crystals in coexistence. The salt water is completely saturated at this point and it is not possible to dissolve more salt into it.

Finally, let us see what happens to the fully saturated salt water, represented by a point on the boundary between the salt water phase and the phase with salt water and salt crystals, as we lower its temperature. The amount of salt that can be dissolved goes down with temperature. As a result, some salt crystals will start separating, giving rise to a mixture of salt water and salt crystals. The concentration of salt is high enough to keep the freezing point around $-21.1\,^\circ\mathrm{C}$. As we cool below this temperature we end up in the phase with ice and salt crystals.

It should be appreciated that the freezing point can not be lowered arbitrarily just by increasing the concentration. Two factors come in the way of this; firstly one can not increase the concentration of salt indefinitely. Secondly, when the concentration becomes high, the system can no longer be treated as a dilute solution.

10.4 Phases of Carbon

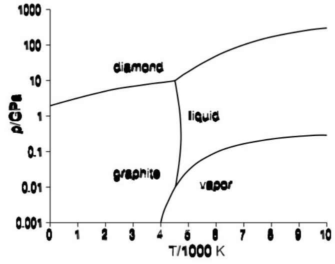

FIGURE 10.3 Phase diagram of carbon.

As another example of an $n = 1$ system, let us look at the phases of Carbon. In some sense, this is even more striking, as chemically this is a single component while water had two chemically distinct components, namely, Hydrogen and Oxygen. A rough phase diagram of Carbon is shown in Fig.(10.3). It consists of *four* distinct phases, namely, Graphite, Diamond, liquid Carbon and Carbon vapor. It's a rough, or crude, phase diagram in the sense that a lot of fine structure that may actually be present has been averaged out. An application of the phase rule gives as $f \leq 3$, as otherwise the number of degrees of freedom turns *negative*. Indeed, we see that there is no point in the phase diagram where all the four phases are coexisting. On the other hand, there are two triple points where Graphite, liquid and vapor on the one hand, and Graphite, Diamond and liquid on the other, coexist. This is completely in accordance with the Gibbs phase rule.

It should however be emphasized that the phase rule does not say that four phases for a $n = 1$ system can never coexist. There could certainly exist some very special material for which the two triple points coincide. But that is not *generic*. Even in the Carbon system, one could envisage the presence of some impurities. In fact colouration in diamonds can come out of such impurities. Then, the location of the triple points can depend on the impurity concentration, and for some special impurity concentration the two triple points may coincide giving a $f = 4$ coexistence. But now we have increased n to at least 2, and as per the phase rule, $f = 4$ for a $n = 2$ system is a generic possibility.

Example 10.2: Are diamonds really forever?

A look at the Carbon phase diagram of Fig.10.3 indicates that at room temperatures diamond is stable only at very high pressures, of the order of ten thousand atmospheric pressures! Then how come we see diamonds at room temperature at all, seemingly existing forever? Let us look at another similar 'puzzle.' Ice at atmospheric pressure is a stable phase only below 0°C. Yet, if we pull out a cube of ice from a freezer into room temperature, it does not spontaneously convert into water. It takes some time. A similar thing happens for diamonds at room temperature. They will eventually 'degrade' into the phase that is stable at room temperatures, which is Graphite. But it takes a really really long time for this to happen. How long does it take for diamond to convert to graphite? Equilibrum Thermodynamics, the subject of this book, can not answer that question, mainly because the passage is a non-equilibrium process.

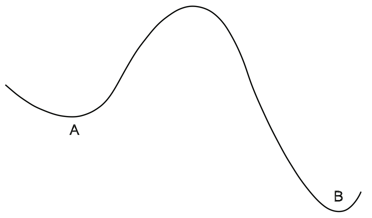

FIGURE 10.4 Gibbs Free Energy Barrier

One can get a feel for what is happening by considering a mechanical anology. What is shown is a potential with a barrier separating two locally stable points **A** and **B**, with **B** lying *lower* than **A**. Therefore **B** is more stable than **A**. But the system, if initially in **A** will not spontaneously roll down to **B**. That is so because in order to get to **B** it has to climb a barrier. The more difficult the barrier, the longer it will take to complete the transition. When one studies enough *Statistical Mechanics* and *Non-equilibrium thermodynamics*, one will see that this is more than a mere analogy. In going from an unstable state like diamond at room temperature to the stable graphite state, the system has to go through many intermediate states whose Gibbs free energies are such that there are several barriers. The nature of these barriers determines the transition rate.

10.5 Helium-3 Phase Diagram

Returning to phase diagrams, one can also ask whether in a system with at least three dinstinct phases, there may be no triple point at all. This is certainly possible and is illustrated by the rough phase diagram of Helium-3 that people had thought to be correct before more accurate measurements at very low temperatures were possible. This is illustrated in the next figure: The phase diagram of Helium-3 has had a fascinating history, which we shall recount here as the physics involved is rather deep, and some of it (the so called *Pomeranchuk Cooling*) will play a crucial role in our later discussion of the experimental techniques to reach the lowest possible temperatures. Even the phase diagram of Fig.(10.5) was only theoretically conjectured at one point. If it is compared, for example, with the phase diagram given in Pippard, it differs from the latter by the non-monotonic (i.e both decreasing and increasing)

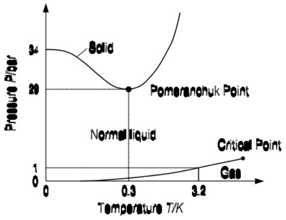

FIGURE 10.5 Older He3 Phase Diagram.

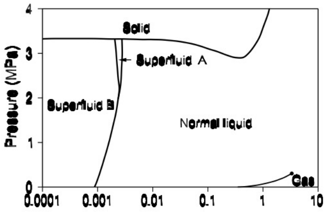

FIGURE 10.6 Recent He3 Phase Diagram.

part of the freezing curve. At the time of Pippard's book, experiments seemed to indicate that the freezing curve had flattened out around 0.5 K. As we shall explain later, close to absolute zero, all freezing curves must flatten out. Hence it was taken that the flattening at around 0.5 K was because of this and that this flattening will continue for the remaining 'short' temperature interval.

The Russian physicist, Pomeranchuk, had however argued that at temperatures much lower than 0.5 K, the solid is the high-temperature stable phase, meaning that an increase in temperature would prefer the formation of the solid phase. This is highly counter-intuitive as we expect the liquid phase to be the one that is high-temperature stable. This would produce the kind of freezing curve shown in Fig.10.5. To test such a hypothesis, one would have to go to temperatures below 0.3 °C, not an easy task then. Assuming such a possibility, one sees that the freezing curve for Helium-3 for such temperatures would resemble the anomalous freezing curve of water. But we will see in the next chapter that as a consequence of the *Clapeyron Equation* (for gases at low temperatures and low pressures it is also referred to as the *Clausius-Clapeyron approximation*), the physics behind the two anomalous situations is drastically different.

We show above a modern phase diagram of Helium-3. This has been made possibly through great technological breakthroughs, particularly in attaining and controlling very low temperatures. The phase diagram shown above extends the lower end of the temperature scale to millikelvin, which is 50 times smaller than the corresponding temperature scale used in the older phase diagram. It certainly upholds the ideas of Pomeranchuk; indeed from mK to about 0.3 K, it is the solid that is high-temperature stable, not the liquid. The phase diagram has, at the same time, become much richer. The liquid phases are now three in number, *normal liquid, superfluid A, superfluid B*. While there is no triple point involving the solid and normal liquid, one involves all the liquid phases, and two involve the solid. The *critical point* as the end point of the liquid-gas coexistence is still at the same location of roughly 3.2 K, and 230 KPa of pressure.

10.6 Helium-4 Phase Diagram

We now turn to a discussion of the phase diagram of Helium-4. Its features are totally different from that of Helium-3. At a fundamental level, Helium-3 is fermionic, whereas Helium-4 is Bosonic. From a purely thermodynamic perspective, this distinction can not be made use of. Helium-4 exists in four phases, solid, vapor, and two liquid phases. There are two triple points and one isolated critical point.

The accompanying figure displays the phase diagram of Helium-4. What is totally new from the Helium-3 case is that now there is a *continuous line* of critical points separating the two liquid phases. This is called the λ-transition line because the specific heat curve at each of these critical points resembles the greek symbol λ. At each of these points, the latent heat vanishes. We will show later how many of these features can be understood from pure thermodynamic arguments using the Clapeyron equation, and its generalizations to the so called *higher order phase transitions*.

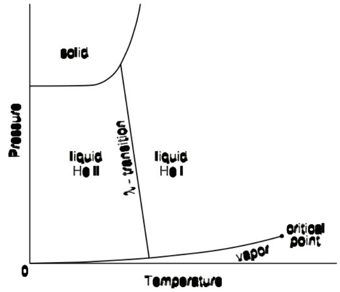

FIGURE 10.7 Helium-4 Phase Diagram.

10.7 QCD Phase Diagram

Lastly we discuss a case to show the tremendous range of thermodynamics, far beyond the types of matter, and their physical conditions, that led to its birth in the first place. We discuss the phase diagram of the so called *Quantum Chromodynamics*. This is the theory considered by many to be the best candidate to explain the strong forces holding together the nucleus of atoms.

By colliding nuclei against each other at high energies, very high temperatures and densities can be created. These are also the conditions that are believed to exist in the very early stages of our universe. The most energetic of such collisions are being carried out at the particle accelerator *LHC* at Geneva. So the span of thermodynamics is truly mind-boggling, from ultra-microscopic to ultra-macroscopic, that is actually cosmic. This phase diagram says that at low temperatures (these are still very high temperatures compared to what we normally encounter!) and fairly high densities, matter exists as nuclei. At somewhat higher temperatures, but still considered 'low' from a nuclear matter perspective, and much higher densities one encounters matter as found in *Neutron Stars*. If nuclei are heated to substantially high temperatures but keeping the density low, one reaches the states as found in very early universe (top left hand side of phase diagram). If heated to somewhat lower temperatures and densities lower

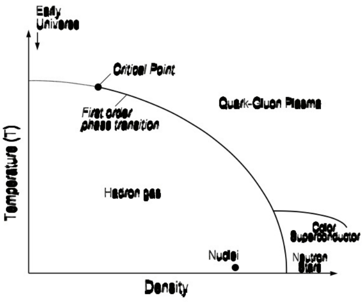

FIGURE 10.8 Quantum Chromodynamics.

than neutron star matter, one gets a gas of protons and neutrons etc. called the *hadron gas*. When this hadron gas is taken to higher temperatures or suitably high pressures, a new phase called *Quark-Gluon Plasma* shows up. Studying the properties of this phase is one of the chief objectives at LHC. The coexistence curve between the gas phase and the plasma phase is expected to terminate at a critical point. Determining the precise location and the properties of this critical point is seen as a challenging test of this theory.

10.8 Superconducting Phase Transitions

One of the most interesting phase transitions, also of far reaching consequences, is the so called *Superconducting Phase Transition*. First let us discuss this fascinating phenomenon. When certain metals like Aluminium or Tin are cooled to rather low temperatures, of the order of a few K, they abruptly lose their DC electrical conductivity *completely*! This was experimentally discovered by Kamerlingh Onnes in 1911.

A complete understanding of this phenomenon requires Quantum Theory. Also, now many variants of the superconducting phenomenon are known. It would be far beyond the scope of this book to even make a modest attempt at that. But the power of Thermodynamics is so incredible that we can understand some of the most salient properties of superconductivity in terms of what we have already covered in this book.

We shall focus attention on the so called *Type-I Superconductors* only. For such a class of superconductors, there is a phenomenon called *Meissner-Ochsenfeld Effect*. It is an effect by which a metal in a superconducting state expels all magnetic field within it. This is explained in figure 10.9. The material becomes a superconductor only below some temperature T_c; above that it is in the normal state. On the left hand side of the figure is a situation where the metal is in a normal state and magnetic field as usual can penetrate the metal. On cooling the sample below T_c, which makes the metal become superconducting, the magnetic field is completely expelled from the material. What is of course happening is that in the superconducting state currents are set up in the body which generate magnetic fields to exactly compensate the applied external magnetic field. These details, though extremely fascinating, are

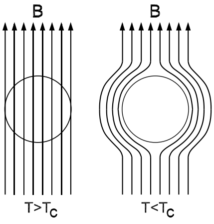

FIGURE 10.9 Meissner-Ochsenfeld Effect.

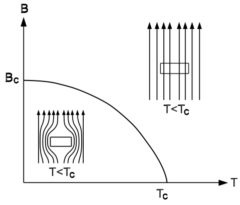

FIGURE 10.10 Critical field B_c vs temperature.

not required for a thermodynamic understanding. But what is of relevance to us, is another aspect of such type-I superconductors. It turns out that if the external field is made stronger and stronger, it eventually destroys the superconducting state, and beyond that *critical field* H_c, the metal ceases to be a superconductor, and as a normal metal allows the penetration of the magnetic field. It is observed that the value of H_c depends on temperature. Quite obviously, above the superconducting transition temperature T_c, the critical field is zero as the metal is anyway in the normal state. Temperature dependence of B_c in typical type-I superconductors has the behaviour shown in the figure 10.10.

The table below gives the numerical values of T_c(K) and $B_c(0)$ in mT(milli-Tesla) for a few familiar superconducting materials: As can be seen from this table, rather small fields are enough to destroy superconductivity. For example, just a field of 3 mT(30 G) is enough to destroy the superconductivity of Aluminium at 1K. We shall see in chapter 11 that the vanishing of B_c at T_c means that the superconducting transition is one with vanishing latent heat. As far as this aspect is concerned T_c here is very much like the critical point in the water phase diagram. At T_c the critical field vanishes. Very close to the critical temperature, B_c falls linearly, i.e $B_c \approx (T_c - T)$. At other temperatures, it is observed that the temperature dependence of the critical magnetic field is well described by the equation

TABLE 10.1

Critical Temperature T_c and Critical Field $B_c(0)$ for some superconductors.

Name	T_c(K)	$B_c(0)$(mT)
Aluminium	1.2	10
Lead	7.2	80
Mercury	4.2	41
Tin	3.7	31
Titanium	0.4	5.6

$$B_c(T) = B_c(0)\left(1 - \frac{T^2}{T_c^2}\right) \tag{10.9}$$

This is referred to as the *Parabolic Law*. This is one of the predictions of the famous Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. Though in principle the critical field is expected to be a function of both temperature and pressure, no appreciable pressure dependence has been seen experimentally [25].

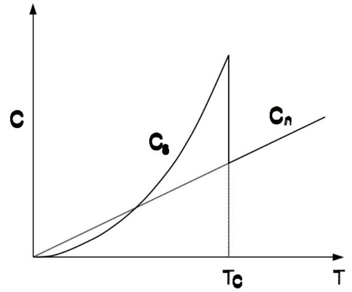

FIGURE 10.11 The specific heats in superconductors.

But a very important difference arises in the behaviour of specific heats which is shown in the figure 10.11. As the temperature is lowered below T_c, the specific heat increases with a jump from the specific heat of the normal metal at that temperature. One may wonder how the specific heat of the normal state could have been probed at temperatures below T_c! The trick is to apply a critical magnetic field at that temperature so that superconductivity is destroyed and one is left with a normal metallic state. The magnetic field could in principle affect the specific heats, but those effects can be accounted for by using the results presented in chapter 10.

For most metals the low temperature specific heat in the *normal state* has the behaviour $aT + bT^3$. In the case of Aluminium, the dependence is practically linear. It vanishes at absolute zero as required by Nernst-Planck theorem. The low temperature specific heat of superconducting state on the other hand is of the form $de^{-\frac{c}{T}}$. Therefore eventually the specific heat again falls below the normal state specific heat. The superconducting state specific heat too approaches zero as one approaches absolute zero, again in conformity with Nernst-Planck theorem.

These are the most important observable effects for us and in chapter 15 we shall see how thermodynamics gives a beautiful and straightforward account of them.

10.9 High-T_c Superconductor Phase Diagram

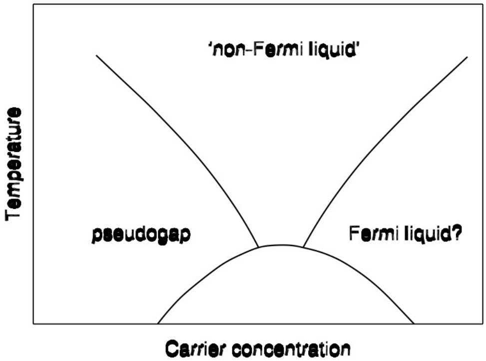

FIGURE 10.12 High T_c Superconductors.

The pursuit of the phase diagrams of high temperature superconductors continues even till today. A phase diagram is shown characterising the so called *High Temperature Superconductors*. Their study is extremely important both from a basic sciences perspective, as well as from a technological perspective. The diagram shown is in a plane spanned by temperature and doping concentration. This continues to be a very challenging problem.

10.10 Problems

Problem 10.1 Consider a chemically homogeneous substance such as, for example CO_2. In its liquid phase, how many degrees of freedom are required for its thermodynamic description? What is the maximum number of coexisting phases for this substance? What could they be?

Problem 10.2 Consider a system consisting of two chemically distinct systems. When they are in a single homogeneous phase, what is the number of degrees of freedom required for a complete description? How many triple points are possible for this system, and how many degrees of freedom are required for their description? What is the maximum number of coexisting phases in this case? Give an example of such a system.

Problem 10.3 An experimenter wishing to study the phase diagram of Carbon is under the mistaken impression that the carbon samples are pure, but it turns out that they do have impurities. If the triple point pressure P_{gdl} where graphite, diamond, and carbon liquid are in coexistence is very sensitive to impurities and has a dependence on impurity concentration x of the type $P_{gdl}(x) = P_{gdl}(0) - \eta\,\mathrm{x}$, while the pressure at the other triple point P_{glv} is totally insensitive to impurities, at what value of x will the two triple points coincide if for all practical purposes the temperatures of the triple points are the same, and also totally insensitive to x? Interpret such a coalescence from the point of Gibbs phase rule.

Problem 10.4 Consider the system of water and salt as discussed at length in section 10.3. Discuss the phase diagram presented there in the light of the Gibbs phase rule

Problem 10.5 Carbon dioxide has a normal freezing curve and its phase diagram has a triple point at $T = 304.25K$ and $P = 74$ bar. At what values of P,T should one start so that upon reduction of pressure solid carbon dioxide directly passes to its gaseous phase (sublimation)? Likewise, what should be the starting P,T such that reduction of pressure first takes the solid to a liquid and then to a gas?

Problem 10.6 Consider a weak salt which only partially ionises in water. Apply the Gibbs phase rule to this system.

11 The Clapeyron Equation

In this chapter we shall derive one of the most important equations in thermodynamics, the so called *Clapeyron Equation*, named after Paul Emile Clapeyron (1799-1864), one of the founders of thermodynamics. The Clapeyron equation is magical in its ability to explain a myriad of facts concerning phase equilibria. Nevertheless, its derivation, at least in its most commonly used form, is rather straightforward. We shall present a few alternative ways of obtaining it. We shall also give a generalization of it due to the Austrian and Dutch physicist Paul Ehrenfest (1880-1933), which enables it to be applied to the so called *continuous phase transitions* (at the critical points).

11.1 Clapeyron's original treatment

As we saw in section 1.5 of chapter 1, Clapeyron derived his famous equation in 1834 even before the nature of heat as understood in modern thermodynamics was known. The equation given by him then, as given in eqn.(1.28) was

$$\frac{dP(T)}{dT} = \mu(T)\,\frac{l(T)}{v_s - v_w} \tag{11.1}$$

This is of the same form as what is currently known as the *Clapeyron equation* except for the appearance of the unknown, but universal, *Carnot function* $\mu(T)$. The great importance of this function, at those early times, has been elaborated at length in chapter 1. It is worth mentioning that many predictions of the modern version of this equation like boiling point elevation and freezing point depression (see later parts of this chapter) already follow, though only qualitatively, from this original equation. As also stressed before, Clapeyron heralded the graphical methods with this work, and these methods form the backbone of modern thermodynamical analyses.

11.1.1 Clausius's improvement

As explained in section 3.2 of chapter 3, it was Clausius who fixed the universal function $\mu(T)$ to be 1/T. To do so, he relied on Carnot's revolutionary idea of the universality of heat engines. As explained in eqn.(3.8), he essentially reconsidered Clapeyron's original treatment, but now with his modern theory of heat, to get this seminal result. In the light of Clausius's important progress, the Clapeyron equation becomes

$$\frac{dP(T)}{dT} = \frac{l(T)}{T(v_s - v_w)} \tag{11.2}$$

We once again stress that this equation should truly be called the *Clausius-Clapeyron equation*, as some sources indeed do. But a vast majority call it the Clapeyron equation and we shall continue with that but in this book that should be understood as just using a shorthand. Also, one should not confuse this with the *Clausius-Clapeyron approximation* discussed later.

11.2 More modern approaches

To begin with, let us note that every phase is characterized by its own Gibbs potential per unit mass $g(T,P)$. This can of course be expressed in terms of any set of independent thermodynamic variables. Since phase transitions take place at a given temperature and pressure, the P-T representation is more convenient.

Before considering the problem of coexistence of phases, let us note some important properties of the Gibbs potential:

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \qquad \left(\frac{\partial g}{\partial P}\right)_T = v \tag{11.3}$$

where s, v are the entropy per unit mass (specific entropy) and volume per unit mass (specific volume), respectively. As both s, v are positive, it follows that at constant pressure $g(T,P)$ must decrease with T and at constant temperature it must increase with pressure.

The condition for phase coexistence is easily determined; we explicitly derive this condition for phase equilibria of a single component system ($n = 1$ in our earlier terminology), as generalization to arbitrary systems is straightforward. Let m_1, m_2 be the masses of this single component in the phases 1,2 respectively. The total Gibbs potential G_{tot} is then

$$G_{tot}(T,P) = m_1 g_1(T,P) + m_2 g_2(T,P) \tag{11.4}$$

If m_1 changes by δm during coexistence, m_2 must change by $-\delta m$. The change in the total Gibbs potential is therefore $\delta G_{tot} = \delta m(g_1 - g_2)$. Since phases in coexistence are in equilibrium, and since at equilibrium the total Gibbs potential is *stationary*, i.e $\delta G_{tot} = 0$, the condition for phase coexistence is

$$g_1(T,P) = g_2(T,P) \tag{11.5}$$

and this must be true all along the coexistence curve. In fact, eqn.(11.5) *defines* the coexistence curve, $P(T)$.

This is a mathematical consequence of the exact equality of the relevant Gibbs potentials g_1, g_2. In reality, such an exact equality will be hard to realize and this means that we may be dealing with situations which are slightly off equilibrium. This departure may be very hard to recognize for all practical purposes. Then we do not expect the pressure to be determined entirely by the temperature. Also, an exact determination of the potentials g_1, g_2 either theoretically or from experimental data (as is often the case in thermodynamics) is also practically impossible. This too leads to an *effective* fuzziness in the coexistence 'curve.'

It is important to get a physical understanding of this fact also. For coexistence of a gaseous phase with other phases, which can be solid, liquid or gas, the pressure above equals the vapor pressure. Now vapor pressure depends only on temperature and not on volume. Superficially, this seems to go counter to the ideal gas behaviour, $PV = nRT$, according to which the pressure depends on both temperature and pressure. In the case of the vapor pressure, n is not fixed. If one increases the volume, more of the solvent goes into vapor form, maintaining the pressure P. At any temperature, what is fixed instead is the ratio $\frac{n}{V}$. In the case of coexistence involving liquids and solids only, the situation is very different, yet leading to similar observations about pressure. Both liquids and solids are highly *incompressible*, making pressure depend very weakly on volume anyway.

But if the equilibrium condition of eqn.(11.5) is rigorously valid, pressure is strictly dependent on temperature only. Even for liquids and solids, this means that what little dependence on volume there is for their pressure, because of their very low compressibilty, must disappear at phase co-existence.

Mathematical aspects Mathematically speaking, the Clapeyron equation is the equation for the tangent of the coexistence curve in the P-T plane. Physics-wise, it tells us the change in pressure ΔP accompanied by a change in temperature ΔT. Clearly, the required condition is

$$\left\{\left(\frac{\partial g_1}{\partial T}\right)_P - \left(\frac{\partial g_2}{\partial T}\right)_P\right\} dT + \left\{\left(\frac{\partial g_1}{\partial P}\right)_T - \left(\frac{\partial g_2}{\partial P}\right)_T\right\} dP = 0 \tag{11.6}$$

On using eqn.(11.3), we get the final (almost) form of the desired equation:

$$\left(\frac{\partial P}{\partial T}\right)_{g_1=g_2} = \frac{s_2 - s_1}{v_2 - v_1} \tag{11.7}$$

In transitions with a latent heat per unit mass l_{21} (which could in principle be temperature-dependent), one has, $(s_2 - s_1) = T\, l_{21}(T)$. Since pressure depends *only* on temperature in the present context, the partial derivative $\left(\frac{\partial P}{\partial T}\right)$ above can be replaced by the total derivative, giving therefore

$$\frac{dP}{dT} = \frac{l_{21}(T)}{T(v_2 - v_1)} \tag{11.8}$$

This is the famous Clapeyron equation. We have added the subscript 21 to clearly indicate that l_{21} is the heat per unit mass *absorbed* by phase-1 in going to phase-2. Depending on how the phases are labelled, it can be negative also. In the ice-water example, if phase-1 is ice and phase-2 is water, ice needs to absorb the *latent heat of melting* (also called latent heat of fusion) of 334 kJ per kg. Hence l_{21} is positive. If the phases had been labelled otherwise, l_{21} would have been negative.

11.2.1 Other demonstrations

There are many demonstrations of the Clapeyron equation available. Some of them may appear much 'simpler' than the one presented here. But on closer examination, one would find that in such proofs some seemingly reasonable facts are assumed.

Also, we shall soon see that the Clapeyron equation of eqn.(11.8) breaks down at critical points of phase diagrams. Then the so called easy proofs, which are highly contextual, do not generalize that easily. We shall, however, provide a few more demonstrations that are quite general. Looking at the same issue from different perspectives is always useful.

Fermi's approach: Let us look at the proof as given by Fermi, which is obtained straightaway from the first law and the meaning of latent heat [17]. For the circumstance considered above, the total volume V of the system is $V = m_1 v_1 + m_2 v_2$. If u_1, u_2 are the internal energies per unit mass, the total internal energy U is $U = m_1 u_1 + m_2 u_2$. Since we are on the coexistence curve, pressure is a function of temperature and consequently all quantities are also functions of temperature only. The variations in U and V are given by $\delta V = \delta m(v_2(T) - v_1(T))$ and $\delta U = \delta m(u_2(T) - u_1(T))$, respectively. Then, from the first law $đQ = dU + PdV$, and the fact that the latent heat $l_{21} \cdot \delta m$ is in this case the same as $đQ$, one gets

$$l_{21} = (u_2 - u_1) + P(v_2 - v_1) \tag{11.9}$$

Since temperature is kept constant throughout these changes, $\frac{\delta u}{\delta v} \rightarrow \left(\frac{\partial U}{\partial V}\right)_T$, but that is given by one of the fundamental identities

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{11.10}$$

Putting all the relations together, indeed one arrives at the Clapeyron equation eqn.(11.8).

Huang's approach Another derivation which is almost as straightforward as the first one, is the following (Huang) [26]: Let $\Delta g(T,P) = g_2(T,P) - g_1(T,P)$. It immediately follows, on using eqn.(11.3), that

$$\frac{\Delta s}{\Delta v} = -\frac{\left(\frac{\partial \Delta g}{\partial T}\right)_P}{\left(\frac{\partial \Delta g}{\partial P}\right)_T} = -\left(\frac{\partial \Delta g}{\partial T}\right)_P \left(\frac{\partial P}{\partial \Delta g}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\Delta g} \tag{11.11}$$

Where we have made use of the results, $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z$, and,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{11.12}$$

whenever $z = z(x,y)$.

Finally, in eqn.(11.11) Δg should be set equal to zero. The reader should note, however, that even though Δg vanishes on the coexistence curve, its partial derivatives occurring in eqn.(11.11) need not vanish *necessarily*. Thus we get exactly the same as eqn.(11.7), and the Clapeyron equation follows as before.

Example 11.1: A skating myth?

One of the interesting consequences of the Clapeyron equation is that under pressure, the freezing point of a liquid is lowered. This means a substance in a solid phase, like *for example ice, can be turned into a liquid if sufficiently high pressure is applied. A popular folklore is that this is how ice skating becomes possible i.e under the weight of the skater spread over the very small area of contact between ice and skates just melts ice forming a liquid layer, facilitating skating. Is this a myth or a reality?*

Let us denote by W the gravitational force due to the weight of the skater in kilo Newtons. For example, if the mass of the skater is 75 Kg, the weight due to gravity will be 75 Kg.9.8 N/Kg = 735 N and W=0.735. Let the area of contact be A in units of 100 square mm. Most ice skates are about 200 mm in length so that if the blade has thickness of 0.5 mm, the area of contact would be 100 sq.mm and A=1. The pressure exerted on ice is then $10W/A$ MPa. Remember that the atmospheric pressure is roughly 100 KPa. Strictly speaking one should integrate the Clapeyron equation from T_i=273.15 K with P_i=1 atm to T_f and $P_f = P_i + 10W/AMPa$. But let us assume that the latent heat of fusion of 330 kJ/kg at 273 K and 1 atm does not change appreciably during the process nor does the change in specific volume of $\Delta v = 10^{-4} m^3 Kg^{-1}$. Then the Clapeyron equation gives

$$\frac{\Delta}{T} = \frac{W\,10^{-4}}{330A}\frac{\mathrm{MPa\,m}^3}{kJ} \simeq 3\cdot 10^{-4} \tag{11.13}$$

So, if we take the blade edge to be 0.5 mm and W=1 (corresponding to a mass of about 102 Kg (a rather heavy skater), the change in freezing point is $\Delta T_F \simeq 0.8K$. On the other hand, if the mass of the skater is 75 Kg but the width of the blade is 3mm so that A=6, then ΔT is only about 0.1 K. But some people have taken the mass of the skater at 70 Kg but A at the improbably low value of 0.25, corresponding to a blade width of 0.12 mm, getting a ΔT of 2 K. But even this exaggerated case would imply that no ice skating would be possible below $-2\,^\circ$C and that is certainly not true! This raises serious doubts about this popular myth, and the reasons for developing that surface water layer must lie elsewhere!

11.3 Freezing curves

As a first application of the Clapeyron equation, let us consider the so called *freezing curves* (also called *melting curves*). These are the coexistence curves for a solid-liquid coexistence. In a majority of cases, it requires heat to take the solid to a liquid. If we denote the phase-1 to be the solid, and phase-2 to be the liquid, as per our conventions, the latent heat l_{21} is *positive*. We saw earlier that $l_{21} = s_2 - s_1$. Hence in all these cases, the specific entropy of the liquid is *higher* than that of the solid. This means, from our discussions of entropy, that the liquid phase is generally more *disordered* than the solid phase. So far, whatever has been said holds for water too.

Now, in most cases, solids are *denser* than the liquids at the freezing or melting points. Therefore, in all such cases, $v_2 > v_1$ or $v_2 - v_1$ is also *positive*. The Clapeyron equation immediately tells us that in these so called normal cases, $\frac{dP}{dT}$ is positive. On referring to the phase diagrams of chapter 14, one sees this for the solid freezing curve of fig. 1, for the diamond-liquid carbon case, for Helium-3 past what may be called the *Pomeranchuk point*, and for Helium-4 also (at very low temperatures the curve is practically flat as demanded by Nernst theorem, to be discussed in a later chapter).

11.3.1 Anomalous freezing curves

An examination of even the small number of phase diagrams shown in chapter 14 tells us that not all freezing curves have positive slope in the P-T plane. A prime case is that of water itself, whose freezing curve has a *negative* slope, although very small in magnitude. The latent heat in going from solid to liquid is positive in this case. But what is anomalous about water is the behaviour of its density below 4 °C; the density *decreases* with temperature. More specifically, at the freezing point the specific volume of ice, the solid phase, is *larger* than that of the liquid phase. Therefore in this case while l_{21} is positive, $v_2 - v_1$ is *negative*. It immediately follows from the Clapeyron equation that the slope of the freezing curve for the ice-water system is negative. the consequences of such a negative slope for the freezing curve of water have already been mentioned before.

Turning to the phase diagram of Helium-3, we once again see that the freezing curve has a negative slope for temperatures below the point at which the coexistence curve has a minimum. We called this the *Pomeranchuk point* as that part of the curve was first proposed by Pomeranchuk, on theoretical grounds.

But for the Helium-3 system, densities behave normally, i.e the solid phase is denser than the liquid phase. So, $v_2 - v_1$ is positive. The Clapeyron equation tells us that the coexistence curve can have a negative slope only if $s_2 < s_1$, but that would imply that the latent heat l_{21} is *negative* in this case. In other words, the solid has to give up heat to become a liquid! This also means that the solid is *more ordered* than the liquid in this case. In thermodynamics this is all that can be said. But a statistical mechanics treatment of this problem explains, as originally shown by Pomeranchuk, this unexpected behaviour. The key to this behaviour is that Helium-3 is *Fermionic*.

A very important consequence of this anomalous freezing curve for Helium-3 is that, upon applying pressure to a liquid it freezes to a solid. But this process now is *endothermic*, i.e heat must be absorbed from the surroundings, leading to a cooling effect. This is the principle behind the Pomeranchuk *compressional cooling* technique. This will turn out to be a very important tool in the march towards absolute zero, to be discussed at length later on.

11.3.2 Boiling and sublimation curves

The Clapeyron equation can be applied to liquid-vapor and solid-vapor coexistences also (in fact it is applicable to a variety of phase coexistences, except for the so called higher order phase transitions, discussed later in the chapter). Again, comparison with all the phase diagrams of chapter 10 reveal that all these coexistence curves have positive slopes. In all these cases, the latent heats (with the convention that we have adopted) are all positive, accompanied at the same time by increases in specific volumes. Thus both the denominators and numerators of the Clapeyron equation are positive, leading to a positive $\frac{dP}{dT}$.

11.3.3 Slope near absolute zero

As will be discussed at length later on , the entropy near absolute zero either vanishes or can be taken to be the same for all systems. Hence as we approach absolute zero, the numerator of the Clapeyron equation vanishes. Generically, there is nothing requiring the denominator to also vanish in this limit. Hence the generic behaviour of coexistence curves near absolute zero is that their slopes must be vanishingly small. This is clearly seen for the solid-superfluid-B coexistence curve for Helium-3, and for both the solid-liquid Helium-II and liquid Helium-II and vapor coexistence curves for Helium-4.

11.4 The Clausius-Clapeyron approximation

Now we derive what is called the *Clausius-Clapeyron approximation* which is a restricted form of the Clapeyron equation, applicable to gases at low temperatures (but still high enough for the gasesous phase to exist), and low pressures. We make two simplifying assumptions, namely, that the specific volume of vapor is much much larger than the specific volume of the liquid , and that the vapor obeys ideal gas law. The consequence of the first approximation is that the specific volume of liquid can be neglected in the Clapeyron equation. Adopting the convention that phase-1 is the liquid and phase-2 is the gas, l_{21}, the latent heat of vaporization is *positive*. As the context is unambiguous, we shall call this $\lambda(T)$ and simply denote the vapor specific volume by v. This yields

$$\frac{dP}{dT} = \frac{\lambda(T)}{T\,v} \tag{11.14}$$

The ideal gas law for the vapour is $Pv = \frac{R}{M}T$; we can rewrite the above equation as

$$\frac{dP}{dT} = \frac{\lambda(T)M}{RT^2}P \tag{11.15}$$

Integrating this between temperatures T_0 and T_1 where the pressures are P_0, P_1 respectively, one gets

$$P_1 = P_0\, e^{\frac{M}{R}\int_{T_0}^{T_1}\frac{\lambda(T)}{T^2}dT} \tag{11.16}$$

If T_0 is taken to be the normal boiling point of the liquid, then by definition P_0 is the atmospheric pressure. We can then use the above equation to give the temperature dependence of the vapor pressure. But to do so requires the knowledge of the temperature-dependence of the latent heat $\lambda(T)$. As a further approximation, we can take $\lambda(T)$ to be a constant equal in value to the latent heat of vaporization λ_0 at the boiling point. In that case, the temperature dependence of the vapor pressure is given by

$$P(T) = P_0\, e^{-\frac{M\lambda_0}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \tag{11.17}$$

This equation works reasonably well in the vicinity of the boiling point.

Example 11.2: Raising boiling points by pressure

Using the Clausius-Clapeyron approximation, calculate the increase in boiling point of water in a domestic pressure cooker if it can build up a pressure of 2 atm., given that the latent heat of vaporization is 2257 kJ/kg at $100\,^\circ\mathrm{C}$ *and 1 atm. of pressure. What would be the boiling point if the pressure could be built up to 5 atm.(rather high!)?*

The Clausius-Clapeyron approximation yields

$$\frac{dP(T)}{dT} = \frac{PL}{RT^2} \tag{11.18}$$

Integrating this between (T_i, P_i) and (T_f, P_f) gives

$$\ln\frac{P_f}{P_i} = -\frac{L}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right) = \frac{2257\cdot 18}{8.314}\left(\frac{1}{T_f} - \frac{1}{T_i}\right) \tag{11.19}$$

It is easy to calculate from this that when the pressure ratio is 2, $T_f = 394K$, and when the pressure ratio is 5, $T_f = 425K$, when T_i is taken to be 373.15 K

11.4.1 Dew, frost and relative humidity: An application

We now discuss a classic application of the Clausius-Clapeyron approximation to the phenomena of *Dew* and *Frost*. This is the phenomemon which manifests, for example, as beautiful water droplets condensing on various surfaces on a cold morning. The vapor pressure discussed in the context of phase equilibrium between liquid and vapor should be more appropriately called the *saturated vapor pressure*. It is so, as under the given pressure and temperature, the liquid keeps on evaporating till the pressure of the vapor equals the external pressure. If there is air over the liquid surface, it is the sum of the vapor pressure and the partial pressure of air that equals the external pressure. We can now consider the gas to be air and water vapor in equilibrium with water. This saturated vapor pressure is then a function of temperature only. The gas constant in the CC-approximation has to be that of the water vapor and we can denote it by R_v.

In contrast to this saturated vapor pressure, there is also the notion of an *unsaturated* vapor pressure. To appreciate this, consider a room at pressure P and temperature T that is filled with *dry* air. Into this dry air, consider introducing a small mass of water vapor. Compared to the amount of water that would have been contained in this body of air had it been filled with saturated vapor pressure, this amount will be much smaller and consequently unsaturated vapor pressure will also be much smaller than the saturated vapor pressure at P, T.

It is clear that if this parcel of almost dry air were to be cooled at pressure P to lower temperatures, the vapor pressure will get closer to the saturated vapor pressure. The temperature at which the original unsaturated vapor pressure exactly *equals* the saturated vapor pressure at the new temperature is called the *Dew point temperature* T_{dew}. Clearly, if the temperature is lowered any further, the air can not hold the original amount of water, and water vapor will begin to condense into water, which is the phenomenon of *dew*. If such conditions happen at some height from the ground, the phenomenon of *fog* takes place. If instead of liquid phase, one substitutes the solid ice phase, the resulting phenomenon is that of *frost.* The physics of all these phenomena is essentially governed by the CC-approximation.

Going back to the coexistence of liquid and vapor at some pressure $P(T)$ corresponding to a temperature T on the coexistence curve, any lowering of the temperature will necessarily result in some of the vapor condensing into liquid. In that sense, every temperature on the coexistence curve is a Dew point! This is so because the starting point is itself a condition of saturation. Thus, it is to be appreciated that Dew point is a temperature that is dictated by the conditions of *unsaturatedness* rather than by any characterstic of the liquid-vapor coexistence. A related concept is that of *relative humidity* which is defined as the fraction of the saturated vapor pressure that equals the given unsaturated vapor pressure. Clearly, given the relative humidity at some temperature, the dew point can be calculated, and vice versa. This is possible if there is a formula which gives the saturated vapor pressure as a function of temperature.

The CC-approximation gives an approximate way of doing so. Clearly, this approximation breaks down when the approximations used in deriving the CC-approximation break down. For example, close to the critical temperature the approximation of neglecting the liquid specific volume compared to the specific volume of the vapor is definitely a very poor approximation. Also, close to the critical point the pressure and temperature are both high so the ideal gas approximation breaks down too. In fact it will be seen later that at the critical point C_P blows up in complete contrast to the behaviour of ideal gases.

In metereological literature, the saturated vapor pressure is denoted by $e_S(T)$, and the unsaturated vapor pressure by $e(T)$. The gas constant R_v for the water vapor is given by $R_v = \frac{R}{M_v}$, where R is the *universal gas constant* with the value of 8.314 Joule/Kg/K and M_v the molecular weight of water which can be taken to be 18.01. Thus the numerical value of R_v is 461.5 J/Kg/K. From the previous discussion it is clear that if e is the *unsaturated* vapor pressure at P,T, the dew point at the same pressure is given by

$$e_S(T_{dew}) = e(T) \tag{11.20}$$

It should be emphasized that the formation of dew need not happen at the same pressure. What is needed is that at the new pressure and temperature, the saturated vapor pressure must equal the original unsaturated vapor pressure. The calculations are a bit more involved, but there is no real complication. All that is needed is to integrate the CC-approximation between T and T_{dew}. We can simply take over eqn.(11.17) with the identifications $M = M_v, T_0 = T, P_0 = e_S(T), T_1 = T_{dew}, P_1 = e_S(T_{dew}) = e(T)$ to get

$$\ln\frac{e(T)}{e_S(T)} = \ln r = \frac{1}{R_v}\int_T^{T_{dew}} \frac{\lambda_v(t)}{t^2}\,dt \tag{11.21}$$

where r is the *relative humidity* at temperature T. An almost identical equation obtains for the frost temperature, T_{fr} on replacing the latent heat for vaporization λ_v by the latent heat of freezing λ_f:

$$\ln\frac{e(T)}{e_S(T)} = \ln r = \frac{1}{R_v}\int_T^{T_{fr}} \frac{\lambda_f(t)}{t^2}\,dt \tag{11.22}$$

To proceed further one must either have a theoretical model for the latent heats $\lambda(t)$, or have empirical data for them. In metereology one also uses empirical equations for the saturation vapor pressure as, for example, the Magnus-Teten equation. But even without going that far, one can make some interesting observations: the positivity of the latent heats guarantees that for a given T, r, one gets a unique value for the dew and frost temperatures.

To get a feel for what is going on, one can solve these equations under the assumption that the latent heats are constant; this is not a very bad approximation in the vicinity of the boiling and melting points. On using the familiar values $\lambda_v = 2250\,kJ/Kg$ at 373 K, and, $\lambda_f = 335kJ/Kg$ at 273 K, one finds

$$T_{dew}^{-1} = T^{-1} - 2.05\cdot 10^{-4}\ln r \qquad T_{fr}^{-1} = T^{-1} - 1.38\cdot 10^{-3}\ln r \tag{11.23}$$

Thus, given the relative humidity r at some temperature T, the dew and frost temperatures can be calculated. It is interesting to note that as $r \to 0$, $T_{dew}, T_{fr} \to 0$, independent of T. Empirically it is found that approximating the latent heats by constants is not so good. The Magnus-Teten empirical equation

$$e_s(T) = 6.1094\exp\left(\frac{17.625T}{T+243.04}\right) \tag{11.24}$$

is seen to perform better. Here the vapor pressure is measured in hPa and temperature in Celsius. This can be seen, on substituting in the CC-approximation, to be equivalent to the *temperature dependent* latent heat of vaporization (now T is temperature in Kelvin):

$$l_v(T) \approx \frac{T^2}{(T-30)^2} \tag{11.25}$$

where T is in degree Kelvin. Near the boiling point of water, this amounts to a latent heat that *linearly decreases* with temperature. Such a trend has also been verified by direct measurements. But for temperatures higher than the boiling point, this predicts an incorrect behaviour. For more accurate calculations, the metereological standard is the so called *IAPWS Formulation 1995* (International Association for the Properties of Water and Steam) (see Wagner and Pruss[77])

$$\begin{aligned} Log\frac{e_S}{22.064\cdot 10^6} &= \frac{647.096}{T}\cdot(-7.85951783t + 1.84408259t^{1.5} - 11.7866497t^3 \\ &+ 22.6807411t^{3.5} - 15.9618719t^4 + 1.80122502t^{7.5}) \end{aligned} \tag{11.26}$$

with T in [K] and ew in [Pa] and $t = 1 - T/647.096$. This equation is expected to be valid all the way to the critical temperature.

11.5 Temperature dependence of latent heats

That latent heats can be temperature dependent should not come as a surprise. In fact that is the generic thermodynamic behaviour. On noting that $l = T(s_2 - s_1)$, and $\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_P}{T}$, one finds

$$\left(\frac{\partial l}{\partial T}\right)_P = \frac{l}{T} + c_{P2} - c_{P1} \tag{11.27}$$

Likewise,

$$\left(\frac{\partial l}{\partial P}\right)_T = T\left(\frac{\partial (s_2 - s_1)}{\partial P}\right)_T \tag{11.28}$$

We now use one of the Maxwell relations, $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P = -v\beta$, where β stands for the *volume expansion coefficient*. Therefore,

$$\left(\frac{\partial l}{\partial P}\right)_T = T(v_1\beta_1 - v_2\beta_2) \tag{11.29}$$

The *total* derivative of l wrt to T is therefore given by

$$\frac{dl}{dT} = \left(\frac{\partial l}{\partial T}\right)_P + \left(\frac{\partial l}{\partial P}\right)_T \frac{dP}{dT} \tag{11.30}$$

Using the earlier expressions and the Clapeyron equation we arrive at the final result for the equation governing the temperature dependence of latent heats:

$$\frac{dl}{dT} = \frac{l}{T} + c_P^{(2)} - c_P^{(1)} + l\,\frac{v_1\beta_1 - v_2\beta_2}{v_2 - v_1} \tag{11.31}$$

Even at this level of generality, the following observations can be made:

- If phase-1 is either liquid or solid, and phase-2 is gas, then $v_1 << v_2$, except perhaps in close vicinity of the critical temperature.
- The thermal expansion coefficients β are the largest for gases, followed by liquids and solids.
- The specific heats at *constant pressure* are typically larger for liquids and solids when compared to the gasesous state at the same temperature and pressure.

If we make use of these well founded approximations, we can recast eqn.(11.31) as

$$\frac{dl}{dT} \approx \frac{l}{T} + c_P^{(2)} - c_P^{(1)} - l\beta_2 \tag{11.32}$$

Additionally, if we are in a range of temperatures and pressures where the gas phase can be described by an ideal gas law, $\beta_2 = \frac{1}{T}$, we see that the first and last terms cancel, leaving

$$\frac{dl}{dT} \approx c_P^{(2)} - c_P^{(1)} \tag{11.33}$$

The rhs, as mentioned above, is generally *negative*. Thus we see that latent heats generally decrease with temperature. It should be cautioned that from this one can not conclude that as critical temperature is approached, latent heat will vanish. Many of the approximations made here, including the ideal gas behaviour for the vapor, are no longer valid there. One has to use eqn.(11.31) or make an ab initio study of the problem. It is worth stating that near the critical point the latent heat drops precipitously.

The meaning of C_P for the gas in the above needs some clarification. By that we mean the specific heat of the *unsaturated* vapor. For a saturated vapor, as we have seen on several occasions, the pressure is determined solely by temperature, and C_P is ill-defined!

It is interesting to see how well some of these considerations work in the familiar example of water. The specific heat C_P for liquid water at 4 °C is roughly 4.2 J/K/gm which translates to a molar specific heat of 75.6 J/K. While there is some variation in this quantity with temperature, it is not very dramatic. On the other hand, the molar C_P of steam around 100 °C is around 36 J/K, so indeed the gas C_P is less than that of the liquid. If steam is approximated as an ideal diatomic gas, this value would have been 28 J/K. On the other hand, around 645.2 K, which is very close to the critical temperature, the molar C_P of water is close to 1800 J/K, while that of steam is close to 3800 J/K and the roles of gas vs liquid get completely reversed!

11.5.1 Fermi's treatment

In general, modelling the liquid state is very difficult. For the solid state, however, reasonably good models like the *Debye model* exist which have been succesful in explaining many observed features of solids. We shall not go into the details of such a model. Instead, we shall simply use the expression for the entropy of solids as given by the Debye model. We shall follow Fermi in describing a solid-vapor phase coexistence along these lines. This particular approach, which we have simply termed the *Fermi model of sublimation* will be used several times in this book, each time to illustrate a different essential concept. Here we use it to discuss the temperature dependence of the latent heat of sublimation.

The entropy of a mole of solid, as given by the Debye model is,

$$S_{solid} = 3R\ln T + a_D \tag{11.34}$$

where a_D is a constant. Though it is explicitly known in the Debye model, it suffices here to treat it as unknown. Following Fermi, we shall treat the vapor as an *ideal monatomic gas*. Consequently, its entropy in the T,P representation is given by

$$S_{gas} = \frac{5R}{2}\ln T - R\ln P + a \tag{11.35}$$

where a is yet another entropy constant whose precise value is not of interest here. The molar latent heat of sublimation is therefore given by

$$\Lambda(T) = T\,(S_{gas} - S_{solid}) = T\,(-\frac{R}{2}\ln T - R\ln P + b) \tag{11.36}$$

We first record the resulting vapor pressure as a function of temperature:

$$P(T) = c\frac{1}{\sqrt{T}}e^{-\frac{\Lambda}{RT}} \tag{11.37}$$

This differs from the solution, eqn.(11.17), of the CC-approximation obtained under the assumption of a constant latent heat. The difference is in the additional factor of $\frac{1}{\sqrt{T}}$. Fermi ascribes this to the fact that in his calculations the temperature dependence of the latent heat has been taken into account. We go a step further and display the exact temperature dependence of $\Lambda(T)$ that is implicit in his model.

To do so we compute $\frac{dP}{dT}$ in his model and compare it to the CC-approximation:

$$\begin{aligned}
\frac{dP}{dT} &= \frac{c}{\sqrt{T}}e^{-\frac{\Lambda}{RT}}\frac{\Lambda}{RT^2} - \frac{1}{2}\frac{c}{T^{3/2}}e^{-\frac{\Lambda}{RT}} - \frac{c}{\sqrt{T}}e^{-\frac{\Lambda}{RT}}\frac{1}{RT}\frac{d\Lambda}{dT} \\
&= \frac{\Lambda P}{RT^2} - \frac{P}{RT}\frac{d\Lambda}{dT} - \frac{P}{2T} \\
&= \frac{\Lambda}{TV_{gas}} = \frac{\Lambda P}{RT^2}
\end{aligned} \tag{11.38}$$

where in the last line we used the Clapeyron equation and ideal gas law (CC-approximation). Hence, in the Fermi model,

$$\frac{d\Lambda}{dT} = -\frac{R}{2} \qquad \rightarrow \Lambda(T) = \Lambda_0 - \frac{RT}{2} \tag{11.39}$$

This too shows a latent heat decreasing linearly with temperature. But it does so everywhere, and predicts a vanishing of latent heat at $\bar{T} = \frac{2\Lambda(273)}{R} + 273$. This is much much higher than the true critical temperature for water. This means that in real life, latent heat falls more rapidly.

We end this discussion by comparing eqn.(11.39) with eqn.(11.33). In the Fermi model, $\beta_{solid} = 0$ (this has to do with the fact that the Debye model neglects anharmonicities). This is consistent with the general trend we discussed that thermal expansions of solids can effectively be neglected. Further, in this model, $C_P^{solid} = 3R$ while $C_P^{gas} = \frac{5R}{2}$. This too agrees with the anticipation that C_P for solids is higher than that for gases. With these values eqn.(11.39) and eqn.(11.33) are in agreement with each other.

11.6 Boiling points of dilute solutions

In chapter 9 on the thermodynamics of dilute solutions, we had shown that upon dissolving N_1 moles of a solute in N_0 moles of a solvent, the lowering of the vapor pressure when the solution is dilute, i.e $N_1 << N_0$, was given by

$$\Delta P = \frac{RT}{\Delta V}\frac{N_1}{N_0} \tag{11.40}$$

As the signs of various effects have been treated very carefully in that chapter, we shall merely deal with their magnitudes. We can derive the magnitude of the elevation of boiling points and depression of freezing points by combining this with the

Clapeyron equation. We will show how it works for the boiling points. Treatment of freezing points is completely parallel.

$$\Delta T = \Delta PT\frac{\Delta V}{\Lambda} = \frac{RT}{\Delta V}\frac{N_1}{N_0}T\frac{\Delta V}{\Lambda} = \frac{RT^2}{\Lambda}\frac{N_1}{N_0} \tag{11.41}$$

This is precisely the expression for the elevation of the boiling point of dilute solutions obtained there.

11.7 Breakdown of the Clapeyron equation

Conditions may certainly arise when both the numerator and the denominator of the Clapeyron equation vanish at the same time. When the numerator vanishes, the latent heat vanishes. There are a countless number of cases where this happens, and we shall discuss them shortly. When the denominator vanishes, there is no change in the specific volumes between the phases. Therefore, in such exceptional cases, the standard form of the Clapeyron equation becomes mathematically meaningless. Before discussing the possible remedies in such cases, let us look at some situations where only the denominator or the numerator vanishes.

When the denominator vanishes, the slope of the coexistence curve becomes *infinite*. The tangent to the coexistence curve is then parallel to the P-axis. In the ice-water case, the entire coexistence curve is almost parallel to the P-axis. In this case, the change in specific volumes remains small throughout. The graphite-liquid coexistence curve in the phase diagram of carbon appears to be such that between the two triple points, the slope of the coexistence line takes both normal and anomalous values. In between, it seems to pass through a point where the slope is infinite, pointing to a vanishing of the denominator of the Clapeyron equation.

When only the numerator vanishes but not the denominator, the tangent becomes parallel to the T-axis. This is what happens at the Pomeranchuk point on the phase diagram of Helium-3. This represents a phase transition where the latent heat vanishes. In fact the latent heat vanishes at all the so called *Critical points*. But at the critical points, the denominators also vanish typically. From that point, the Pomeranchuk point may not be considered a critical point. We will postpone a discussion of this subtle point to a later stage.

Coming back to the situations where the Clapeyron equation breaks down, there are several ways to proceed. One is to expand the Gibbs potential to higher orders in dp, dT, and getting an equation for $\frac{dP}{dT}$ on noting that P is a function of T alone. This typically leads to second and higher order algebraic equations for $\frac{dP}{dT}$. Instead, we shall illustrate an alternative proposed by *Ehrenfest*, and also its possible limitations.

The starting point of Ehrenfest's treatment is that when both the numerator and denominator of the Clapeyron equation vanish simultaneously, one has $s_1(T,P) = s_2(T,P)$; $v_1(T,P) = v_2(T,P)$. These are of the same form as eqn.(11.5), and the same type of analysis applied to it before can now be applied to the pair. The generalization of the Clapeyron equation will now consist in finding the equation for the *common* *tangent* to the two curves $s_1 - s_2 = 0$ and $v_1 - v_2 = 0$. Generically two curves may not have a common tangent at the point of their intersection at all. Thus, critical points are very special indeed.

It easily follows that

$$\frac{dP}{dT} = -\frac{\left(\frac{\partial(s_2-s_1)}{\partial T}\right)_P}{\left(\frac{\partial(s_2-s_1)}{\partial P}\right)_T} = -\frac{\left(\frac{\partial(v_2-v_1)}{\partial T}\right)_P}{\left(\frac{\partial(v_2-v_1)}{\partial P}\right)_T} \tag{11.42}$$

We now use the following relations:

- The definition of the specific heat per unit mass at constant pressure: $\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_P}{T}$,
- The Maxwell relation $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$, and finally,
- The definition of coefficient of volume expansion: $\left(\frac{\partial v}{\partial T}\right)_P = \beta$
- The definition of *isothermal compressibility*: $\left(\frac{\partial v}{\partial P}\right)_T = \kappa$

We can then recast eqn.(11.42) as

$$\frac{dP}{dT} = \frac{1}{vT}\frac{c_{P2} - c_{P1}}{\beta_2 - \beta_1} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1} \tag{11.43}$$

A consistency condition is

$$vT(\beta_2 - \beta_1)^2 = (c_{P2} - c_{P1})(\kappa_2 - \kappa_1) \tag{11.44}$$

In this section we have discussed how the standard Clapeyron equation can fail, and have shown that the so called *Ehrenfest Second Order* phase transitions can be handled despite this breakdown. It is clear from the various restrictions encountered that this treatment will not be generally applicable. The superconducting phase transition is a case to which these considerations can be applied.

The so called λ*-transitions* in Helium-4 are examples where the discontinuity of c_P at the transition is not*finite*, and eqn.(11.43) can not be applied to it. Nevertheless, an examination of the phase diagram of Helium-4 reveals that the slope of the co-existence line is indeed finite though both the numerator and the denominator of the standard form of the Clapeyron equation vanish, hinting at some treatment similar to that of Ehrenfest. In fact, the reader may see a sort of resemblance to the *L'Hospital rule* from calculus. We shall elaborate this point later.

11.8 Magnetic Clapeyron equation

Now we discuss some simple application of these ideas to phase equilibrium between magnetic systems. That the Gibbs potential per unit mass of the various phases must all be equal at the phase coexistence point was so general that hardly any details about the nature of the systems went into that. In particular, details like whether a system is magnetic or not also did not enter those considerations. Of course, for magnetic systems, one must include B_e in addition to (P,T) as the independent variables. As explained in chapter 10, it is the *magnetic Gibbs potential* $G_{\mathscr{M}}$ that has to be used for determining the equilibrium conditions, rather than the usual Gibbs potential G. More precisely, it is the magnetic Gibbs potential per unit mass $g_{\mathscr{M}}$ that needs to be used. As explained in chapter 10, the contribution of the magnetic field energy density $\frac{B_e^2}{2\mu_0}$ need not be explicitly included in the internal energy. Just so that there is no confusion about this, we shall, following Pippard, use u' instead of u for the internal energy per unit mass. The appropriate magnetic Gibbs potential per unit mass will likewise be denoted by $g'_{\mathscr{M}}$.

Therefore

$$du' = Tds - Pdv + B_e dm \tag{11.45}$$

Likewise, the magnetic Gibbs potential per unit mass and its variation are given by

$$g'_{\mathscr{M}} = u' - Ts + Pv - B_e m \qquad dg'_{\mathscr{M}} = -sdT + vdP - mdB_e \tag{11.46}$$

These immediately lead to the relations

$$\left(\frac{\partial g'_{\mathscr{M}}}{\partial T}\right)_{P,B_e} = -s \qquad \left(\frac{\partial g'_{\mathscr{M}}}{\partial P}\right)_{B_e,T} = v \qquad \left(\frac{\partial g'_{\mathscr{M}}}{\partial B_e}\right)_{T,P} = -m \tag{11.47}$$

Unlike the non-magnetic situation, not all the partial derivatives are of definite sign; the last one can be both positive or negative. It can vanish too.

Now we discuss phase equilibrium between two phases of a magnetic system. At this stage we keep the discussion very general. In the next subsection we shall focus specifically on superconducting phase transitions. As before, the condition for the coexistence of two phases, labelled 1 and 2, is that $g'_{\mathscr{M},1}(T,P,B_e) = g'_{\mathscr{M},2}(T,P,B_e)$. This defines a *two dimensional* surface of coexistence unlike the phase coexistence curve that we have treated so far. Therefore, we can in principle define *three* different types of tangents; one lying in (T,P)-plane, one in (P,B_e)-plane and finally, one in the (B_e,T)-plane, so the single Clapeyron equation for a phase coexistence curve now becomes three Clapeyron-like equations. Other than this additional detail, our earlier methods for obtaining the Clapeyron equation go through. This time we will illustrate with only one way of getting the Clapeyron equation, the one based directly on the Gibbs potential. The reader is however urged to try and derive these results for the magnetic systems by as many different methods as possible.

The differential form of the phase coexistence condition is

$$-s_1dT + v_1dP - m_1dB_e = -s_2dT + v_2dP - m_2dB_e \tag{11.48}$$

It immediately follows that the three equations, the magnetic analog of the Clapeyron equation, are given by

$$\left(\frac{\partial B_e}{\partial T}\right)_P = -\frac{s_2 - s_1}{m_2 - m_1} \quad \left(\frac{\partial P}{\partial T}\right)_{B_e} = \frac{s_2 - s_1}{v_2 - v_1} \quad \left(\frac{\partial B_e}{\partial P}\right)_T = \frac{v_2 - v_1}{m_2 - m_1} \tag{11.49}$$

It is easy to explicitly evaluate the triple product of partial derivatives:

$$\left(\frac{\partial B_e}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{B_e} \left(\frac{\partial T}{\partial B_e}\right)_P = \left(\frac{\partial B_e}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{B_e} \left(\frac{\partial B_e}{\partial T}\right)_P^{-1} = -1 \qquad (11.50)$$

which is the triple product rule for partial derivatives that we have heavily made use of. This demonstration should help demystify the triple product rule, i.e the product being -1 instead of a naive expectation of 1.

The second of the equations in eqn.(11.49) is indeed of the same form as the Clapeyron equation encountered in the mechanical case; however, there is an important difference. While the earlier one was a total derivative, the magnetic analog is a partial derivative. This is simply because the third independent variable B_e has to be kept constant while the variation of P corresponding to a variation in T is computed.

11.8.1 Superconducting transitions

We have already described the phenomenon of superconducting phase transitions in chapter 10. We shall apply the magnetic analog of the Clapeyron equation to explain and understand a number of its features. We shall take B_e to be the critical magnetic field $\mu_0 H_c$. As described earlier, in the superconducting state (we shall restrict attention to the so called Type-I superconductor, a terminology that has also been introduced in the same chapter), the magnetic field vanishes totally, i.e $B = 0$ for all B_e below a certain critical strength $\mu_0 H_c$. This is what is usually referred to as a state of *perfect diamagnetism*, as the induced magnetization (or currents) completely cancels the external field. In particular, this means that in the superconducting state $\chi_m = -1$, which is several orders of magnitude larger than the susceptibility in the non-superconducting, or normal, state.

As also explained in chapter 14, when the external field exceeds the critical value, superconductivity is destroyed and the substance returns to its normal state. Instead of labelling the states as 1 and 2, which is not very informative, we shall label them by S for the superconducting state, and by N for the normal state. Then, s_N, v_N, m_N refer respectively to specific entropy, specific volume and specific magnetization for the normal state, and likewise, s_S, v_S, m_S for the superconducting state. At this point, it is clear why defining susceptibility through $M = \chi_m B$ would be inappropriate, as that would have either implied $m_S = 0$ or $\chi_m^S = \infty$. It is also clear that for the normal state whose susceptibilities are very small, it would not have mattered that much as to which of the two ways was used to define the susceptibility, i.e $M = \chi_m H$ or $M = \frac{\chi_m}{\mu_0} B$.

In what follows we shall adapt the very lucid analysis of this situation as given by Pippard. Let us first consider the equation

$$\left(\frac{\partial B_e}{\partial T}\right)_P = -\frac{s_S - s_N}{m_S - m_N} \qquad (11.51)$$

The specific magnetization for the superconducting state is simply given by $m_S = v_S M_S = -v_S \frac{B_e}{\mu_0}$ whereas $m_N = v_N \chi_m^N \frac{B_e}{\mu_0}$. The specific volumes do not change that dramatically during these transitions. Since $\chi_m^N << 1$, we can, to a very good approximation, take $m_N \approx 0$. Putting these together, eqn.(11.51) can be recast as

$$s_S - s_N = \mu_0 v_S H_c \left(\frac{\partial H_c}{\partial T}\right)_P \tag{11.52}$$

Before interpreting this equation, a subtle point, as explained by Pippard, needs to be discussed. As they stand, all the quantities (s_S, s_N, v_S, v_N) are at coexistence points, and will in general depend on H_c. But a closer inspection reveals that their field dependences are weak, and that to a good approximation they can be taken to have the values in zero field. This is an important point as otherwise comparison of many of the equations with data would become very difficult. So let us analyse this in some detail.

First consider the field dependences of the specific entropies. Recall from our discussions in chapter 10 that entropy of a magnetic system was affected by magnetic fields. But that effect was driven by the susceptibility in the normal phase. In the present analysis, effects of the susceptibility of the normal phase are being treated as very very small. It is in this sense that one can claim that the field dependence of s_N is very weak. We can make this argument more precise by considering the magnetic analog of Maxwell's relation as contained in the second of the eqn.(8.58), which for the present circumstance can be rewritten as

$$\left(\frac{\partial s}{\partial H_c}\right)_{T,P} = \mu_0 \left(\frac{\partial m}{\partial T}\right)_{P,H_c} \tag{11.53}$$

Therefore, for s_N, the field dependence can be ignored because $m_N \approx 0$. It is curious that it is this weak field dependence of s_N that underlies the *Adiabatic Demagnetization*, but in the context of superconducting phase transitions, it can just be ignored. But what about the field dependence of s_S then? The diamagnetic susceptibility here is in a sense the largest ever possible! But now, $m_S = -v_S H_c$, and the partial derivative on the rhs of the above equation is nonzero only because of a temperature dependence of v_S. In other words, the field dependence of s_S is of the same order as the *thermal expansion* effect, which is usually very small.

Likewise, to discuss the possible field dependence of v_S, v_N, we make use of the other magnetic Maxwell's relation:

$$\left(\frac{\partial v}{\partial H_c}\right)_{P,T} = -\mu_0 \left(\frac{\partial m}{\partial P}\right)_{H_c,T} \tag{11.54}$$

It again follows from the rhs of this equation that for v_N there is no field dependence as long as $m_N \approx 0$. For the superconducting phase, the only contribution comes from $-\left(\frac{\partial v_S}{\partial P}\right)_T$ which is nothing but $v_S \kappa_T$, where κ_T is the isothermal compressibility or the bulk modulus. This too is a very tiny effect. Thus both v_S, v_N are also practically field independent. The practical consequence is that we can use zero field values for these quantities wherever they make sense.

Let us return to eqn.(11.52) to understand its consequences. To get a better feel for them, let us use the phenomenologically succesful formula for the temperature dependence of H_c, the parabolic law.:

$$H_c(T,P) = H_c(0,P)\left(1-\frac{T^2}{T_c^2}\right) \tag{11.55}$$

Experimentally very little pressure dependence has been seen for the parabolic law [25]. Nevertheless, we have included a pressure dependence of a very specific type above. The reader should appreciate that sometimes it is necessary to see and appreciate how thermodynamics works. For such purposes, even a model, such as the presumed pressure dependence above, is very helpful, notwithstanding its actual observational status. Substituting this in eqn.(11.52), one gets

$$s_S - s_N = -2\mu_0 v_S(T,P)\frac{H_c(0,P)^2}{T_c^2}T\left\{1-\frac{T^2}{T_c^2}\right\} \tag{11.56}$$

We now make several remarks about this important equation. Firstly, notice that at absolute zero, the rhs vanishes. This is what Nernst theorem would require. According to it, all entropies must vanish at absolute zero. A weaker version of it requires that differences between all entropies must vanish at absolute zero, and the above relation satisfies it. The above relation is valid at all temperatures below T_c. The rhs then is *negative* except at T_c and 0 K, where it vanishes. This means that the specific entropy of the superconducting phase is *lower* than the specific entropy of the normal phase. From our earlier discussions of entropy this implies that the superconducting state is *more ordered* than the normal state.

While the vanishing of the difference in specific entropies at absolute zero is demanded by the Nernst theorem, its vanishing at the critical temperature T_c is simply a characterstic of the superconducting transition. Let us try to understand its significance. It means that this zero field transition takes place with vanishing latent heat. But we can recall two other circumstances where too the latent heat vanished. One was at the critical point of the phase diagram of water, and the other at the Pomeranchuk point in the phase diagram of He-3. There was however a fundamental difference between those two situations.

At the Pomeranchuk point, while the latent heat vanished, the difference in specific volumes remained nonzero. This allowed the Clapeyron equation to be applied without any modifications. On the other hand, at the critical point of the phase diagram of water, not only the latent heat vanished, so did the difference in specific volumes. Consequently, the Clapeyron equation could not be applied in its original form, and higher order modifications were necessary. To settle this issue, use can be made of the last of the magnetic Clapeyron equations,

$$\mu_0\left(\frac{\partial H_c}{\partial P}\right)_T = \frac{v_S - v_N}{m_S - m_N} \tag{11.57}$$

By substituting eqn.(11.55) into eqn.(11.57) and using the expressions for m_N, m_S, we get

$$v_S - v_N = -\mu_0 H_c(0,P) H_c'(0,P)\left(1-\frac{T^2}{T_c^2}\right)^2 \tag{11.58}$$

where the prime indicates differentiation wrt P. This equation tells us the very important fact that at the superconducting transition, the specific volumes of both phases are the same, i.e $v_S(T_c) = v_N(T_c)$. This is exactly what happens at the critical point of the water phase diagram too where the specific volumes of the water phase and steam phase become equal. Therefore the superconducting transition is also a *critical point*, and the standard form of the Clapeyron equation can not be applied to it.

If the parabolic law has no pressure dependence at all, the lhs of eqn.(11.57) trivially vanishes and so does the equality of the specific volumes (in fact at all temperatures). But even with the hypothetical P-dependence introduced in eqn.(11.55), the difference in specific volumes vanishes at T_c. It is to be noted that $v_S - v_N$ is vanishing as $\simeq (s_S - s_N)^2$ as T_c is approached. We will explain the significance of this shortly.

We have already encountered critical points of different kinds, as for example the critical point in water, the λ-transitions of He-4 etc. Can we say, purely from a thermodynamic analysis, whether the superconducting transition is of one of these types, or of a totally different type? The clue to that comes from an examination of the specific heats. Recall that both at the λ-transition and at the water critical point, the specific heat *diverged*. By specific heat here, we specifically mean the specific heat c_P at constant pressure and per unit mass. To avoid clumsiness in expressions, we shall drop the pressure subscript, and simply write it as c. This is given by $c = T\left(\frac{\partial s}{\partial T}\right)_P$.

It straighforwardly follows from eqn.(11.52) that

$$c_S - c_N = \mu_0 T v_S \left\{\left(\frac{\partial H_c}{\partial T}\right)_P^2 + H_c\left(\frac{\partial^2 H_c}{\partial T^2}\right)_P\right\} + \mu_0 \frac{T}{2}\left(\frac{\partial v_S}{\partial T}\right)_P\left(\frac{\partial H_c^2}{\partial T}\right)_P \tag{11.59}$$

The discontinuity in the specific heat at T_c follows on noting that $H_c(T_c) = 0$ and is given by

$$(c_S - c_N)(T_c) = \mu_0 T_c v_S(T_c)\left(\frac{\partial H_c}{\partial T}\right)_P^2 \tag{11.60}$$

It is to be noted that the lhs is *positive* even without invoking the parabolic law.

Thus the thermodynamic analysis, originally due to Gorter and Casimir [21], states that there should be a sudden jump in the specific heat at T_c. Not only that, it even predicts that c_N should be *lower* than c_S. Actually, Keesom and collaborators [30] had observed this effect experimentally in 1932 at the same laboratory in Leiden where Kamerlingh Onnes originally discovered superconductivity, called *supraconductivity* by the Leiden group. The thermodynamic analysis by Gorter and Casimir actually came a year later.

The BCS theory too, naturally predicts such a discontinuity in specific heats. In fact, thermodynamics may contradict a theory, but no theory can contradict thermodynamics. However, BCS theory goes further in predicting that the ratio $\frac{c_S - c_N}{c_N}$ has the *universal* (meaning the same value for all materials) of 1.43. In actuality, the value differs from material to material. This should not be of concern as the BCS prediction involves some material dependent assumptions. The BCS value has been shown to be in excellent agreement with the high precision experimental values obtained by Phillips for Aluminium.

The general trend is of course seen in all materials. For Aluminium the graph depicting the variation of the specific heats with temperature was shown in chapter 10. One sees that as the temperature is lowered from T_c, a temperature is reached where the two specific heats become equal, i.e $c_S = c_N$. Beyond that, c_S becomes smaller and smaller compared to c_N. Of course, both of them approach zero as absolute zero temperature is approached, in accordance with Nernst theorem.

Before we analyse the issue of applying the higher order Clapeyron equation to this transition, we wish to make some comments on the significance of the temperature at which the two specific heats become equal. Quite generally, since $c_S - c_N = T\left(\frac{\partial s_S - s_N}{\partial T}\right)_P$, it is clear that the point at which the two specific heats match, is a temperature at which the difference in specific entropies is either maximum or minmum. Since the entropy difference is zero at absolute zero as well as at T_c and it is negative everywhere else, it follows that if there is only one crossover point (experimentally that is indeed the situation), that must be a minimum. Therefore this is the point at which *maximal ordering* of the material happens. If we assume that effects of *thermal expansion* are negligible, so the last term of eqn.(11.59) can be dropped, the parabolic law of eqn.(11.55) predicts that this crossover must happen at $T^* = \frac{T_c}{\sqrt{3}}$, quite universally. Examination of data shows that this is quite accurately true.

We finally address the issue of the type of higher order Clapeyron equation that is applicable for the superconducting transition. The fact that c_P is discontinuous at the transition but the discontinuity is *finite* suggests that Ehrenfest's second (or higher) form of the Clapeyron equation may be the right one. For this we need to examine the behaviour of the difference in thermal expansion coefficients $\beta_S - \beta_N$ as well as the difference in isothermal compressibilities $\kappa_S - \kappa_N$ at the critical temperature. We shall first analyze the situation rather generally, and then use the parabolic law for a more explicit analysis. In particular, we wish to understand how the consistency condition of eqn.(11.44) is satisfied for the superconducting transitions. We shall restrict the analysis to only $T = T_c$.

As a first step, we recast eqn.(11.57) into a form that does not assume the parabolic law:

$$v_S - v_N = -\mu_0 v_S H_c \left(\frac{\partial H_c}{\partial P}\right)_T = -\frac{\mu_0}{2} v_S \left(\frac{\partial H_c^2}{\partial P}\right)_T \approx -\frac{\mu_0}{2} v \left(\frac{\partial H_c^2}{\partial P}\right)_T \tag{11.61}$$

This equation is of course valid at all (T,P) on the coexistence surface. From this we can obtain both $\beta_S - \beta_N$ and $\kappa_S - \kappa_N$. Let us consider the expansion coefficients first:

$$\beta_S - \beta_N = \frac{1}{v_S}\left(\frac{\partial v_S}{\partial T}\right)_P - \frac{1}{v_N}\left(\frac{\partial v_N}{\partial T}\right)_P \approx \frac{1}{v}\left(\frac{\partial (v_S - v_N)}{\partial T}\right)_P \tag{11.62}$$

Following Pippard, we have approximated the denominators $\frac{1}{v_S}, \frac{1}{v_N}$ by $\frac{1}{v}$ and further taken v to be a constant. The reader is advised to carefully check the appropriateness of this approximation. If this is acceptable, the following result follows for $\beta_S - \beta_N$:

$$\beta_S - \beta_N \approx -\frac{\mu_0}{2}\frac{\partial^2}{\partial P \partial T} H_c^2 \tag{11.63}$$

Likewise

$$\kappa_S - \kappa_N \approx \frac{\mu_0}{2}\left(\frac{\partial^2}{\partial P^2} H_c^2\right)_T \tag{11.64}$$

At the critical temperature, where $H_c = 0$, these relations take the simplified forms

$$c_S - c_N = \mu_0 T_c v \left(\frac{\partial H_c}{\partial T}\right)_P^2 \quad \beta_S - \beta_N = -\mu_0 \left(\frac{\partial H_c}{\partial P}\right)_T \left(\frac{\partial H_c}{\partial T}\right)_P \quad \kappa_S - \kappa_N = \mu_0 \left(\frac{\partial H_c}{\partial P}\right)_T^2 \tag{11.65}$$

It is seen that the Ehrenfest consistency condition, eqn.(11.44) is indeed satisfied. It finally follows that the slope in the fixed H_c plane is given by

$$\left(\frac{\partial T_c}{\partial P}\right)_{H_c=0} = v T_c \frac{\beta_S - \beta_N}{c_S - c_N} = \frac{\kappa_S - \kappa_N}{\beta_S - \beta_N} \tag{11.66}$$

So far we did not invoke the parabolic law of eqn.(11.55). On making use of it, one finds, at T_c,

$$c_S - c_N = 4\frac{\mu_0 v}{T_c} H_c^2(0,P) \qquad \beta_S - \beta_N = 0 \qquad \kappa_S - \kappa_N = 0 \tag{11.67}$$

Consequently

$$\left(\frac{\partial T_c}{\partial P}\right)_{H_c=0} = 0 \tag{11.68}$$

Even if one allows for a pressure dependence in parabolic law, T_c is seen to be independent of P. Though both $\beta_S - \beta_N$ and $\kappa_S - \kappa_N$ vanish as $T \to T_c$, the latter vanishes faster than the former. In fact the latter vanishes as the square of the former.

11.9 Problems

Problem 11.1 Consider a cylindrical needle of radius 1 mm with a rectangular platform attached to it at right angles. By placing weights on the platform, pressure can be applied to a block of ice, and if the pressure is sufficient, ice will become liquid, allowing the needle to go through. Derive a relationship between the temperature of the ice block and the weight that has to be placed for the needle to go through. How can this be used to measure the latent heat of fusion of ice?

Problem 11.2 The vapor pressure of mercury in two different ranges of temperature is seen to be: a) 0.0127 torr at 50 °C and 0.0253 torr at 60 °C, b) 247 torr at 300 °C and 505 torr at 310 °C. Calculate the latent heat in each of these ranges by applying the Clausius-Clapeyron approximation. Assuming a linear interpolation between the low and high temperature regions, find the formula for vapor pressure as a function of temperature. What is the boiling point at 1 atm. = 760 torr?

Problem 11.3 In a solid-liquid phase transition such as the one between water and ice, it is given that P_0, T_0 lies on the coexistence curve. The slope of the coexistence curve at this point is given to be b. If the latent heat at P_0, T_0 is l_0, calculate the latent heat at a nearby point with temperature $T_0 + \delta T$ under the assumption that the specific volumes, the coefficients of volume expansion, isothermal compressibilities, and constant pressure specific heats of both phases are known in the vicinity of these points.

Problem 11.4 In a so called second order phase transition it is observed that there is no change in specific entropy, specific volume between the two phases. Calculate the difference in c_P for the two phases in terms of the differences between the coefficients of volume expansion and isothermal compressibilities.

Problem 11.5 Determine the temperature dependence of the saturated vapor pressure above a solid under the assumption that the vapor behaves like an ideal gas, and that all specific heats are constant. Show how the difference in specific heats can be measured this way.

Problem 11.6 Determine the change in the volume of a vapor with temperature along its coexistence curve with a liquid. The vapor may be assumed to obey ideal gas law.

Problem 11.7 If one treats the atmosphere isothermally, there is a characteristic decrease of pressure with height as determined by g, the acceleration due to gravity and the mean molecular weight. If these are given to be g $= 9.81N/Kg$ and $M = 0.029Kgmol^{-1}$, calculate the boiling point of water at a height of 5 kms. The latent heat of vaporization can be taken to be 40 kJ/mol. Since the true atmosphere is not really isothermal, what is a reasonable value to be used for the temperature?

Problem 11.8 Repeat the above problem by giving up the assumption of an isothermal atmosphere, and instead basing it on the more realistic case of an adiabatic atmosphere.

Problem 11.9 If the latent heat, specific volumes of the liquid, and vapor are all known as a function of pressure, show that the equation for the coexistence curve can be used to find out the absolute temperature along the coexistence curve in terms of pressure. This can be thought of as a thermometer.

Problem 11.10 Find the equilibrium vapor pressure for a liquid-vapor coexistence when the latent heat of vaporization is known to be well approximated by $L(T) = L_0 - aT - bT^2$ in a certain range of temperatures. The Clausius-Clapeyron approximations may be made here too. Compare this with the observed behaviour of the vapor pressure of liquid He_4.

Problem 11.11 The vapor pressure of a liquid is given by $\ln P(T) = a_l + b_l/T$, while the vapor pressure over the solid phase of the same substance is given by $\ln P(T) = a_s + b_s/T$. Find the a) temperature and pressure of the triple point and b) the three latent heats at the triple point, using the Clausius-Clapeyron approximation and assuming the constancy of various latent heats.

Problem 11.12 Water boils at 92 °C at the top of a hill while it boils at 100 °C at its bottom where the pressure is 100 KPa. If the atmosphere is taken to be isothermal with a characteristic temperature of 300 K, find the height of the hill given that the latent heat of vaporization and the mean molecular weight of air are 2200 kJ/kg and 28 respectively.

Problem 11.13 The specific heat per unit volume of a metal is described by $C_s = aT^3$ in the superconducting state, and by $C_n = cT + bT^3$ in the normal state. Find the transition temperature i) in zero field, ii) the critical magnetic field, and iii) the difference in internal energies of the two states at zero magnetic field.

12 The van der Waals Equation

In 1873, a little over two decades after the formulation of the first and second laws of thermodynamics, van der Waals in Leiden published a thesis entitled *The Continuity of the Gaseous and Liquid States*. He introduced the now famous *van der Waals equation* in that work. This equation has had a great impact on our understanding of phases and their equilibria, apart from being a much more succesful description of the gaseous phase than the ideal gas law. This came nearly two centuries after Boyle's law and a century after Charles's law.

This work also marked a transition from purely thermodynamic treatments to ones invoking the atomic nature of matter. Interestingly it came around the same time as Boltzmann's great works on the statistical origins of thermodynamics. Though atomism had been conjectured by the early Greeks (Democritus) and the Indian philosopher Kanada, and surmised as the basis of chemistry by Dalton, it took several decades more even after van der Waals to experimentally vindicate the atomic hypothesis. In fact, even after Boltzmann's works there was great opposition to atomic theory from such stalwarts as Ernst Mach and Wilhelm Ostwald. The issue was conclusively settled only by Einstein and Perrin's works on Brownian motion. What is remarkable about van der Waal's work is that it used atomism in a rather minimal way, yet with great effect. He introduced two essentially different modifications into the ideal gas law $PV = nRT$. For the first, he argued that atoms or molecules constituting matter have *finite size* and for this reason replaced the volume V by $V - nb$ to account for the *effective* volume available for the motion of the constituents.

The second is somewhat more elaborate, and attempts to take into effect the mutual attraction between the elementary constituents. His analysis of this is surprisingly modern in its spirit. The forces of *cohesion* were taken to be of *short range*. Taking the spatial distribution to be *uniform*, it becomes obvious that in the interrior of a volume, the cohesive forces balance each other and the net effect is as if there were no cohesive forces. But near the boundary, essentially only a hemisphere (if the walls are planes) of atoms or molecules exerts an influence on those at the boundary. Hence the net effect is a pull towards the interior which has the effect of reducing the *pressure*. The effect per constituent is obviously proportional to the number density $\frac{n}{V}$, and on the pressure with an additional factor of $\frac{n}{V}$. Therefore, van der Waals argued, the pressure P in the ideal gas law must be replaced by $P + \frac{an^2}{V^2}$. Combining the two effects, the equation proposed by van der Waals is

$$(P + \frac{an^2}{V^2})(V - nb) = nRT \tag{12.1}$$

The constants a, b are characteristic of the particular substance. It should be noted that the n factors are such as to ensure *extensivity*. Clearly, in the limit $a, b \to 0$, the ideal gas law is recovered.

In the ideal gas case every solution of the equations of state is an *equilibrium state*.

Is this so for the vdW case also? The answer turns out to be negative. The meaning of this will be explained in detail later.

While we have briefly explained the microscopic modelling that went into getting the equation, as far as thermodynamics is concerned, we can forget about that reasoning and simply take eqn.(12.1) as one of the *equations of state* characterizing the thermodynamic system. It is like specifying the *force* or equivalently the *potential* in Newtonian mechanics. Interestingly, Boltzmann is supposed to have called van der Waals the Newton of real gases!

12.1 Thermodynamic aspects

As already emphasized in chapter 6, structurally this is a single constituent system with *two* thermodynamic degrees of freedom. Consequently, one must have *two* equations of state for a complete determination of its thermodynamics. The van der Waals equation is only one of them. For the second, we need an independent equation involving T. In the case of the ideal gas, this was that the internal energy $U(T)$ is a function of temperature alone. The second equation of state could not have been specified completely independently. The restriction, in fact, came from the first law.

To see the analog in the present context, let us use the relation (see eqns.(3.7, 3.9, 3.41))

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{12.2}$$

Substitution of eqn.(12.1) in this yields

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \tag{12.3}$$

whose solution is

$$U(T,V) = f(T) - \frac{a}{V} \tag{12.4}$$

The physically interesting deviation from the ideal gas case is that now the internal energy depends both on (V,T). From the microscopic point of view, the volume dependence of energy is to be expected because of the cohesive forces, but the power of thermodynamics is that it can give that conclusion purely based on its fundamental laws and the equation of state.

Two things to notice about this result are: (i) the internal energy is independent of the parameter b, which in the microscopic picture was a measure of the size of the constituents; (ii) even in this case, the only freedom in specifying the second equation of state is a function of T alone, which was the same in the ideal gas case too. Therefore, the parameters defining a vdW system are not just (a,b) but in addition all the parameters that enter $f(T)$.

An important consequence is that the specific heat C_V of a *generic* vdW system is determined by only the temperature:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = f'(T) \tag{12.5}$$

The specific heat at constant pressure C_P can be obtained on using the general identity (see eqn.(3.52)

$$C_P - C_V = \{\left(\frac{\partial U}{\partial V}\right)_T + P\}\left(\frac{\partial V}{\partial T}\right)_P \tag{12.6}$$

It is easy to show that this reduces to

$$C_P - C_V = \frac{R}{1 - \frac{2a}{RT}\frac{(V-b)^2}{V^3}} \tag{12.7}$$

It is interesting at this stage to ask about the consistency of the vdW system with Nernst theorem. Recall that in the ideal gas case with $C_P - C_V = R$, it is impossible for both $C_P, C_V \to 0$ as absolute zero is approached. To examine this issue for the vdW case, let us rewrite the above equation as

$$C_P - C_V = \frac{R}{1 - \frac{2a}{V^3}\frac{RT}{(P+\frac{a}{V^2})^2}} \tag{12.8}$$

Now, as $T \to 0$, the volume tends to b, and the above equation says that even for the vdW system, $C_P - C_V \to R$, and therefore compatibility with Nernst theorem is not possible. At high temperatures anyway the vdW behaves like an ideal gas, and $C_P - C_V \to R$. It is only in intermediate regions that the behaviour of the difference in specific heats differs from the ideal gas case.

12.1.1 Thermodynamic potentials

As a first step towards determining all the thermodynamic potentials, let us calculate the entropy of a generic vdW system (meaning for an arbitrary choice of $f(T)$). Let us first consider the ratio $\frac{đQ}{T}$:

$$\begin{aligned}\frac{đQ}{T} = dS = \frac{1}{T}(dU + PdV) &= \frac{1}{T}\left(C_V(T)dT + \frac{a}{V^2}dV + \frac{RT}{V-b}dV - \frac{a}{V^2}dV\right) \\ &= \frac{1}{T}C_V(T)dT + \frac{RdV}{V-b} \end{aligned} \tag{12.9}$$

Clearly this ratio is a *perfect differential* by virtue of the two equations of motion only. Integrating this yields the entropy S:

$$S(T,V) = \int_0^T \frac{C_V(T)}{T}dT + R\ln(V-b) + S_0 \tag{12.10}$$

It is significant that the entropy is *independent* of the constant a! The a-dependent contributions to dU and PdV exactly cancel. There is a statistical mechanical significance to it which is beyond the scope of this book to explain.

So far the discussion has been quite general. In what follows, we restrict attention to cases when C_V is a constant.Then clearly the integral does not exist due to a logarithmic divergence near the lower limit of integration, i.e $T = 0$. But it is obvious that a constant C_V will be a good description only at high enough temperatures. Thus, with the proviso that we shall apply these considerations to only cases with reasonably high T, the entropy can be taken to be

$$S(T,V) = C_V \ln(\frac{T}{T_0}) + R \ln \frac{(V-b)}{b} \tag{12.11}$$

Here T_0 is an arbitrary temperature scale. Except for the replacement $V \to V - b$, this is the same as that of the ideal gas. The Helmholtz free energy has the form

$$F(T,V) = U - TS = C_V(T - T\ln\frac{T}{T_0}) - RT\ln\frac{(V-b)}{b} - \frac{a}{V} + U_0 \tag{12.12}$$

U_0 is a possible arbitrary constant in the internal energy, which is *independent* of the entropy constant T_0. The enthalpy and the Gibbs free energy follow likewise.

$$\begin{aligned} H(T,V) &= C_V T - \frac{2a}{V} + RT\frac{V}{V-b} + U_0 && (12.13) \\ G(T,V) &= C_V(T - T\ln\frac{T}{T_0}) - \frac{2a}{V} + RT\frac{V}{V-b} - RT\ln\frac{V-b}{b} + U_0 && (12.14) \end{aligned}$$

We end this discussion with a totally different method for calculating the Gibbs potential G. We saw from chapter 6 that the Euler's equation says that the Gibbs potential and the *chemical potential* μ are basically one and the same. In particular, the *Gibbs-Duhem* relation in the *entropy representation* was

$$d\left(\frac{\mu}{T}\right) = Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) \tag{12.15}$$

for one mole of the substance in which case $\mu = G$. Recall that we had $dG = -SdT - VdP$ which is nothing but the Gibbs-Duhem relation in the *energy representation*. But integrating that would require solving for the entropy S first. The Gibbs-Duhem relation in the entropy representation avoids that. But we need an explicit representation of the internal energy U. To illustrate how things work, let us specialize to the case when C_V is constant, so that $U(T,V) = C_V T - \frac{a}{V}$. Explicitly working out the details

$$\begin{aligned} d(\frac{\mu}{T}) &= Ud(\frac{1}{T}) + Vd(\frac{P}{T}) = -(C_V T - \frac{a}{V})\frac{dT}{T^2} + Vd(\frac{R}{V-b} - \frac{a}{TV^2}) \\ &= -C_V d(\ln T) - d(\frac{2a}{VT}) - Rd(\ln(V-b)) + bRd(V-b)^{-1} && (12.16) \end{aligned}$$

which is easily integrated to give

$$\mu = const.T - C_V T\ln\frac{T}{T_0} - RT\ln\frac{V-b}{b} + b\frac{RT}{V-b} \tag{12.17}$$

This is, not surprisingly, the same expression as for G in eqn.(12.13) if the constant in eqn.(12.17) is chosen to be $C_V + R$.

12.1.2 Various isoparametric processes

Now we consider various processes with one of the quantities, like S, P, V or T, held fixed. Let us consider *adiabatic processes* characterized by $đQ = 0$. Obviously these are also *isentropic* with $dS = 0$. Using the explicit expression for entropy obtained above, we see that these are described by the curve in the (V,T) plane

$$C_V \ln \frac{T}{T_0} + R \ln \frac{V-b}{b} = const. \quad \rightarrow T(V-b)^{\frac{R}{C_V}} = const. \tag{12.18}$$

The equation for this adiabat in the (P,V) plane is easily seen to be

$$(P + \frac{a}{V^2})(V-b)^{\frac{R+C_V}{C_V}} = const. \tag{12.19}$$

The corresponding equation for ideal gases is also called the *Poisson Equation*. Meteorologists, for whom this equation has great significance, are more familiar with this naming. It should be recalled that the adiabat for an ideal gas in the (P,V) plane had the volume exponent $\gamma = \frac{R+C_V}{C_V}$. In the vdW case, even though the corresponding exponent is still $\frac{R+C_V}{C_V}$, it is not the same as the ratio $\gamma = \frac{C_P}{C_V}$ of the specific heats except at very high and very low temperatures.

Next we consider *isochoric* or constant volume processes. Then, only the curve in the (P,T) plane is nontrivial, and is given by

$$T = B(P + A) \tag{12.20}$$

where the constants (A,B) depend on both the fixed volume as well as the vdW constants (a,b). When the fixed volume is b, the constant B must vanish.

The *isobaric* or fixed pressure (at, say, P_0) processes are described in the (V,T) plane by the curve

$$AV^3 + B(T)V^2 + CV + D = 0 \qquad A = P_0; B(T) = -(bP_0 + RT); C = a; D = -ab \tag{12.21}$$

Finally we consider *isothermal processes* characterized by fixed temperatures. The equation of an isotherm in the (P,V) plane is given by

$$(P + \frac{a}{V^2})(V-b) = const. \tag{12.22}$$

This is also a cubic equation in V like the isobar.

Example 12.1: Comparing pressures of ideal and vdW gases

Given that one mole of a gas occupies 10 liters at 300 K, find a relation between the vdW constants if the pressure of this gas, treated as a vdW gas, is bigger, equal to, or smaller than its pressure if treated as an ideal gas.

The pressure formula for a vdW gas shows that if the constant b is zero but the constant a $\neq 0$, the pressure in the vdW case is always smaller than the corresponding ideal gas case. On the other hand, if a $= 0$ but b is not, the vdW pressure is always greater than the ideal gas pressure. In the interesting cases where both the parameters are non-vanishing, it can go both ways. Let us compute the difference in the pressures

$$P_{ideal} - P_{vdW} = \frac{RT}{V} - \frac{RT}{V-\mathrm{b}} + \frac{\mathrm{a}}{V^2} = -\frac{RT\mathrm{b}}{V(V-\mathrm{b})} + \frac{\mathrm{a}}{V^2} \tag{12.23}$$

It is easy to see that the ratio $\mathrm{r} = (a(V-\mathrm{b})/RTV\mathrm{b})$ determines the required answer, i.e $P_{ideal} > P_{vdW}$ if $\mathrm{r} > 1$, the two pressures equal if $\mathrm{r} = 1$ and $P_{ideal} < P_{vdW}$ if $\mathrm{r} < 1$. The constant b for many known gases is very small compared to 10 L, so we can approximate r to just $(\mathrm{a})/(RT\mathrm{b})$. It should be appreciated that this is not the same as ignoring b in the vdW pressure formula. The ratio r has the interesting interpretaion of $(27T_c)/(8T)$. The unit we shall use for b is L, and for a is atm.L^2. The value of the gas constant R is 0.0821 atm.L/K, so that RT in this case is 24.63 atm.L. The ideal gas pressure is therefore 2.463 atm.

Let us apply our criterion to water, CO_2, and Helium. In the case of water, a=5.45 and b=0.03, giving r=7.47. We therefore expect the vdW pressure to be less than 2.463 atm. Indeed, a direct evaluation yields P_{vdW}=2.42 atm. For CO_2, a= 3.59 and b= 0.0427, giving r= 3.41, while a direct calculation of pressure gives P_{vdW}= 2.137 atm. Lastly, we consider the case of Helium for which a= 0.034 (a very small value), while b= 0.0237. One gets, for this case, r= 0.056, and one gets P_{vdW} to be 2.483, which is larger than the ideal gas pressure, and this is what $\mathrm{r} < 1$ should indeed give. In Helium, the pressure difference is almost entirely dominated by b effects while in the case of water it is the other way around.

Example 12.2: Joule and Joule-Kelvin effects for vdW gases

Explicitly show that both during the Joule expansion as well as Joule-Kelvin process for vdW gases, entropy increases. Calculate the Joule coefficient η and Joule-Thomson coefficient μ_{JT} and show that while in the former case there is always a drop in temperature, in the latter the temperature change can be of either sign.

Both processes occur under adiabatic conditions, i.e $đQ = 0$. From this one should not conclude that $dS = 0$ and hence that there is no change in entropy. Recall from section 3.4.1 of chapter 3 that integrating dS gives the entropy change only along reversible paths, and along irreversible paths the integral is actually less than the entropy difference between the initial and final states. So how can we show that both the processes are irreversible?

Consider the ideal gas case as an illustration. The final volume is greater than the initial volume but the temperature has not changed. From earlier chapters we know that under an isothermal expansion of an ideal gas, entropy increases. Therefore, the Joule expansion for ideal gases is irreversible. This has to be so quite generally as from first law $TdS = dU + PdV$, and when $dU = 0$, dS is always positive (as long as temperatures and pressures are positive). The meaning of $dS \neq 0$ in this analysis, even when analysing the Joule expansion for which $đQ = 0$, is the following: once the Joule (or for that matter, any process) takes the system from one state to another, the entropy difference between these two states can be computed by considering any reversible path between them and integrating dS along that path. This dS is of course, non-zero in general.

The Joule coefficient is given by $\eta = \left(\frac{\partial V}{\partial T}\right)_U$. It obviously vanishes for ideal gases as U is a function of T only. For the vdW case it can be calculated, for example, from the explicit result for U from eqn.(12.4):

$$\eta_{vdW} = -\frac{C_V(T)V^2}{a} \tag{12.24}$$

This is always negative, showing that during free expansion of a vdW gas, temperature always drops. In this particular case the finite drop in temperature for a finite increase in volume can be computed either by integrating this expression or directly from eqn.(12.4). Taking C_V to be constant, for example, it is easy to show

$$C_V(T_f - T_i) = -a(\frac{1}{V_i} - \frac{1}{V_f}) < 0 \tag{12.25}$$

Likewise, using $TdS = dH - VdP$, where H is the enthalpy, it follows that for the Joule-Kelvin processes for which $dH = 0$, a lowering of pressure is always accompanied by an increase of entropy, i.e the process is irreversible. The quantifier for this process is the Joule-Thomson coefficient μ_{JT}. First let us derive a general expression for this in terms of C_P and α. The following equations are to be made use of:

$$\begin{aligned} dH &= TdS + VdP \to T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP + VdP \\ &= C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP \end{aligned} \tag{12.26}$$

on using one of the Maxwell relations. Hence

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{VT}{C_P}(\alpha - \frac{1}{T}) \tag{12.27}$$

From this it clearly follows that for ideal gases, for which $\alpha = 1/T$, the Joule-Thomson coefficient vanishes. For the vdW case it follows that (when V, T are high),

$$\mu_{JT-vdW} = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right) \tag{12.28}$$

Clearly this does not have a definite sign, and in the vdW case the porous plug experiment can lead to both lowering and raising of temperatures depending on circumstances.

12.1.3 Properties of the vdW isotherms

We had earlier raised the issue of whether every solution of the vdW equations of state corresponds to an equilibrium state. We address this important issue and issues related to it by examining a family of vdW isotherms, which are displayed in fig.(12.1).

In the vdW case, there is a natural scale for volume which is b, and a natural scale for pressure, which is $\frac{a}{b^2}$. When volumes are large compared to their natural scale, and pressures are small compared to their scale, the vdW equation becomes the same as the ideal gas equation, and hence the isotherms also coincide with ideal gas isotherms at the same temperature. At very high temperatures, it can be seen from the family of isotherms that to each pressure there corresponds only one V. Thus, indeed the solution to the equation of state in these regimes corresponds to an unique equilibrium state.

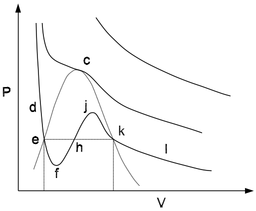

FIGURE 12.1 A family of vdW isotherms.

But at low enough temperatures, in the sense to be made precisely, the isotherms are such that to a given P, there correspond three distinct values of V. Just as there were natural scales $(b, \frac{a^2}{b})$ for volume and pressure, there is of course a natural scale $\frac{a}{Rb}$ for temperatures also. But we shall soon come across another set of scales. So, low temperatures means T is much lower than this natural scale of temperature. That three values of V correspond to a single P is just a consequence of the isotherm equation being a cubic.

In between the three points where the horizontal axis (P=const.) intersects the isotherm, there ought to be pairs of *maxima* and *minima*. In the present case there is exactly one such pair, again due to the cubic nature of the equation involved. The explicit condition for stationarity $\frac{dP}{dV} = 0$ is:

$$\frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \tag{12.29}$$

This is again a cubic equation. It is clear from the figures that the lower the temperature, the farther apart is the maximum from the minimum. This implies a temperature, to be called *Critical Temperature* T_c, where the maximum and minimum coalesce into a *point of inflexion*. At that point, denoted by P_c, V_c on the isotherm at T_c in the (P,V) plane, both $\frac{dP}{dV}$ and $\frac{d^2P}{dV^2}$ are zero. It is an elementary exercise to show at the point of inflexion, the vdW equation written as

$$P_cV^3 - (bP + RT_c)V^2 + aV - ab = 0 \tag{12.30}$$

must be a *perfect cubic*, i.e of the form $P_c(V - V_c)^3 = 0$. Compared with the previous equation, it is easily seen that

$$V_c = 3b \quad P_c = \frac{a}{27b^2} \quad RT_c = \frac{8a}{27b} \tag{12.31}$$

This is the other scale we had referred to. One immediately notices $\frac{P_cV_c}{RT_c} = \frac{3}{8}$ for *all* vdW fluids even though their individual P_c, V_c, T_c or equivalently their (a,b) may be different. This may be reminescent of the ideal gas law $PV = RT$ but the numerical factor is different. This relation could be used to test whether a substance belongs to the vdW class or not. The quantity PV/RT is often referred to as the *compressibility factor* Z.

At this moment, the critical point is emerging only as some mathematical aspect of the vdW equations. But we shall soon see that there is a very rich physics (thermodynamics) associated with this point. Because of these features, the critical point (T_c, P_c, V_c) is easily distinguished experimentally.

Example 12.3: vdW theory for water

Calculate the observed value of (P_cV_c/RT_c) for the water-steam critical point, and compare it to the prediction of the van der Waals theory. The observed critical parameters for the water-steam critical point are : $T_c = 647K$ (to a very good approximation), $P_c = 22MPa$ (again to a good approximation), and the critical density is very close to $323Kg/m^3$. Hence the critical molar volume V_c is

$$V_c = \frac{18}{323} m^3/Kg \cdot gms = 5.6 \cdot 10^{-6} m^3 \tag{12.32}$$

where we used the molecular weight of water to be 18. Hence the critical compressibility factor Z_c for vdW fluids is

$$Z_c = \frac{P_cV_c}{RT_c} = \frac{2.2 \cdot 10^7\, 5.6 \cdot 10^{-6}}{6.47 \cdot 10^2\, 8.31} N/m^2\, m^3/J = 0.22 \tag{12.33}$$

When contrasted with the value of $3/8 = 0.375$ predicted by van der Waals theory, we see that the latter is quite a bit off.

It should be noted that an experimental determination of the critical point allows one to immediately determine the vdW constants (a,b) through the inverse relations: $b = \frac{V_c}{3}, a = 3P_cV_c^2 = \frac{9}{8}RT_cV_c$. A very interesting feature emerges on scaling (P,V,T) by (P_c, V_c, T_C) and introducing $P_r = \frac{P}{P_c}, V_r = \frac{V}{V_c}, T_r = \frac{T}{T_c}$(these ratios are sometimes called *reduced* quantities). The vdW equation in terms of these scaled quantities takes the form

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r \tag{12.34}$$

What is special about this equation is that it is completely *universal*, i.e it has no, unknown constants in it, and takes the same form for all substances obeying vdW equation of state. Expressed differently, it establishes a correspondence between thermodynamic states of different substances. Therefore, for given pairs of values, say, P_r, V_r, one can associate many (P,V) values. One needs only to study thermodynamics with the variables P_r, V_r, T_r, and then the thermodynamics of all vdW substances follows. Kamerlingh Onnes and van der Waals called this *the law of corresponding states*. Henceforth, we shall only use this universal equation.

Example 12.4: vdW thermodynamics in reduced variables

Express all the basic thermodynamic relations of the vdW system in terms of reduced variables, and define in the process, expressions for reduced internal energy, reduced *entropy, reduced Gibbs potential, and reduced enthalpy. Write down the first law in reduced form.*

Let us start with the expression for the molar internal energy given by eqn.(12.4). We wish to find a reduced internal energy U_r which is dimensionless and expressed in terms of the reduced variables.

$$U = C_V T - \frac{a}{V} = \frac{8a}{27b}\left(\frac{C_V}{R}T_r - \frac{9}{8V_r}\right) = \frac{8a}{27b}U_r \rightarrow U_r = \frac{C_V}{R}T_r - \frac{9}{8V_r} \tag{12.35}$$

Clearly there is no uniqueness to U_r but it has been designed so that it resembles the form of the unreduced U as much as possible.

Next consider the entropy as given in eqn.(12.11). It is straightforward to write down the reduced molar entropy S_r:

$$S = RS_r \rightarrow S_r = \frac{C_V}{R}\ln T_r + \ln(3V_r - 1) \tag{12.36}$$

Likewise, it is easy to see that the reduced Helmholtz free energy, reduced Gibbs free energy, and the reduced enthalpy (all molar) are given by

$$F = \frac{8a}{27b}F_r \rightarrow F_r = U_r - T_r S_r \quad G = \frac{8a}{27b}G_r \rightarrow G_r = F_r + \frac{3}{8}P_r V_r \quad H_r = U_r + \frac{3}{8}P_r V_r \tag{12.37}$$

The explicit expressions for F_r and G_r are

$$\begin{aligned} F_r &= \frac{C_V}{R}(T_r - T_r \ln T_r) - T_r \ln(3V_r - 1) - \frac{9}{8V_r} \\ G_r &= \frac{C_V}{R}(T_r - T_r \ln T_r) - T_r \ln(3V_r - 1) - \frac{9}{8V_r} + \frac{3}{8}P_r V_r \end{aligned} \tag{12.38}$$

The first law in reduced form would read

$$T_r\, dS_r = dU_r + \frac{3}{8}P_r dV_r \tag{12.39}$$

If we denote by $V_r^{max}(T_r), V_r^{min}(T_r)$ the volumes at which the maximum and minimum occur for the reduced isotherm (P_r vs V_r), the universal vdW equation gives two pressures, $P_r^{max}(T_r)$ and $P_r^{min}(T_r)$, which are characterstic properties of vdW isotherms. The location of these stationary points is given by the eqn.(12.29). Denoting them collectively by $\tilde{V}_r$, the reduced pressure at the stationary points, $\tilde{P}_r$, can be calculated:

$$\tilde{P}_r = \frac{8T_r}{3\tilde{V}_r - 1} - \frac{3}{\tilde{V}_r^2} = 4T_r \frac{(3\tilde{V}_r - 2)}{(3\tilde{V}_r - 1)^2} \tag{12.40}$$

It is also instructive to calculate the second derivative $\frac{d^2P_r}{dV_r^2}$ *at the stationary points* to check whether the stationary points in question are a maximum or a minimum:

$$\frac{d^2P_r}{dV_r^2} = 72T_r \frac{1 - \tilde{V}_r}{\tilde{V}_r(3\tilde{V}_r - 1)^3} \tag{12.41}$$

The important conclusion that follows is that all maxima occur at $V_r \geq 1$ and that all minima occur at $V_r \leq 1$. This further has the very important consequence that P_r^{max} is *always positive*. On the other hand, P_r^{min} can be positive or negative depending on whether $\tilde{V}_r$ is greater than $\frac{2}{3}$ or lesser than it, while still being lesser than 1. These points will assume significance while discussing the issue of *negative pressures* in vdW systems.

For pressures above P_r^{max} as well as for pressures below P_r^{min}, the cubic equation determining the intersection of a vdW isotherm with $P_r = const.$ has only one root. This can be checked by applying the well known rules for the roots of a cubic equation. For intermediate pressures one can also check that there are three real roots.

Now we address a number of *seemingly unphysical* features of the vdW isotherms. Firstly, it is odd that at a given pressure there can be three points of intersection with an isotherm. One would expect that fixing both P and T should fix the state of the system. But at this stage, this in itself need not be considered an undesirable feature as it could well turn out that only one of these points of intersection is *stable*.

Since at the maximum and minimum, $\frac{dP}{dV} = 0$, it follows that this derivative must change signs at these points. Let us divide the volume range into three regions: region I by $b \leq V \leq V_{min}$, region II by $V_{min} \leq V \leq V_{max}$, and finally region III by $V_{max} \leq V \leq \infty$. As already remarked,in the low P high V regions, the vdW equation becomes closer and closer to the ideal gas equation for which $\left(\frac{\partial P}{\partial V}\right)_T$ is *always negative*. But this is region III, which means in region II this partial derivative must be *positive*, and in region I it must again be *negative*.

To explicitly show that the derivative is negative in region I is rather cumbersome, so the above argument is a nice short cut. Recall that the *isothermal compressibility* κ_T is defined as $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. This means that in regions I and III, this compressibility is positive which is physically sensible. But in region II, this compressibility is *negative*. This does not seem physically sensible as it implies that on increasing pressure P, the volume also increases! This is a very serious drawback of the vdW equation if one interprets it literally. The cure, which really turns a problem into a victory, is discussed next. The occurrence of *negative pressures* is another serious drawback of the vdW system. A fuller discussion of that issue is possible only after we have discussed the next section.

12.2 Existence of Phases in the vdW system

Now we address the central issues concerning the vdW equation, namely, the multivalued solutions to the equation of state, and the unphysical behaviour of the isotherms. If more than one solution to the equation of state is thermodynamically *stable*, it is tempting to interpret them as different *phases* of a single component system. Of course, it will not be evident that this interpretation will automatically fix the bad behaviour of the isotherms.

To gain some intution in the matter, let us look at a one component system existing in both liquid and gaseous phases, for example, CO_2. The phase diagram of this substance exhibits a critical point at 304 K (room temperature in many parts of the world!). In figure 12.2, isotherms are shown for both above and below the critical temperature. It is seen that well above the critical temperature, the real life isotherms do indeed resemble the vdW ones. Even the one at the critical temperature (the thick curve) looks like the vdW critical isotherm, though the curve at the critical point is much *flatter*.

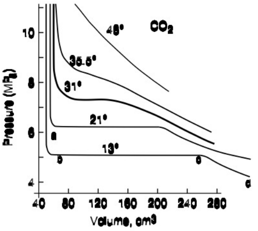

FIGURE 12.2 Carbon Dioxide Isotherms

But where the real life isotherms differ markedly are when temperatures are *below* T_c. What distinguishes the real life isotherms are regions where the isotherms are *flat* and run parallel to the V-axis(P=const.). These are clearly absent in the vdW case. Before focusing attention on this part, let us note that to both the left as well as the right of the flat part, the isotherms sort of resemble the vdW ones, though the shapes are not exactly the same. But what is of importance is that in both these regions the isothermal compressibility is normal (positive).

The region to the left is characterized by small volumes, or equivalently higher densities, and is the *liquid* part. Likewise, the region to the right is marked by considerably larger volumes for the same P and T, and this should be identified with the gaseous phase. To be more precise, this corresponds to the region of *unsaturated vapor*. What that means is that there is only vapor without any liquid accompanying it.

With these identifications, we can now understand the flat part of the real isotherms. From our detailed study of phase equilibria we know that two phases can coexist at the same P and T if their Gibbs potentials *per unit mass* are equal at those (P,T). On the other hand, the specific volume (volume per unit mass) of the gas, v_g, is much larger than that of the liquid,v_l. Now imagine x mass units of liquid coexisting at (P,T) with 1 − x mass units of gas so that the total mass is still unity. But the volume now is $xv_l + (1-x)v_g$ and for each value of x one has a *stable* phase. Thus in the/ P-V diagram, this entire collection of stable phases appears as a line with one end being pure liquid and the other end being pure gas.

Let us follow the isotherm marked abcd to get a better grasp of things. The point d is in the unsaturated vapor region with $T < T_c, P < P_c$ and $V > V_c$. Let us consider compressing this isothermally. As we increase the pressure, the system moves up along the isotherm, with decreasing volume, till it reaches c. This point is on the flat coexistence curve bc. The vapor pressure now equals the *saturated vapor pressure*.

Any further compression at this point leads to *condensation* so that a decrease in volume is accompanied not by an increase in pressure but by formation of liquid. Therefore the decrease in volume has to be accomplished by taking away *latent heat*. As this process is carried on, more and more liquid will be formed while maintaining the pressure at the saturated vapor pressure, and one eventually reaches the point b, where the system is completely in the liquid phase which is practically *incompressible*. Volume can now be lowered only by increasing pressure, and the isotherms tell us that the pressure increases steeply.

At this point we have the situation that real life isotherms have something that the vdW isotherms do not, i.e the flat parts, and they do not have something which the vdW isotherms do have, namely, the kink over part of which the compressibility is unphysical. The main task of reconciliation is to bring to vdW isotherms what is missing, and to get rid of the unphysical sectors.

There is a subtlety that we address now. If instead of taking away heat at c, let us consider compressing the system *very slowly*.Then the vapor becomes *supersaturated* meaning the liquid content in the vapor is more than what would have been in the saturated case. This clearly has to be an *unstable* state as all the possible stable points have been accounted for by the flat part. In practical terms, liquefaction requires the so called *nucleation centres*; these could be dust particles or in their absence even fluctuations in temperature, density etc. By removing such nucleation centres, it is possible to supersaturate the vapor. These supersaturated, unstable, states are the part of the vdW isotherms that would not be part of the stable states of real isotherms. The instability manifests itself by the fact that any slight disturbance of the system through minute dust particles, fluctuations etc. would result in condensation to the stable states. In principle, by a very very careful method more and more such unstable states may be produced whose locus will reproduce the original vdW isotherms (provided of course that the substance strictly obeys the vdW equation). But in practice, unstable states ’far away’ from stable ones are extremely difficult to produce.

With this discussion a plausible resolution of the unphysical features of vdW case suggests itself; it is that the vdW equation does not always represent a single component homogeneous phase. There are two phases of the system, and regions where they coexist, and in those regions the original vdW isotherms have unstable states that should be replaced by stable states of coexisting phases.

This also gives meaning to the multiplicity of the roots for V of the vdW equation at a given P. Where the equation has only one root, for example when $P > P_{max}$ or $P < P_{min}$, there is no issue. But for $P_{min} \leq P \leq P_{max}$, the smallest volume solution is to be associated with the liquid phase and the largest volume solution with the gas phase. At only one P, will both the phases be stable. At all other pressures even in the range of multiple solutions, only *one* root will represent the stable phase.

All this does not say how exactly this replacement is to be achieved. In other words, where exactly should one locate the flat part of the isotherms? The answer to this is one of the most beautiful developments in thermodynamics worthy of being called another *pearl of theoretical physics* (Lorentz is said to have described Boltzmann's thermodynamic derivation of the Stefan law as a *veritable pearl of theoretical physics*). We describe this in the next section.

12.2.1 The Maxwell construction

So the main task is to find a method for determining, for a given T, the pressure at which the liquid and gas phases coexist. Then all the points in region I of the isotherm below this line, all the points in region III above this line and the *entire* region II will represent unstable phases.

We discuss three different ways of tackling this problem: first is a very elegant construction discussed by Fermi which requires only the existence of the coexistence part and does not require any calculations at all. Next, we use the fact that the Gibbs potential per unit mass of the two phases must be equal to determine the flat part, also called the *Maxwell line*. Finally, we use Helmholtz free energy considerations towards the same end.

Fermi method: Consider the isotherm marked d*efhjkl* in fig.(12.1). Let the solid line e*hk* be the flat part we are seeking. The important point to remember is that if it were so, every point along it, from e to k, represents a stable state. Consequently, *infinitesimal reversible* changes can link two neighbouring points. Even though the states along the original part of the vdW isotherms are all unstable, nearby points can still be connected by reversible isothermal changes.

Now consider performing a *reversible isothermal cycle* h*kjhfeh*. From our considerations of chapter 3, it follows that $\oint \frac{đQ}{T} = 0$ along this cycle, and because T is constant throughout, $\oint đQ = 0$. From first law, it then follows that the total work done in traversing the cycle must also vanish, which means $\oint PdV = 0$, i.e the total *area* of the curve must vanish. Our sign convention for work is such that the area of the *closed curve* h*kjh*, traced in the anti-clockwise direction, should be considered *negative*, while the area of the closed curve h*feh*, traced in the clockwise direction, should be considered *positive*. Therefore, the total area being zero means that the geometrical areas of h*kjh* and h*geh* should be equal. Therefore the way to find the coexistence line is to draw it such that it produces two curves of equal area. This is called *the Maxwell Construction* [43, 44].

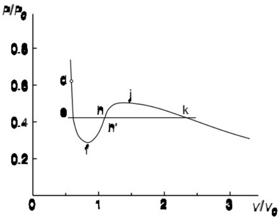

FIGURE 12.3 The Maxwell Construction.

The Gibbs potential construction Now let us turn to this construction from the point of view of g(T,P). The ends e and k of the coexistence line represent the pure phases (liquid and gas in this case). Hence their Gibbs potentials per unit mass must be equal, i.e $g_e(T,P) = g_k(T,P)$. This implies $f_e(T,P) + Pv_e(T,P) =$

$f_k(T,P) + Pv_k(T,P)$ where (f,v) stand for the unit mass Helmholtz free energy and volume, respectively. Now recall that $df = -sdT - Pdv$ where s is the specific entropy. It therefore follows, since T is constant throughout, that

$$f_e - f_k = -\int_e^k P dv \qquad (12.42)$$

This integral is just the area of the *open* curve e$fhjk$. It is elementary to see that this is equal to $P(v_k - v_e) + Area(hjkh) - Area(hfeh)$. Therefore, the equality of g at the points e and k implies the equality of the two closed areas, exactly as before. For ease of later references, let us call hfeh the *lower closed curve*, and hjkh the *upper closed curve*.

But it is possible to go beyond this geometrical construction to explicitly write down the equation for the Maxwell line. There are several ways of doing this. Let us illustrate by explicitly using the expressions for entropy and internal energy of vdW fluids as given in eqn(12.11) and eqn.(12.4) respectively. One could have used the explicit expression for the Gibbs potential of eqn.(12.13), but that particular expression does not contain P explicitly. Therefore, the condition $g_e - g_k = 0$ becomes

$$P(v_e - v_k) + u_e - u_k - T(s_e - s_k) = p(v_e - v_k) + RT\ln\frac{v_k - b}{v_e - b} + \frac{a}{v_k} - \frac{a}{v_e} = 0 \quad (12.43)$$

Solution of this equation gives the coexistence curve $P(T)$. But what makes solving this equation difficult is that the roots v_e, v_k of the cubic equation for finding v given (T,P) are themselves dependent on (T,P) in a very complicated way. However, we shall work out these details in the vicinity of the critical point later on.

The Free energy construction We now turn to an explanation of the Maxwell construction based on Helmholtz free energy considerations. It should be appreciated that all these different outlooks are related deep down. They are included to give the reader as many different perspectives as possible. First let us consider the case where P has any value lying between P_{max} and P_{min}, as shown in the figure. Let the points of intersection be at $1, m, n$. Recall the relation $\left(\frac{\partial f}{\partial v}\right)_T = -P$. This means that if we plot f as a function of v at a fixed T, the *slope* of the tangents at the points 1,m, and

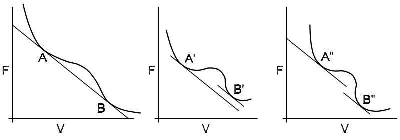

FIGURE 12.4 Maxwell Construction based on Helmholtz free energy.

n are the same, and equal to -P. Let us concentrate only at the end points l and n. Therefore, there are three possibilities: i) the points l and n have a *common tangent*, ii) the one at n lies *above* that at l, or iii) the tangent at n lies *below* that at l. Let us consider possibility ii) first. Let (f', v_n) be a point on the tangent at l. In other words, the tangent at l intersects the vertical line $v = v_n$ at f'. Clearly, $f_n > f'$. Since the slope of the tangent at l is -P it follows that

$$\frac{f' - f_l}{v_n - v_l} = -P \to -P(v_n - v_l) = f' - f_l < f_n - f_l \to g_l < g_n \tag{12.44}$$

This means that ii) represents the case when the liquid phase is more stable. In this case the area of the upper closed curve is lower than the area of the lower closed curve. Likewise, the case iii) would imply $g_l > g_n$, in which case it is the gas phase which is more stable. Then the area of the upper closed curve is larger than the area of the lower closed curve.

Thus the g's at the endpoints would be the same only if case i) holds, i.e the free energy curve has a common tangent at the end points. In that case, it follows that

$$\frac{f_n - f_l}{v_n - v_l} = -P \to \int_l^n P dv = P(v_n - v_l) \tag{12.45}$$

which has already been shown to be the same as the equal area rule of the Maxwell construction.

It is interesting to enquire about the third point of intersection whose volume lies intermediate to the volumes of the liquid and gas phases. It turns out that its Gibbs potential per unit mass is *higher* than g_l, and hence higher than g_g too. Therefore it is an *unstable* phase. From the free energy point of view too, it can be shown that the free energy of the homogeneous phase represented by h is *higher* than the coexistence phase (represented by the point h' which is geometrically at the same point h, but represents a different state).

Finally, it is important to note that the common tangent referred to while discussing the method based on Helmholtz free energy has the same physical interpretation as the line representing the free energies of the various coexistence states. It is worth emphasizing that while all these have the same g, they have different f's with f_n being *lower* than f_l. The fact that f_n is lower than f_l certainly does not mean that n is more stable than l (they are in fact both stable). A lower f means greater stability only when comparisons are made at the same (T,V). Therefore it made sense to compare the free energies of h and h' for stability.

12.2.2 Stable and unstable states of the vdW system

Now we summarize our discussion so far as to which of the states of the vdW system are stable and which of them are not. For $T > T_c$ or equivalently $T_r > 1$, for each pressure there is only one point on an isotherm which is stable. Therefore all points on all isotherms above T_c are stable states.

For temperatures below T_c the issue is more involved. Now we have two distinct pressures $P_{max}(T)$ and $P_{min}(T)$. For pressures *above* P_{max} there is only one root to isotherm which again is a stable state. Inspection shows that this happens for V much less than V_c and these stable states are in the liquid phase. Likewise, for pressures *below* P_{min} there is a single root which represents a stable state, and this time in the gaseous phase.

When pressures are in the range $P_{min} \leq P \leq P_{max}$, we have to analyse case by case. Let us start when $P = P_{min}$. Now there are two points of intersection, the point l being at the location of the minimum itself. Now the area of the lower curve is zero and obviously the area of the upper curve is the larger. From our earlier discussion, it is n which is more stable and this is in the gaseous phase. This is in fact what one would expect from continuity, as for P slightly lower than this value the stable phase is gaseous. As we increase P from P_{min} all the way to the Maxwell line, this will be the situation and we will get a sequence of stable states in the gas phase. But now each of these stable states is accompanied by *two* unstable states. In terms of g, the gas phase has a lower Gibbs potential than the *potential* liquid phase.

Then we come to the Maxwell line, when the areas of the upper and lower curves equal. Here both l and n have the same g, and they can coexist as liquid and gas phases. The entire line ln now represents stable states of liquid-gas coexistence. Attention has already been drawn to the point h which is geometrically the point of intersection between the line ln and the isotherm. We can, by convention, take h to be the homogeneous state lying on the isotherm. Then the intersection point h' lying on the line ln, though geometrically coincident with h, represents a completely different state which is the stable state in which both liquid and gas phase coexist (with the mass ratio of liquid to gas being $\frac{lh'}{h'n}$). The Gibbs potential g of h is much higher than that of h'. The difference in these g-values is what was referred to as the *barrier* in the chapter on phase equilibrium.

Immediately after the Maxwell line, the situation is akin to what it was immediately before, but with the roles of liquid and gas reversed. Now we get a series of stable states in the liquid phase, with each stable state accompanied by two unstable states. This will continue till one reaches $P = P_{max}$ where again (just as in the case $P = P_{min}$) there is a stable liquid state accompanied by only one unstable gaseous phase.

It is useful to look pictorially at how the Gibbs potential profile of both the stable and unstable states progresses as we go through the abovementioned sequence. In the following figures we have plotted g vs v. This idea is sometimes presented through continuous curves of g as a function of v. But we point out that at any combination of (T,P) values, the vdW equation has at best three solutions, which means the manifold of states with fixed (T,P), inclusive of both stable and unstable states, can at best have three points. Now it can be appreciated that the two-phase structure of the vdW system owes it to the multivaluedness of solutions for volume at fixed (T,P). The ideal gas, being singlevalued in this respect, can not obviously exhibit more than one phase. This also means that the vdW system can not possess a *triple point*. For that to happen, the relevant equation must have at least *five* solutions or in other words, the equation of state must at least be a *quintic*.

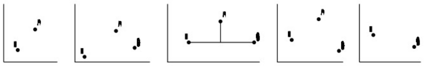

FIGURE 12.5 The relative Gibbs potentials.

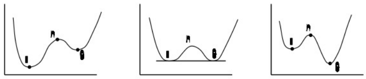

FIGURE 12.6 Another plot of G.

12.2.3 Phases of the vdW system

Now we discuss the vdW phase diagram in the P-V plane. The critical isotherm forms one boundary, above which the system is always in the *unsaturated vapor* phase, which we call the *gas* phase. All isotherms above T_c lie entirely in this region. This means that if the temperature is even slightly higher than T_c, no matter how large a pressure one applies, one can not *liqueify* the gas, a rather remarkable feature of the critical temperature. At P_c and above, the critical isotherm marks the *phase boundary* between the liquid and gas phases.

Below P_c there are three distinct regions and we now discuss the boundaries separating these regions. For this, consider the locus of all liquid state endpoints of the Maxwell lines. This is one of the boundaries of the region we are talking about. Likewise, the other boundary is the locus of all the gas state endpoints. These two boundary lines obviously merge at the critical point. The region bounded by these two lines marks the two-phase coexistence region where the liquid is in coexistence with its *saturated vapor*. This can be called the *liquid-vapor* region. We are making a distinction between the saturated vapor which we are calling *vapor*, and the unsaturated vapor which we have already called *gas*.

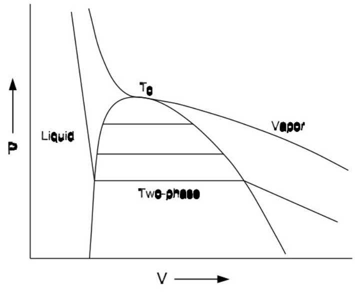

FIGURE 12.7 Stable phases of vdW.

The locus of liquid endpoints marks the phase boundary between the purely liquid phase and the liquid-vapor coexistence phase. In the same way, the locus of gas endpoints marks the boundary between the purely gas phase and the liquid-vapor coexistence phase.

12.3 Negative pressures in vdW systems

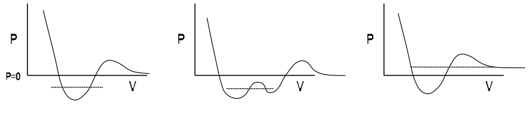

FIGURE 12.8 Negative pressure.

Now we discuss the occurrence of *negative pressures* in vdW systems, and whether these have any physical significance, or provide another unphysical aspect of vdW isotherms. By drawing the vdW isotherms at a low enough temperature one can explicitly verify that the isotherm goes through negative values for pressures. Let us analyze this issue as analytically as possible.

It is clear that if at some temperature $T_{r,neg}$ (we shall henceforth use reduced variables, so our conclusions hold for all vdW systems), $P_{min}(T_{r,neg})$ becomes zero, then for temperatures lower than this the isotherm will have points with negative pressure. To determine this characteristic temperature, let us recall that the pressure $P_{r,S}$ at the stationary points is given by $P_{r,S} = 4T_r\frac{(3V_{r,S}-2)}{(3V_{r,S}-1)^2}$. Clearly, this can vanish at $V_{r,S} = \frac{2}{3}$. As this volume is less than unity, the stationary point, as per our earlier discussions, can only be a minimum. In fact we have already shown that P_{max} is always *positive*.

In other words, while P_{min} can indeed be negative, P_{max} can never be. If both P_{max} and P_{min} could have become negative at some temperature, then there would have been the possibility that the Maxwell construction would yield stable coexistence states at negative pressure. But the fact that P_{max} can never be negative, precludes such a possibility.

It is easy to work out the value of $T_{r,neg}$ since there $P_r = 0$ and $V_r = \frac{2}{3}$. An elementary calculation using the universal form of the vdW equation in terms of reduced variables yields $T_{r,neg} = \frac{27}{32}$, which is a surprisingly large value!

We next examine whether with a negative P_{min} and a positive P_{max}, the Maxwell line which has to lie in between can be at a negative value of P. Firstly, since P_{max} is positive, and for large V $P \to 0$ from above, there can not be any intermediate points where P can be negative without the isotherm having at least an additional pair of maximum and minimum, something that a cubic vdW equation can not accommodate. Hence, if at all there is a Maxwell line at negative P, it must intersect the isotherm at only two points. It is easy to show, using methods described so far, that the point with the lower g (more stable) is the one with unphysical isothermal compressibility. This precludes having a coexistence curve at negative P.

Lastly, we have to consider the possibility that even with a negative P_{min} and a positive P_{max}, as well as a Maxwell line at positive P, there may be a stable state with negative P. But the same argument that was given above to show that the point with lower g was unphysical holds here too.

Thus one can confidently conclude that no stable state with negative P exists in the vdW system. Such states have to be unstable. But even as unstable states, do they make sense? Some have argued that the concept of a negative pressure can be physically sensible. Some point to the pumping of water by tree roots despite the pressure by the already present water column as evidence in favor of such a concept. But in that particular case, causes such as capillarity as well as partial vacuum created by various processes mimick a negative pressure. They certainly do not point to absolute pressure turning negative. For isolated thermodynamic systems, negative absolute pressure should be considered *unphysical.*

Unfortunately, there is no experimental way to address this issue as no real life system is actually described by the vdW equation. The real life equations of state have various corrections and very likely these modifications also take away the source of negative pressure.

However, there is one circumstance where a negative absolute pressure is taken very seriously. That is in the context of *Cosmology* where the so called *positive cosmological constant* in Einstein's equations for the universe have the effect of a negative absolute pressure. What is more, recent data based on Supernovae has given good evidence that this is the case with our universe. The observable manifestation is an expanding universe that is also accelerating.

12.4 Surface tension

We now discuss the phenomenon of *surface tension* from two rather distinct perspectives. First is that this phenomenon, in contrast to everything that has been considered so far, is a purely *surface* effect. It becomes important while considering interfaces between coexisting phases. It can be characterized as a *tendency* to minimize interfacial surfaces. One of its descriptions is in terms of a *force per unit length* acting on a line on the surface in a direction normal to it. For example, when a leaf is found floating on water, it is not the force of *buoyancy* that is holding it up, as the leaf is not even partially submerged. An even clearer example is a razor blade floating on water, as the density of steel making up the blade is far higher than that of water.

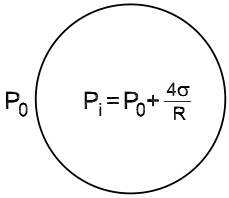

FIGURE 12.9 Bubble pressure

This means that the *net effect* of the fluid surface on the blade is to exert an *upward* force cancelling the force due to gravity. It will therefore require work to be done to lift the blade out. The force required to pull the blade out is proportional to its *perimeter*, and for a circular blade of radius a, the required force is $4\pi a\sigma$ (not $2\pi a\sigma$!), where σ is called the *surface tension* of the liquid and has the units of *Newton/meter*. What could be confusing is that the force on the blade acts normal to it.

An experiment that can also be used to measure σ can clarify this. If we prepare a rectangular soap film with an arrangement to, say, change the height of the rectangle, it can be seen that a force is required, along the direction of the height, to increase the height and hence the area of the film. This gives the alternative definition of surface tension as *the work done* to increase the area of the surface by a unit. Equivalently, an internal energy of surfaces of the form $U_s = \sigma A$ can be introduced.

Let us consider a bubble made of a liquid with its vapor both inside and outside it, as shown in figure (12.9). In the absence of any surface tension, *mechanical equilibrium* would require the pressures inside and outside, P_i and P_O, to be *equal*. But with surface tension, there can be a pressure difference. This pressure difference can be qualitatively understood as follows: a *positive* pressure difference $\Delta P = P_i - P_O > 0$ has the tendency to *increase* the surface of the bubble. This can be countered by a surface tension which tends to decrease the surface, so there can be equilibrium when these two tendencies equal each other.

We make this reasoning quantitative from alternative viewpoints. The bubble, like a soap bubble, has *two* interfaces- a vapor to liquid *and* a liquid to vapor. Let us simplify the problem by considering a *single* interface. We take this to be the surface of the spherical cavity with vapor inside and liquid outside. First, let us apply the principle of *virtual work*, a method used for determining mechanical equilibrium. For this, imagine changing the radius of the bubble r by δr; the work done by the pressure difference ΔP is $\Delta P \cdot \Delta V = 4\pi \mathrm{r}^2 \delta\mathrm{r} \cdot \Delta P$. The work done *against* surface tension is $-\sigma\,\delta A = -8\pi R\sigma\,\delta\mathrm{r}$. The principle of virtual work requires the *total* work to be zero. This leads to the well known equation in *capillarity*:

$$\Delta P = \frac{2\sigma}{\mathrm{r}} \tag{12.46}$$

ΔP in this equation, which is $P_i - P_O$, is always *positive* else or no bubble can form. In this case, $P_i = P_v$ and $P_O = P_l$, where the subscripts v, l refer to the vapor and liquid, respectively. When the bubble consists of liquid in a vapor environment, $\Delta P = P_l - P_v$. In the case of the soap bubble, if the *outer* vapor pressure is P_O and the inner vapor pressure P_i and the pressure of the liquid in between is P_l, one has, $P_l - P_O = 2\sigma/\mathrm{r}$, and, $P_i - P_l = 2\sigma/\mathrm{r}$! Therefore, for a soap bubble, $P_i - P_O = 4\sigma/\mathrm{r}$!

When we pull films out of a liquid too, there are *two* interfaces due to the unavoidable wetting of the surface that is pulled out. This explains why the required forces are *twice* as large as a naive expectation. We shall also derive eqn.(12.46) from *thermodynamic* arguments, which form our second perspective on the issue.

Example 12.5: Work required for aerosol spray

1 Kg of water at $20^\circ\mathrm{C}$ *is initially in a container 10 cm x 10 cm x 10 cm. This is completely atomized into spherical droplets of average radius of* 10^{-4} *cm. The whole process takes place isothermally. Calculate the work required for this process as well as the heat transferred. The dependence of surface tension with temperature is very accurately given by eqn.(13.3).*

The initial surface area is 600 sq.cm. Since all droplets are spherical, the ratio of surface area to volume of each droplet is just $3/R$. Hence the new total surface area of water is simply $A = 3.0 \cdot 10^3 m^2$. This is a huge increase in area. The increase in surface energy is therefore $\sigma \Delta A \simeq \sigma A$, as the initial area is completely negligible in computing the increase in area. Now we use the high accuracy interpolation formula for the surface tension of water at various temperatures (see eqn.(13.3) [75]). According to this σ at $20^\circ\mathrm{C}$ is $72.72 \cdot 10^{-3}$ N/m. Thus, it requires $W = \sigma A = 72.72 \cdot 3 = 218.16$ Joules.

From the same interpolation formula one finds that $d\sigma/dT$ at $20^\circ\mathrm{C}$ to be -$0.15 \cdot 10^{-3} Nm^{-1}K^{-1}$. The surface entropy is given by eqn.(12.62) to be $S_s = -d\sigma/dT \cdot A$. In this case this turns out to be $S_s = 0.45$ J/K. The heat absorbed by water at $20^\circ\mathrm{C}$ is, therefore, 131 J.

Example 12.6: Coalescing soap bubbles

If two soap bubbles of radii r_1 *and* r_2 *coalesce to form a single bubble, what will its radius be if all other physical conditions like pressure and temperature are unchanged.*

Since all other conditions are identical, upon coalescing the new bubble must be of such a radius that the total surface energy is conserved. Before coalescence, this was $4\pi(\mathrm{r}_1^2 + \mathrm{r}_2^2)$. Hence the radius of the final bubble is $R = \sqrt{\mathrm{r}_1^2 + \mathrm{r}_2^2}$.

Example 12.7:

Consider a spherical drop of radius r_1 *of a liquid with surface tension* σ. *It is found that the drop has inside it a spherical bubble of radius* r_2 *concentric with the drop. If* P_o *is the pressure outside the drop, and* P_i *the pressure inside the bubble, find the radius of a single bubble such that the pressure difference between the inside and outside of that bubble is equal to* $P_i - P_o$.

Applying the formula for the pressure differences obtained in the text, $P - P_o = 2\sigma/\mathrm{r}_1$, and $P_i - P = 2\sigma/\mathrm{r}_2$, where P is the pressure of the liquid in the annular region. Hence, $P_i - P_o = 2\sigma(1/\mathrm{r}_1 + 1/\mathrm{r}_2)$. This must be equal to $4\sigma/R$, where R is the radius of the single bubble. Hence $R = (\mathrm{r}_1\mathrm{r}_2)/(2(\mathrm{r}_1 + \mathrm{r}_2))$.

12.5 Thermodynamics of inhomogeneous substances.

The first perspective presented above is purely *mechanical*. All it needed was the existence of surface tension. We now turn to the second perspective, which is *thermodynamical*. Any process that has a tendency to increase the interfacial area must perform work. Therefore, the first law must be modified to include this additional source of work:

$$TdS = dU + PdV - \sigma dA \tag{12.47}$$

the negative sign for the extra term follows from the fact that while the PdV tends to increase the area, the surface tension term tends to decrease it. This seemingly innocuous modification has, however, some very subtle consequences. Firstly, surface terms spoil the *extensivity* that has played such an important role so far. In fact the Euler and the Gibbs-Duhem relations of chapter 6 are no longer valid for the whole system! We shall soon find that entropy has a part growing with area. In consequence, all thermodynamic potentials too will have surface dependent terms.

While deriving the conditions for the equilibrium of coexistence of phases, the Gibbs potential G played a central role, and the Euler relation forced this to be the same as the chemical potential μ. But a central feature then was the *equality* of the pressures in the two phases. But now, because of eqn.(12.46), the pressures in the two phases are *different*. This necessitates a rethink on this very central issue. In the usual cases referred to, the equal pressures also equalled the *externally applied* pressure; but now, in general, all these can be different and careful distinction between them has to be made.

In fact, the issues go beyond this. So far, only *homogeneous* substances had been considered, and for them, density and molar fraction n, being uniform, contains the same information for a given volume. The interface, being the transitional region between two phases, must necessarily be described in terms of *varying* density. Therefore, a reformulation is needed replacing n by density ρ, which, however, is no longer constant. This also means that the chemical potential introduced traditionally via the $\mu\, dn$ term, loses its meaning in the interface. Though there is a pressure difference between the phases, each phase on its own continues to be homogeneous with a meaningful chemical potential. But what is far from obvious is the relationship between the chemical potentials.

Gibbs, around 1875, was the first to give a systematic treatment of this problem of the thermodynamics of heterogeneous systems in his foundational work [19]. All the essential results are contained in that work. In 1894, van der Waals gave another treatment of the problem in what is considered to be a monumental paper on capillarity [74, 62]. Gibbs had based his work on *discontinuities* in the density profile, while van der Waals theory uses only smooth variations. An additional noteworthy feature of van der Waals's work is that he treated, as best as he could for his times, the singular behaviour of surface phenomena near *critical temperature*. Van der Waals points out some conceptual errors that even a great master like Gibbs made regarding the chemical potentials.

12.5.1 van der Waals theory of surface tension

We shall follow the treatment of van der Waals. We shall only state the principal results, but encourage the reader to go through the original. In the modification to the first law considered above, the surface tension σ entered at the level of an empirical description. In an *ab initio* treatment such as that of Gibbs or van der Waals, it has to emerge as an *effective* description of *inhomogeneity*. It proves useful to consider systems with some *symmetry* so that density varies only as a function of *one* parameter. If the interface is *planar*, this parameter will be the height h measured along the normal to the plane; if the interface is *spherical*, the parameter is the radial distance r. Let us generically denote it as z.

For reasons already mentioned, i.e pressures not being the same in the two phases, Gibbs potential can be problematic in determining phase equilibrium. Van der Waals bases his analysis on Helmhotz free energy instead. It should be noted that the temperature is taken to be constant throughout, thereby justifying the use of F. But now one has to reckon with a fundamental difference when compared to the traditional uses of F; a *local* variant of it has to be used which not only depends on the local value of the density, but also on its variation wrt z. Denoting the Helmholtz free energy per unit mass (recall that in treating phase equilibria one has to consider various thermodynamic potentials per *unit mass*) by $f(\rho(z))$, the total free energy is $\int \rho f(\rho) dV$. If the phase is *homogeneous* this would have been essentially -PV (for isothermal conditions).

Instead of viewing the problem as that of coexistence of two phases, with their respective Gibbs potentials (or equivalently, chemical potentials), van der Waals' mastery lay in viewing it as the problem of equilibrium of a *single* substance, albeit of varying density, at some given temperature. The minimization of the total F should still be valid as nothing in the derivation of that criterion really made any assumptions about the density profile.

Thus according to van der Waals, the equilibrium condition should result upon minimizing F subject to the constraint that the *total mass* of the system does not change, i.e

$$\delta \int \rho f(\rho) = 0 \qquad \int \rho = C \tag{12.48}$$

This is a familiar problem in the *calculus of variations* and is solved through the introduction of a *Lagrange multiplier*, say μ (with a deliberate choice of the symbol!), to handle the condition of constant total mass. The resulting variational problem is

$$\delta \int \{\rho(f(\rho) - \mu)\} = 0 \tag{12.49}$$

When f depends only on ρ, and not on the derivatives of ρ wrt z, the solution to this variational problem is straightforward, and is given by

$$f(\rho) + \rho f'(\rho) = \mu \tag{12.50}$$

where f' denotes the derivative of f wrt to ρ. When f also depends on some or all the derivatives of ρ, it is still possible to write down the solution to the variational problem. Instead of doing this in all generality, we shall restrict ourselves to the particular modifications that are thought to be sufficiently accurate in [74, 62]. This amounts to keeping only second derivatives of ρ wrt z, and neglecting all higher ones (due to the symmetry assumed, there can be no first derivatives). The relevant variational problem is

$$\delta \int \left\{ \rho(f(\rho) - \frac{c_2}{2}\frac{d^2\rho}{dz^2} - \mu) \right\} = 0 \tag{12.51}$$

where c_2 is taken, following common practice, to depend only on temperature. It has to be *positive* as otherwise every interface will *spontaneously* disappear. In other words, equilibrium configurations will be those with uniform densities.

The solutions to the variational problem are slightly different for the planar case and the spherically symmetric cases. This has to do with the partial integrations needed to solve the problem, and the different volume factors in the two cases. We present both of them, side by side, in the next equation;

$$f + \rho f' - c_2\frac{d^2\rho}{d\mathrm{z}^2} = \mu \qquad f + \rho f' - c_2\frac{d^2\rho}{d\mathrm{r}^2} - \frac{2c_2}{\mathrm{r}}\frac{d\rho}{d\mathrm{r}} = \mu \tag{12.52}$$

When phases are homogeneous, i.e when density does not depend upon z, both these become a single equation

$$u - Ts + \frac{P}{\rho} = \mu \tag{12.53}$$

The lhs is nothing but the Gibbs potential g per unit mass, and the above equation, when applied to coexisting phases, is the familiar equality of chemical potentials. But that equality had been derived ignoring capillarity. With capillarity taken into account, when eqns.(12.52) are applied to the homogeneous phases adjoining the interface, one still comes to the highly non-trivial conclusion that Gibbs potentials (also chemical potentials) of the homogeneous phases *separated* by an interface, are still equal! This holds irrespective of the geometry of the interface, i.e planar or spherical. Applying this to the bubble problem, one gets,

$$\mu = \mu_l = u_l - Ts_l + P_l v_l = \mu_g = u_g - Ts_g + P_g v_g \tag{12.54}$$

What happens in the interface? The governing equation is still eqn.(12.52), but several complications arise. In the homogeneous phases as above, $\rho f' = P/\rho$ by virtue of the relation $\left(\frac{\partial F}{\partial V}\right)_T = -P$; but in the interface, this is no longer true. One could continue to call $\rho f'$ as P/ρ, but such a P has no bearing to the real pressure inside the interface nor to the externally applied pressure. As such complications tend to obscure the real issues when the geometry is also more involved, let us consider the planar case first, where the difficulties with the interface are already present. Also, in that case $P_l = P_g$, offering an additional simplification.

For that case, with the abovementioned understanding about P, one can show, with the help of eqn.(12.52) that (I denoting the interface)

$$u_I(h) - Ts_I(h) + P_I(h)v_I(h) = \mu + \frac{c_2}{2}\frac{d^2\rho(h)}{dh^2} \tag{12.55}$$

With $P_I(h)$ not even being interpretable as the pressure in the interface, the lhs can not be given the meaning of a chemical potential for this region. In fact, it is hard to make any sensible use of this equation. Remarkably, van der Waals manages to derive the following relation (again for planar interfaces)

$$u_I(h) - Ts_I(h) + P_e v_I(h) = \mu + \frac{c_2}{2}\left\{\frac{1}{\rho_I(h)}\left(\frac{d\rho_I(h)}{dh}\right)^2 - \frac{d^2\rho_I(h)}{dh^2}\right\} \tag{12.56}$$

Where P_e is the external pressure. The reversal in the sign of the second derivative term will be seen to be *crucial.* The crucial observation of vdW is that neither with P nor with P_e is this expression equal to the common chemical potential for the liquid and gas phases. Gibbs had assumed the chemical potential in the interface to be also the same as the other two.

One can integrate this (after multiplying with ρ_I) to arrive at

$$U_I - TS_I + P_e V_I = M_I \mu + \sigma A \tag{12.57}$$

with

$$\sigma = c_2 \int dh \left(\frac{d\rho(h)}{dh}\right)^2 \tag{12.58}$$

and U_I, S_I, V_I being the internal energy, entropy, and volume of the interface. The symmetry of the problem was crucial for getting the integral to be proportional to the total area. In fact, in the spherical case, it does not happen (see [74, 62] for details). However, for large enough radii, the two cases converge. We shall discuss the quantitative aspects of this later on.

12.5.2 Surface thermodynamics in vdW theory

The natural question that arises in ones mind is whether the two σ's of eqn.(12.58) and eqn.(12.47) are one and the same. As a first step towards this, let us clarify the meaning of eqn.(12.57). Clearly, the interface has a certain fraction as liquid, and the remainder as gas. If U_I, S_I, V_I were just the weighted sums of the corresponding quantities for the liquid and gas, there could not have been the additional σA term; this clearly means that there are additional contributions over and above the *bulk* contributions, which can be ascribed to a *surface*. But as Landau and Lifshitz [34] point out, this division into bulk plus surface is problematic. There are several ways of seeing this; the masses and volumes of the liquid and gas are ambiguous because these quantities can be *exchanged* with the interface. Thus, a surface tension coupled with geometric information about the surface is *not enough* for a complete thermodynamic description of the entire system.

Even without attempting this rather delicate split into bulk and boundary, one can address the issue of the equality of the two σ's. For this we write down the expressions for the *total* Gibbs potentials for the liquid and gas phases:

$$U_l - TS_l + P_1 V_l = M_l \mu \qquad U_g - TS_g + P_1 V_g = M_g \mu \tag{12.59}$$

Next we consider some *reversible* process where all relevant quantities undergo *infinitesimal* changes while maintaining the *total mass* $M_l + M_g + M_I$; it is easy to see that $U = U_l + U_g + U_I$ and $V = V_l + V_g + V_I$ satisfy just the same equation as eqn.(12.47), so indeed σ of eqn.(12.58) is the *surface tension*.

Returning to the issue of the bulk plus surface split, this can indeed be down as shown in the worked example. It amounts to an explicit realisation of the suggestion made by Landau and Lifshitz [34] and is expressed through the equation

$$F_s = U_s - TS_s = \sigma A \qquad (12.60)$$

where the subscript s refers to the *surface* which is now characterized by having *no* mass and volume, unlike the interface, which had both. Consequently, the *surface Gibbs potential* G_s is given by

$$G_s = \sigma A \qquad (12.61)$$

All the thermodynamic aspects of the surface follow from eqns.(12.60) and (12.61). Using the familiar relations of thermodynamics one finds that the surface entropy S_s, surface internal energy U_s, and the surface enthalpy H_s to be

$$S_s = -\frac{d\sigma(T)}{dT}A \qquad U_s = (\sigma(T) - T\frac{d\sigma(T)}{dT})A = H_s \qquad (12.62)$$

The heat absorbed during a reversible change of area, and the corresponding work done are given by

$$\Delta Q = T\frac{d\sigma}{dT}(A_2 - A_1) \qquad \Delta W = -\sigma(A_2 - A_1) \qquad \Delta U_s = \Delta Q - \Delta W \quad (12.63)$$

Analogous results for spherical layers is left as an exercise.

The relation derived earlier, i.e eqn.(12.46), gave only the pressure *difference* between the inside and outside of a spherical bubble. We now disuss how to determine both these pressures individually when the applied pressure is P_e, which is also the pressure of the two phases when the interface is planar, i.e when $R \to \infty$.

Before that we show how eqn.(12.46) can also be derived by minimizing the *total* free energy $F = F_l + F_g + \sigma A$. The area for a spherical bubble is $A = 4\pi \mathrm{r}^2$. Since the total volume $V = V_l + V_g$ is fixed, $\delta V_l = -\delta V_g = \Delta V$. Recalling $\left(\frac{\partial F}{\partial V}\right)_T = -P$, one finds

$$0 = \delta F = (P_g - P_l)\Delta V + \sigma dA \to \Delta P = \frac{2\sigma}{\mathrm{r}} \qquad (12.64)$$

Recall that when the vapor is outside the liquid drop, $\Delta P = P_l - P_g$. In fact, this exactly mimics the virtual work calculation. While the former was purely mechanical, the present one is thermodynamical.

12.6 Revisiting the bubble pressure

The starting point for a separate evaluation of P_l, P_g is the equality of the chemical potentials (taken to be Gibbs potential *per mole*) as given by eqn.(12.54), i.e

$$\mu_l(P_l, T) = \mu_g(P_g, T) \qquad (12.65)$$

When the interface is planar, i.e r $\to \infty$, $P_l = P_g = P_e$, where P_e is the external pressure. Hence

$$\mu_g(P_g,T) - \mu_g(P_e,T) = \mu_l(P_l,T) - \mu_l(P_e,T) \tag{12.66}$$

Recalling that $d\mu = -sdT + vdP$, and the fact that for liquids entropy is almost a function of T alone, it follows that

$$\mu_l(P_l,T) - \mu_l(P_e,T) = \int_{P_e}^{P_l} v_l(P,T)dP \approx v_l(P_l - P_e) \tag{12.67}$$

where the further, reasonable, approximation that liquids are very nearly *incompressible*, i.e v_l is independent of P, has been made. For the vapor, it is a good approximation to use the ideal gas law to obtain

$$\mu_g(P_g,T) - \mu_g(P_e,T) = RT \ln \frac{P_g}{P_e} \tag{12.68}$$

Thus one obtains the fundamental equation

$$RT \ln \frac{P_g}{P_e} = v_l(T)(P_l - P_e) \tag{12.69}$$

Using the ideal gas condition $P_g \mathrm{v}_g = RT$, this can be recast in the following very useful form:

$$\ln(1 + \frac{\Delta P_g}{P_e}) = \frac{P_e}{P_g} \frac{\mathrm{v}_l}{\mathrm{v}_g} \frac{\Delta P_l}{P_e} \tag{12.70}$$

This is valid for bubbles and drops of *all* sizes.

We analyze the situation for two extreme cases, one of which is when (i) $\Delta P_l = P_l - P_e << P_e$ and $\Delta P_g = P_g - P_e << P_e$, and the other when (ii) $\Delta P_g >>, P_e$. Clearly, case (i) is characteristic of *large* bubbles or drops. It is pertinent to ask what one means by *large* or *small* sizes in this context. It is obvious that $\mathrm{r}_c = 2\sigma/P_e$ has dimensions of length, and this can be taken to set the scale for largeness or smallness. We shall point out that the relevant scale for (ii) is much smaller.

Let us analyse the case (i) now. It immediately follows from eqn.(12.70) that

$$\frac{\Delta P_g}{P_e} = \frac{P_e}{P_g} \frac{\mathrm{v}_l}{\mathrm{v}_g} \frac{\Delta P_l}{P_e} \tag{12.71}$$

In this regime $P_g \approx P_e$. Using this, and $\Delta P_l - \Delta P_g = 2\sigma/\mathrm{r}$, it is easy to arrive at

$$\Delta P_l \approx \frac{2\sigma}{\mathrm{r}} \qquad \Delta P_g \approx (\frac{P_e \mathrm{v}_l}{RT}) \frac{2\sigma}{\mathrm{r}} \approx 0 \tag{12.72}$$

Therefore, for large enough bubbles, i.e r $>>$ r_c, the vapor pressure is hardly changed from the external pressure (for a planar surface the vapor pressure is *exactly equal* to external pressure), while the pressure in the liquid increases.

Let us now turn to the other limit (ii) where $\Delta P_g >> P_e$. This means that $P_g >> P_e$ too. It should of course be remembered that if P_g is too high, the vapor would have condensed completely, and there would not be a liquid drop anymore! As long as the vapor has not liquefied completely, $\mathrm{v}_l < \mathrm{v}_g$. It therefore follows from eqn.(12.70) that whenever $\Delta P_g >> P_e$, ΔP_l is *much greater than* ΔP_g. This again implies that ΔP_l is very close to $2\sigma/\mathrm{r}$, which was the case also when r was *large*! But unlike then, ΔP_g, though negligible in comparison to ΔP_l, can still be much larger than P_e.

It is easy to determine how large this can be, again from eqn.(12.70); on the lhs of that equation, ΔP_l can be replaced by $2\sigma/\mathrm{r}$, and P_gV_g by RT, since the vapor has already been taken to obey ideal gas law. Hence

$$P_g(\mathrm{r}) = P_e e^{\frac{2\sigma}{\mathrm{r}}\frac{\mathrm{v}_l}{RT}} = P_e e^{\frac{\mathrm{r}_c}{\mathrm{r}}\frac{P_e\mathrm{v}_l}{RT}} \tag{12.73}$$

We see that the *effective* size scale for small bubbles (drops) is no longer r_c, but the *much smaller* scale $(P_e\mathrm{v}_l/RT)\mathrm{r}_c$. This has the effect of slowing down the rate of increase of P_g with decreasing r. This concludes our discussion of bubble pressures.

12.7 Problems

Problem 12.1 Express various identities involving C_P,C_V of eqns.(3.52–3.56) in terms of the reduced variables, and the reduced versions of isothermal compressibility κ_T^r and the coefficient of volume expansion α^r.

Problem 12.2 Determine the critical parameters T_c, P_c, V_c for the Clausius equation of eqn.(1.16). Show that this equation too admits a law of corresponding states by determining the reduced equation.

Problem 12.3 The compressibility factor Z is defined as $\frac{PV}{RT}$, and has the significance that it is the ratio of the pressure P to the ideal gas pressure at the same V and T. We have seen that the value of Z at the critical point of all vdW fluids is 3/8. But there is another kind of universality too; show that Z satisfies a cubic equation whose coefficients are functions of only the reduced pressure P_r and reduced temperature T_r. Show that at the critical point $P_r = 1, T_r = 1$ this cubic becomes a perfect cubic equation.

Problem 12.4 Apply the previous problem to the solved example 12.1.

Problem 12.5 It often becomes necessary to calculate the volume given P and T, for equations like the van der Waals, Clausius, Dieterici etc. In the next chapter 13, one such method is adopted for the vdW case. Show that an iterative method for all such equations is available which consists of writing the volume (assume one mole) formally as $V = f(P,T,V)$ (which of course does not solve the problem in itself), and some value V_0 as the first guess and calculating the next value by substituting this in f(P,T,V), and so on. For these classes of equations, what will be the best guesses for V_0? Does this depend on the phase for which the volumes are required? Does the iteration converge eventually?

Problem 12.6 Calculate the entropy of mixing when n_1 moles of a vdW gas is mixed with n_2 moles of an ideal gas at T,P. Show that the mixing entropy has the form encountered in Flory-Huggins theory (example 9.2). Also calculate the enthalpy of mixing, volume of mixing, as well as the Gibbs potential of mixing in this case. Can this mixing be called ideal or not?

Problem 12.7 Repeat the previous problem when both the gases are vdW.

Problem 12.8 One of the main uses of the Joule-Kelvin process is in the liquefaction of gases. There it is desirable to achieve cooling, i.e $\Delta T < 0$ upon expansion $\Delta P < 0$, i.e the Joule-Thomson coefficient μ_{JT} must be positive. But we already saw, in the vdW case, that this can have both signs. The curve in the P-T plane separating regions of $\mu_{JT} > 0$ from $\mu_{JT} < 0$ is called an inversion curve. Determine the inversion curve for vdW gases. Express it in terms of the reduced variables.

Problem 12.9 Repeat the previous exercise for a gas obeying the Clausius equation.

Problem 12.10 Consider a fixed volume V_0 of a vdW gas. Show that knowing the pairs (T_1,P_1) and (T_2,P_2) is sufficient to determine the vdW constants a, b. If one does not know whether a gas obeys the vdW equation or not, show that the triplet of pairs (T_1,P_1), (T_2,P_2), and (T_3,P_3) can determine whether a gas obeys the vdW equation or not. Find the relationship between the three pairs of values so that the gas obeys a vdW equation.

Problem 12.11 Consider an ideal gas as well as a vdW gas both having the same constant C_V. Show that the difference in their Helmholtz free energies at the same values of (T,V,n) can be expressed as a suitable integrable of the compressibility factor Z (see problem 12.3)

Problem 12.12 Gilbert Lewis introduced the notion of fugacity f in such a way that the chemical potential expressed in terms of T and P has the form $\mu(T,P) = A(T) + RT\ln \mathrm{f}(T,P)$ for all substances. For ideal gases fugacity equals the pressure. Calculate the fugacity of a vdW gas.

Problem 12.13 Calculate the pressure corresponding to an inversion temperature of 10 K for Helium assuming it to behave like a vdW gas with constants as used in example 12.1.

Problem 12.14 Show, using the explicit expression for enthalpy of a vdW gas of eqn.(12.13), that the integral Joule-Kelvin effect for i a vdW gas leads to the temperature drop

$$C_V(T_f - T_i) = P_iV_i - P_fV_f + a(\frac{1}{V_f} - \frac{1}{V_i}) \tag{12.74}$$

Show that integrating the Joule-Thomson coefficient μ_{JT} leads to the same expression.

13 The Critical Point

13.1 Overview

Now we address one of the most profound of phenomena in Thermodynamics as well as Statistical Mechanics, namely, *Critical Phenomena*. In plain terms, this is a study of the occurrence of the so called *critical points* and their properties. In this book we have encountered critical points in many different contexts. We start by briefly recalling these contexts as this will not only put the contents of this chapter in its proper perspective, but also give the reader an idea of the great importance of this topic.

At the earliest instance, we noted in section 4.2 that at the critical point in the phase diagram of water, the specific volumes of the liquid and gas phases become equal. The critical point in the water-saturated steam system occurs at roughly 647.29 K and a pressure of 22.09 MPa. Considering that at even the boiling point of water at 373.15 K and 0.101 Mpa (1 atm.), the density of water is nearly 1600 times that of steam, it is rather remarkable that at T_c they become *equal*. Then in section 5.5.3, the occurrence of a critical point even for the case of an ideal gas, albeit quantum mechanical, was noted and discussed. The specific heat vs temperature displayed a *cusp* at this *Bose-Einstein transition* temperature. In the same section, the general behaviour of specific heats at critical points was discussed. It was seen that specific heats show a variety of very fascinating behaviours at critical points; some of them blow up with characterstic *critical exponents*, i.e $C \simeq |T-T_c|^\alpha$, while others become discontinuous, as at the λ-transition in He4. The cusp behaviour means that while the specific heat is in itself *continuous*, its temperature derivative is *discontinuous*.

The critical point in He3 occurs at 3.2 K, while an *isolated* critical point occurs at 5.19 K in He4. In He4, one also observes the remarkable phenomenon of a *line of critical points*. In carbon dioxide, as noted in chapter 12, the critical temperature occurs at 304 K! Thus critical points are rather *ubiquitous*!

In water, the critical point is a *termination* of the phase coexistence curve $P(T)$ in the P-T plane. As we shall see soon, the latent heat, which is around 2257 J/mole at the boiling point, monotonically decreases to zero at T_c! The vanishing of the latent heat is also characterized by an exponent, i.e $L(T) \simeq (T_c-T)^\beta$, with β being very close to $1/3$ for water. This vanishing of latent heat at the critical point is not just restricted to the water system, and is in fact seen in many diverse systems. For example, the *superconducting transitions*, discussed in section 10.8, also share this feature. In chapter 10, a brief mention has also been made of the phases of *Quantum Chromodynamics*, with characterstic temperature scales of $10^{13}\,K(!)$, where too a critical point is expected. Vigorous research is on to determine its location and properties. This exemplifies the astronomical range of temperatures where all these concepts hold.

The *Clapeyron equation* exhaustively discussed in chapter 11 nicely ties up the various features of critical phenomena. For example, according to this equation, the observed fact that the *slope* of the coexistence curve for water is *finite* and *non-vanishing* at T_c means that if the entropy difference, which is the latent heat, vanishes at T_c, so must the difference in densities, which of course it does, as already mentioned. Strictly speaking, this leads to a $0/0$ problem, and formally, the Clapeyron equation breaks down. In section 11.7 of that chapter, we discussed Ehrenfest's proposals to modify the Clapeyron equation at such critical points. His *second order* phase transitions, however, required C_P to be *continuous*. This, as seen in section 10.8, is indeed what happens in superconducting transitions. Ehrenfest theory demanded certain *consistency conditions* as discussed in that section. In the later section 11.8 on the *magnetic Clapeyron equation*, it was shown that these conditions for the superconducting transitions follow from the thermodynamics of magnetic systems.

These considerations show that a substantial amount of even the details of critical phenomena are captured quite well from general thermodynamic considerations. As already pointed out in these earlier chapters, even the Ehrenfest second order theory is not sufficient to understand all of the critical phenomena. In fact, it fails to explain the λ-transitions in He, as the change in C_P in these transitions is not *finite*. However, as clearly emphasized by Pippard [54], it is possible to suitably modify the Clapeyron equaton to handle any critical phenomena, while staying entirely within the thermodynamical framework.

A word of explanation may be necessary to qualify the previous remark; thermodynamics is, of course, incapable of even revealing the existence of critical exponents discussed in the next paragraph. But consistency with thermodynamics would require that different exponents match.

But the most remarkable aspect of phase transitions is their *universality*. For example, even in Xenon, chemically and structurally very different from water, the difference in densities of the liquid and vapor phases vanishes as $|T - T_c|^\beta$ with $\beta \simeq 0.317$, a value very close to the one found in water; both are close to 1/3, whose significance will be discussed in the last part of this chapter. In fact all *liquid-vapor* transitions are described by the same value for this exponent! Not only that, even unrelated problems like the behaviour of *binary alloys*, and certain ferromagnetic transitions, all possess the same exponent.

This universality is so amazing that it is worthwhile to look at a few more aspects. Liquid water at the melting point of ice has a density of 1000 Kg/m^3, but at its T_c of 647.29 K it reaches a *critical density* of 316.96 Kg/m^3. carbon monoxide, on the other hand, has the much lower T_c of 133.15 K, but still its critical density is 301 Kg/m^3; carbon dioxide, its close cousin has its T_c at the rather high value of 304 K, room temperature in many parts of India! Nevertheless, its critical density is 464 Kg/m^3. Thus while all critical liquid densities are of comparable magnitude, critical temperatures show a wide variation. Neither T_c nor ρ_c are by themselves universal in the sense the exponents are; their universality is far more precise.

What we wish to do in this chapter is to give a three-fold view of critical phenomena. In the first part, we simply display various experimental data for water. We have chosen to concentrate on the phase-coexistence curve $P(T)$, the latent heat of vaporisation $L(T)$, and surface tension $\sigma(T)$, over a wide range of temperatures, all the way upto T_c. We then look at the *van der Waals equation* as an *analytical model* for the critical properties of a thermodynamic system. In particular, we solve for the densities of the two phases near criticality by exhibiting a Taylor series in suitable variables for both the *mechanical equation of state* in the terminology of chapter 6, as well as the *Maxwell line* describing the coexistence of phases within this model. From this, we compute the *coexistence curve* $P(T)$, the latent heat $L(T)$, the surface tension $\sigma(T)$, and the *interface thickness*. It is shown that the vdW model captures many essentials of the observed data for water, though the exponents do not come out correct.

In a subsequent section we briefly explain the basis for the observed universality of exponents in terms of the famous *scaling laws* arising out of the so called *renormalisation group*. This theory says that the exponents of the liquid-vapor system must be the *same* as those of the *three dimensional Ising model*. The notion of a *scaling function* is also explained. We then discuss how a simple parametrization for the latent heat of water given by Torquato and Stell [73] that is motivated by the 3-d Ising model fits the observed data for water over a very wide range of temperatures.

13.2 Critical properties of water:data

13.2.1 The coexistence curve

We shall only concentrate on the liquid-vapor aspect of the phase diagram of water, shown in fig. (10.1), as only that branch ends in a *critical point*. Of course, other parts of the phase diagram are fascinating too, like the *triple point* at 273.16 K and a pressure of 0.006028 atm., the *anomalous freezing curve* etc., but they are not governed by any universality. As emphasized during our discussion of *thermometry* in section 1.1, the triple points are a good way of calibrating thermometers as they occur at a unique combination of temperature and pressure. For reference, it may be noted that the triple point of carbon dioxide occurs at 216.55 K and a considerably higher pressure of 5.112 atm.

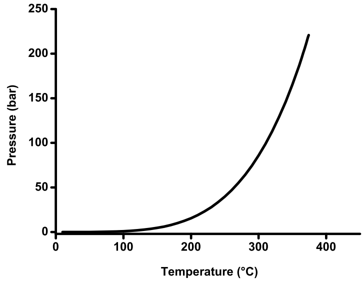

FIGURE 13.1 Steam pressure data.
Source: The Dortmund Data Bank

Let us start with the coexistence curve. The figure 13.1 presents the data (with the kind permission of the Dortmund Data Bank) for temperatures ranging from the 0 °C to T_c. The important thing to notice is the *slope* of this curve at T_c. It is neither 0 nor ∞, but has a finite value. Up to the boiling point of water the saturated vapor pressure has a very slow growth, but beyond that it rises steeply to reach a pressure nearly 250 times higher than at the boiling point. It is such high pressures that make working with steam at higher temperatures so difficult.

13.2.2 Latent heat

Next we consider the *latent heat* data (also courtesy of the Dortmund Data Bank). Its value at the boiling point of 100°K or 373.15 K is, as is well known, 540 cal/gm or 40,688 J/mole. In the next figure, the data is plotted for the *molar latent heat* from the boiling point all the way to T_c. The latent heat decreases *monotonically* throughout the range.

In section 11.5 we gave a general derivation for the *total derivative* $dL(T)/dT$ as expressed in eqn.(11.31). At temperatures far away from T_c, this general equation could be simplified to eqn.(11.33). This latter equation was based on a number of approximations, like the fact that at such temperatures $v_l << v_g$, that the *thermal expansion coefficients* β are higher for gases than liquids, and finally that the gases can be taken to obey ideal gas laws. Under those approximations it was found there that

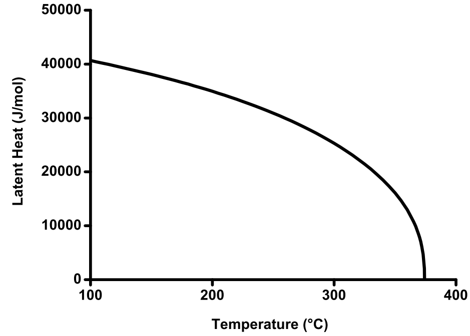

FIGURE 13.2 Latent heat data for water.
Source: The Dortmund Data Bank

$$\frac{dL(T)}{dT} \approx C_P^{gas} - C_P^{liq} \tag{13.1}$$

Since at such temperatures, C_P for gases is *lower* than those for liquids, it followed that L(T) must decrease with temperature, thus explaining the observed decrease of L(T).

Recalling the worked example there, the molar C_P for water at 100°C was 76 J/mole, while that for steam was 36 J/mole, and indeed the rhs of eqn.(13.1) is *negative*. Recall that molar specific heat C_P for an ideal triatomic gas is 4R under the approximation that its C_V is 3R (which is a very good approximation at low temperatures); this works out to 33.2 J/mole, not far from the actual value. The difference can be attributed to the *rotational* degrees of freedom of the water molecule.

This simple analysis of why latent heat should decrease with temperature, breaks down in the vicinity of the critical temperature for a variety of reasons. In fact, close to criticality it is the C_P of the gas that is *higher*! For example, at 645.20 K, just a few degrees away from T_c, the C_P for liquid water is 1776 J/mole, while that for steam is 3865 J/mole! [39]. Furthermore, the specific volume of the gas is no longer much larger than that for the liquid; in fact they become *equal* at T_c. The vapor can hardly be treated as an ideal gas. For all these reasons, it becomes rather difficult to apply eqn.(11.31) to understand the observed fall of the latent heat near T_c.

A noteworthy feature of the latent heat at T_c is that while it vanishes, its derivative *blows up* as revealed by the fact that the plot meets T_c with a tangent that is perpendicular to the T-axis. This means that as $T \rightarrow T_c$, the latent heat must vanish as $L(T) \rightarrow L_0(T_c - T)^\beta$ with β *positive* and *less than unity*. The fit to the data gives $\beta = 0.325$. Of course, in practice, fits are also compatible with $\beta = 1/3$. We shall return to this point later on.

13.2.3 Surface tension

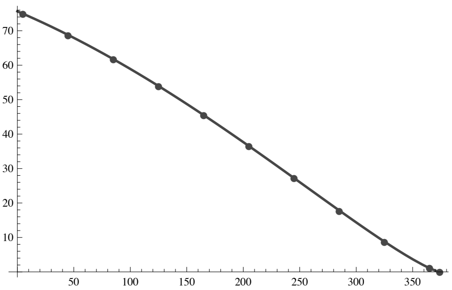

FIGURE 13.3 Surface tension of water vs T.
Source: IAPS tables (1975)[27]

We finally turn to the issue of the critical behaviour of *surface tension*. As per the van der Waals theory, described in section 12.5.1, surface tension must *vanish* near criticality. This is because the density profile, the source of surface tension in the vdW theory, disappears at criticality as the density of both phases become equal. Thus, one should expect that surface tension must vanish as $(T_c - T)^{\beta'}$, with β' a new exponent. At this stage, we can only say that β' must be *positive*.

However, as per discussions of section 12.5.2, and in particular of eqn.(12.62), the *surface entropy* is given by

$$S_s = -\frac{d\sigma(T)}{dT} A \tag{13.2}$$

Accordingly, the surface tension exponent β' can not be less than *unity*, as otherwise the surface entropy would *blow up*! The minus sign in this equation is important, and it makes surface entropy *positive* near T_c. But what is to be noted is that the surface entropy *vanishes* at T_c.

What has been plotted is the data as per the international table of values of surface tension released by the *International Association for the Properties of Steam* (IAPS) [27]. A selection of data points, representative of the temperature range under consideration, is shown by dots; the solid curve is based on the interpolation formula obtained by by N.B. Vargaftik, B.N. Volkov, and L.D. Voljak [75]:

$$\sigma(T) = 235.8 \left(\frac{T_c - T}{T_c}\right)^{1.256} \left\{1 - 0.625 \frac{T_c - T}{T}\right\} \tag{13.3}$$

In the above σ is given in units of $10^{-3} N/m$. The agreement between the data points and the interpolation formula is *excellent* despite the extreme simplicity of the formula. For temperatures lower than about 275° C, the formula yields a marginally higher than *linear* growth, while for temperatures higher than this, the formula yields a marginally *lower* than linear growth. It is clear from the formula that the curve must touch the T-axis with *zero slope*, but this is very hard to see from the graph. Thus the observed surface tension exponent is $\beta' = 1.256$, which is indeed greater than unity as required by entropic considerations discussed earlier.

13.3 Critical behaviour of van der Waals theory

The vdW equation is easily the simplest equation of state for a system that displays *liquefaction* of gases, as discussed at length in chapter 12. In fact, it was the first of any equation to be able to do that. As already noted, the vdW equation also admits a *critical temperature*. This was easily seen as a property of its *isotherms*. Through the *Maxwell construction*, the seemingly unphysical branches of these isotherms were replaced by lines of *phase coexistence* At that level, the critical point played the role of dividing the isotherms into two regions, i.e for $T > T_c$, and the system existed only in the gas phase, while for $T < T_c$, the system could exist in both gas and liquid phases. The fact that above T_c the gas phase could not be liquefied no matter how high the pressure, was a remarkable prediction of the vdW equation! This experimentally well founded fact had indeed appeared baffling till then.

In the vdW system, the critical point appears as a *point of termination* of the phase coexistence curve. This is also a feature that is experimentally observed in many systems. This has a certain subtle consequence of the phases: it means that one can continually pass from a liquid phase to a gas phase (and vice versa) without ever crossing a *phase boundary*!

Because of all these features, the vdW equation would provide an easily analyzable model for phase coexistence *and* critical phenomena. Due to the *law of corresponding states* discussed in section 12.1.3, the vdW equation also predicts that all vdW systems have the same critical exponents. Let us recall those arguments once more: the vdW equation (for one mole)

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{13.4}$$

had its critical point at

$$P_c = \frac{a}{27b^2} \qquad V_c = 3b \qquad RT_c = \frac{8a}{27b} \tag{13.5}$$

In terms of the so called reduced variables $P_r = P/P_c, V_r = V/V_c, T_r = T/T_c$, the vdW equation assumes the particularly simple *reduced form*

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \tag{13.6}$$

Naturally, for all vdW systems the critical point occurs at the same location in terms of the reduced variables, i.e $T_r^c = 1, P_r^c = 1, V_r^c = 1$. What's more, if, say, the latent heat vanishes as $(T_r^c - T_r)^\beta$, the latent heat exponent for *all* systems obeying vdW equation is the same β!

This may appear to be the explanation for the observed universality of universal exponents, but it is not. In fact, we shall see that the exponents predicted by vdW theory do not agree with the observed values. That the vdW equation can not adequately describe the observed critical phenomena *quantitatively* is already evident from the fact that vdW theory predicts the universal value $(P_cV_c/RT_c) = 3/8 = 0.37$ for *all* liquid-gas critical phenomena. As already worked out in the example 12.3, the observed value is only 0.22.

Therefore, one should not expect very accurate numerical agreements between observed critical phenomena and vdW theory. The best that can be hoped for is that gross features of physical phenomena like the vanishing of the latent heat at T_c with an exponent less than unity, vanishing of surface tension with an exponent greater than unity, the slope of the coexistence curve etc. are reproduced by the vdW theory. In this, we shall see, the vdW theory indeed does very well, and in fact it gives the correct trend even far from T_c.

The critical point in vdW theory is governed by the vanishing of the derivatives

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = 0 \qquad \left(\frac{\partial^2 P_r}{\partial V_r^2}\right)_{T_r} = 0 \tag{13.7}$$

The strategy is to examine the system in the vicinity of T_r^c. For that purpose we introduce the variables

$$T_r = 1 - t \qquad V_r = 1 + v \qquad P_r = 1 - p \tag{13.8}$$

So, for fixed t we wish to obtain expressions for v_l for the liquid phase and v_g for the gas phase. As a first step in this direction, let us write down the vdW equation in the reduced form, as given in eqn.(13.6), by *naively* treating all of $(\mathrm{t},\mathrm{p},\mathrm{v})$ to be *small*. Let us take (t,p) to be the *independent* variables; then one can always take (p,t) to be small, but the smallness of the *dependent* variable needs care.

It is straightforward to obtain an expansion for p to the *leading* order:

$$p = 4t - 6\,\mathrm{v}\,\mathrm{t} + \frac{3}{2}\mathrm{v}^3 + \dots \tag{13.9}$$

Here is the subtlety in treating v as also small. Since t,p have been taken to be independent, there is no reason why $p - 4t$ has to be vanishingly small. On the other hand, if v is indeed small, the -6vt will be small compared to 4t, and things will be consistent only if $p - 4t \approx 0$, which it has no reason to! The resolution is clear, for *generic* changes t,p away from the critical point, there is no reason why v, as defined by eqn.(13.8) has to be small. In fact it can be arbitrarily large, as a consequence of the vanishing derivatives in eqn.(13.7).

However, it is clear from the nature of isotherms of the vdW theory (see section 12.1.3, and the figure 12.1 therein), that an isotherm in the vicinity of T_c (but of course with $T < T_c$), will have the liquid and gas volumes *close* to V_c which is another way of saying that v will be small if t,p are both small and lie on the *coexistence curve*. Even in the vicinity of the coexistence curve, but not necessarily on it, v can still be treated as being small.

The coexistence curve itself is given by the locus of points in the P_r, T_r plane such that the Gibbs potentials per unit mass of the two phases are equal. In fact this defines the so called *Maxwell line*, already introduced and discussed in subsection 12.2.1, with the explicit equation for the line given in eqn.(12.43), with the proviso that ek there refer to the liquid and gas phases, respectively. Since we are dealing with a single component system, phase equilibrium can equally well be characterized by the equality of *molar* Gibbs potentials at a given $T\,P$. For this we need the expression for the molar Gibbs potential in *reduced form* worked out in eqn.(12.37). We reproduce it here for better readability:

$$G_r = \frac{C_V}{R}(T_r - T_r \ln T_r) - T_r \ln(3V_r - 1) - \frac{9}{8V_r} + \frac{3}{8}P_r V_r \tag{13.10}$$

Thus the Maxwell line at the point $T, P(T)$ of the coexistence line is defined by

$$G_r^{liq}(T,P) = G_r^{gas}(T,P) \tag{13.11}$$

where V_r takes the value V_r^{liq} in the liquid phase, and V_r^{gas} in the gas phase. It is clear that the part of G_r that only depends on T_r has no role to play, and the equilibrium condition can be stated as:

$$M(V_r^{liq}, T_r) = M(V_r^{gas}, T_r) \tag{13.12}$$

where the truncated 'Maxwell function' $M(V_r, T_r)$ is given by

$$M(V_r, T_r) = -T_r \ln\frac{(3V_r - 1)}{2} - \frac{9}{4V_r} + \frac{T_r}{3V_r - 1} \tag{13.13}$$

In arriving at this equation, P_r has been expressed in terms of V_r, T_r using the reduced vdW eqn.(13.6). Therefore, in order to find $\mathrm{v_l}$, $\mathrm{v_g}$ at a given pressure and temperature, not necessarily in the vicinity of T_c, both $p(\mathrm{v_g}, \mathrm{t}) = \mathrm{p}(\mathrm{v_l}, \mathrm{t})$ have to be solved at the same time. Already, for a given temperature and pressure, the equation satisfied by the volume is a *cubic*, which can, however, be solved analytically. But the difficulty arises in solving the Maxwell line condition in addition, which, when the analytical solution for the cubic is substituted is not even a polynomial equation any longer.

In the vicinity of the critical point, however, both conditions can be handled *perturbatively*. The expansion for $M(\mathrm{v}, \mathrm{t})$ to the same order of accuracy as eqn.(13.9), is

$$M(\mathrm{v}, \mathrm{t}) = -\frac{\mathrm{t}}{2} + \frac{9}{4}\mathrm{v}\,\mathrm{t} - \frac{9}{16}\mathrm{v}^3 + \ldots \tag{13.14}$$

The analysis proceeds as follows: equilibrium at a given temperature requires that the pressures of the liquid and gas phases be the same, i.e

$$-\frac{3}{2}\mathrm{v}_g^3 + 6\mathrm{t}\mathrm{v}_g = -\frac{3}{2}\mathrm{v}_l^3 + 6\mathrm{t}\mathrm{v}_l \quad \rightarrow 4\mathrm{t} = \mathrm{v}_g^2 + \mathrm{v}_l^2 + \mathrm{v}_g\mathrm{v}_l \tag{13.15}$$

It is easily seen that to this accuracy

$$p(\mathrm{v},\,\mathrm{t})+\frac{8}{3}\mathrm{M}(\mathrm{v},\,\mathrm{t})=\frac{8}{3}\mathrm{t} \tag{13.16}$$

As this is *independent* of v, to this accuracy the Maxwell line condition is the same as eqn.(13.15), which does not determine $\mathrm{v_g}, \mathrm{v_l}$ separately. However, even at this stage it is clear that the leading order coexistence curve is given by

$$p(\mathrm{t})=4\mathrm{t} \tag{13.17}$$

We can check the consistency of this with the Clapeyron equation, even without knowing the individual volumes, as long as they are both small. It follows from eqn.(12.36) that ΔS_r, the change in reduced entropy from the gas phase to the liquid phase is $\Delta S_r = 3/2(\mathrm{v_g}-\mathrm{v_l})$. The reduced Clapeyron equation is given by

$$\frac{dP_r}{dT_r}=\frac{8}{3}\frac{\Delta S_r}{\Delta V_r} \qquad \to \frac{dp}{dt}=4+\ldots \tag{13.18}$$

To determine the two volumes separately, we develop both p and M to one higher order:

$$\begin{aligned} p(\mathrm{v},\mathrm{t}) &= 4t-6\mathrm{v}\mathrm{t}+\frac{3}{2}\mathrm{v}^3+9\mathrm{t}\mathrm{v}^2-\frac{21}{4}\mathrm{v}^4+\ldots \\ M(\mathrm{v},\mathrm{t}) &= -\frac{\mathrm{t}}{2}+\frac{9}{4}\mathrm{v}\mathrm{t}-\frac{9}{16}\mathrm{v}^3-\frac{9}{4}\mathrm{t}\mathrm{v}^2+\frac{99}{64}\mathrm{v}^4+\ldots \end{aligned} \tag{13.19}$$

The analog of eqn.(13.16) now reads

$$p(\mathrm{v},\,\mathrm{t})+\frac{8}{3}\mathrm{M}(\mathrm{v},\,\mathrm{t})=\frac{8}{3}\mathrm{t}+3\mathrm{t}\mathrm{v}^2-\frac{9}{8}\mathrm{v}^4 \tag{13.20}$$

Consequently the coexistence condition becomes

$$3\mathrm{t}(\mathrm{v_g^2}-\mathrm{v_l^2})-\frac{9}{8}(\mathrm{v_g^4}-\mathrm{v_l^4})=0 \quad \to (\mathrm{v_g^2}-\mathrm{v_l^2})(8\mathrm{t}-3(\mathrm{v_g^2}+\mathrm{v_l^2})=0 \tag{13.21}$$

This immediately yields $\mathrm{v_g}=-\mathrm{v_l}$. Combining with eqn.(13.15) yields the leading order solution

$$\mathrm{v_g}=2\sqrt{\mathrm{t}}+\ldots \qquad \mathrm{v_g}=-2\sqrt{\mathrm{t}}+\ldots \tag{13.22}$$

13.3.1 Critical exponents of vdW theory

Therefore, the *reduced latent heat* to leading order is given by

$$L_r(t)=6\sqrt{t} \tag{13.23}$$

Therefore the exponent β for vdW theory is 0.5 as against the observed value for fluids and binary mixtures which is close to 1/3. The satisfactory aspect of the vdW theory is that it gets this exponent to be less than unity. The surface tension close to criticality can be worked out from van der Waals celebrated paper [74, 62]; we shall simply work with the results obtained there.

$$\sigma(t) \simeq (\mathrm{v_g} - \mathrm{v_l})^3 \simeq \mathrm{t}^{\frac{3}{2}} \tag{13.24}$$

The vdW theory also predicts the prefactor, but we shall only focus on the exponent. Thus the prediction of the theory for the surface tension exponent β' introduced above is 1.5, whereas the observed value is 1.256. Again the exponent is larger than unity as expected on grounds of finite surface entropy. In fact, the surface entropy near criticality, as given by vdW theory is

$$S_s \simeq \mathrm{t}^{0.5} \tag{13.25}$$

Curiously, this is also the leading behaviour near criticality of *bulk entropy* too! The interface thickness, according to the vdW theory is given by

$$\mathrm{h} \simeq \ln\Lambda(\mathrm{v_g} - \mathrm{v_l})^{-1} \simeq \ln\Lambda\mathrm{t}^{-0.5} \tag{13.26}$$

Unfortunately, van der Waals analysis of the interface thickness near criticality is not as clean as his other derivations, and he had to introduce a *cut off* Λ to obtain meaningful results. This expression is for planar interfaces only. We shall discuss the behaviour of interfacial thickness in real life later on.

13.3.2 Even more exponents

An additional exponent, δ, is defined by the behaviour as one approaches the critical point along a *critical isotherm*, defined by $t = 0$, or equivalently by the behaviour along a *critical isobar* defined by $p = 0$ [3, 34]:

$$t = 0; \quad p \simeq |\mathrm{v}|^{\delta} \qquad \mathrm{p} = 0 : \mathrm{t} \simeq |\mathrm{v}|^{\delta} \tag{13.27}$$

From eqn.(13.9), it is clear that both give $\delta = 3$. The *critical isochore* is given *exactly* by $\mathrm{p} = 4\mathrm{t}$ even arbitrarily far from the critical point.

There is also the so called *susceptibility exponent* which for the liqid-gas system is essentially the exponent governing the behaviour of the *isothermal compressibility*:

$$\kappa_T^r = -\frac{1}{V_r}\left(\frac{\partial V_r}{\partial P_r}\right)_{T_r} \simeq \mathrm{t}^{-\gamma} \tag{13.28}$$

using eqn.(13.9) it follows that $\gamma = 1$ for vdW theory.

Another interesting issue is the behaviour of C_P near the critical point. It should be noted that C_V in vdW theory is an input; for *ideal* vdW case, $C_V(T) = const.$, so there is no special critical behaviour. The exponent α, defined via $C_V(\mathrm{t}) \rightarrow \mathrm{t}^{-\alpha}$, is therefore zero. To investigate C_P, we make use of the reduced form of one of the identitities in eqn.(3.52) (see problem 12.1):

$$C_P - C_V = \frac{3RT_r}{8}\left(\frac{\partial P_r}{\partial T_r}\right)_{V_r}\left(\frac{\partial V_r}{\partial T_r}\right)_{P-r} \rightarrow -\frac{3R}{8}\left(\frac{\partial p}{\partial t}\right)_{v}\left(\frac{\partial v}{\partial t}\right)_{p} \tag{13.29}$$

For this purpose, it is useful to recast eqn.(13.9) in the form

$$2\mathrm{p} - 8\mathrm{t} + 3\mathrm{v}\mathrm{p} - 3\mathrm{v}^3 = 0 \tag{13.30}$$

Using this, it is easy to see that in the vicinity of the critical point

$$C_P - C_V = 8R\frac{1}{\mathrm{p} - 3\mathrm{v}^2}\frac{1}{2 + 3\mathrm{v}} \tag{13.31}$$

Approaching along the critical isochore:
Along this line $\mathrm{v} = 0, \mathrm{p} = 4\mathrm{t}$ (in fact this is true even if one is not in the vicinity of T_c). Hence $C_P - C_V \simeq \mathrm{t}^{-1}$. For the ideal vdW case, since C_V remains finite by choice, one concludes that $C_P \simeq \mathrm{t}^{-1}$. If an additional exponent α' is introduced via $C_P(\mathrm{t}) \to \mathrm{t}^{-\alpha'}$, one concludes that for approach along the critical isochore $\alpha' = 1$.
Approaching along the critical isobar:
Along the critical isobar $\mathrm{p} = 0, \mathrm{v}^3 = -8\mathrm{t}/3$. It should be noted that p, t were *positive* only along the coexistence curve. Away from it, they can take both signs. However, along the critical isobar a negative t is only compatible with a positive v, i.e a gas phase, and likewise a positive t is only compatible with a liquid phase. In either case $|\mathrm{v}| \simeq |\mathrm{t}|^{1/3}$, and one sees that $C_P \simeq |\mathrm{t}|^{-2/3}$ so that $\alpha' = 2/3$ now. Since C_P does not have a finite discontinuity, Ehrenfest second order theory is *not applicable* to the vdW critical point!
Approaching along a critical isotherm:
We have already seen that along a critical isotherm $2\mathrm{p} = 3\mathrm{v}^3$. So we can investigate the behaviour of C_P along an isotherm by introducing yet another specific heat exponent via $C_P \simeq p^{-\tilde{\alpha}}$. Then, using the relations above it is easy to see that along a critical isotherm $C_P \simeq p^{-2/3}$, so that $\tilde{\alpha} = 2/3$.

In fact critical exponents can be introduced for any approach along a given path so that there is only one *dependent* variable, and study how some physical quantity like latent heat, surface tension etc. behaves as one approaches the critical point. To reiterate, if the path is the coexistence curve, one takes temperature as the independent variable; if the path is a critical isotherm, one takes the independent variable to be the pressure etc.

13.3.3 Beyond the critical region of vdW theory

The advantage of an explicitly analytic model like vdW theory is that one can study the behaviour of any physical quantity one is interested in any region of the space of thermodynamic variables. The essential ingredients involved are simultaneous solutions to the liquid equation of state $P = P(V_l, T)$, of the gas equation of state $P = P(V_g, T)$, and the Maxwell line, or equivalently, the equality of the Gibbs potentials in the two phases.

In this age of computers, one can envisage carrying this out *numerically*. A good starting point is where the solution is $P = P_c, V_l = V_g = V_c, T = T_c$. Then the numerical implementation will be to go to temperature very close to T_C, but lower than it, and *self-consistently* determine P, V_l, V_g at this new temperature from the three mentioned

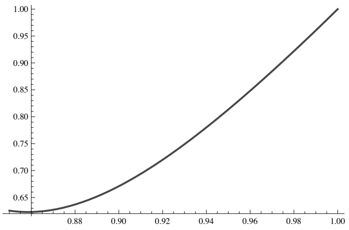

FIGURE 13.4 Coexistence curve in vdW theory.

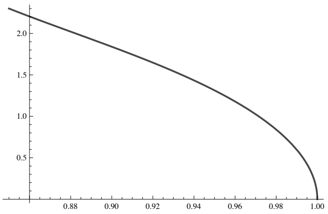

FIGURE 13.5 Latent heat in vdW theory.

equations. In this manner, one goes on *iteratively* solving the relevant equations to any desired accuracy. The initial stages of the iteration, however, require great care because of the vanishing of the derivatives as in eqn.(13.7).

An analytical approach to the problem consists in essentially adding more and more terms in the *perturbative* expansons of the functions $p(\mathrm{t},\mathrm{v})$ and $M(\mathrm{t},\mathrm{v})$, and iteratively solve the equations. In this manner one obtains $\mathrm{v_l}, \mathrm{v_g}$ as series expansions in powers of $\sqrt{t}$. Once the series expansions for the two volumes are obtained, any thermodynamic quantity of interest can also be obtained as a series expansion by simply substituting the expressions for the volumes. The main drawback of such an analytical expression, in general, is that the manipulations become extremely tedious as one goes to higher and higher orders. More seriously, one has to contend with issues like *radius of convergence* for the series etc. There are questions of *unphysical behaviour* even while staying within the radius of convergence. For example, $V_l = 1 + \mathrm{v_l}$, being the *physical volume* of the liquid, should never be *negative*. Actually, for the vdW case the reduced volume V_r should always be greater than 1/3. The pressure too should only show a *monotonically increasing* behaviour.

A third, hybrid, approach is to perform the initial steps analytically using the perturbative method around a small neighbourhood of the critical point to avoid the numerical pitfalls due to the vanishing derivatives exactly at T_c, and then perform the rest numerically.

We shall not present the details and systematics of this perturbative approach, but urge the interested reader to work them out!. In the two plots in figs. (13.4,13.5) we have presented the results for the coexistence curve and the latent heat as a result of a series expansion upto $\mathrm{t}^{5/2}$:

$$\begin{aligned}\mathrm{v_g} &= 2\mathrm{t}^{1/2} + \frac{18}{5}\mathrm{t} + \frac{147}{25}\mathrm{t}^{3/2} + \frac{7992}{875}\mathrm{t}^2 + \frac{34183}{2500}\mathrm{t}^{5/2} + \ldots \\ \mathrm{v_l} &= -2\mathrm{t}^{1/2} + \frac{18}{5}\mathrm{t} - \frac{147}{25}\mathrm{t}^{3/2} + \frac{7992}{875}\mathrm{t}^2 - \frac{34183}{2500}\mathrm{t}^{5/2} + \ldots \qquad (13.32)\end{aligned}$$

The radius of convergence was around $\mathrm{t}^{1/2} = 0.66$, but within this the volumes remained physically sensible. However, the resulting equation for the coexistence curve:

$$P(t) = 1 - 4\mathrm{t} + \frac{24}{5}\mathrm{t}^2 - \frac{816}{875}\mathrm{t}^3 + \frac{5212128}{21875}\mathrm{t}^4 + \ldots \qquad (13.33)$$

appears to have a very low radius of curvature of $\mathrm{t} = 0.004$; but this could be misleading, and as the terms are alternating in sign, a reliable estimate for the radius of convergence may only obtain with the next term. It is a healthy sign that the series for P has only integer powers in it.

Above $\mathrm{t} = 0.15$, the pressure starts showing unphysical behaviour like rising with decrease of temperature. But in the range $\mathrm{t} = (0.15, 0.0)$, the plotted curves look remarkably like observed data. It is clear that a fuller treatment of the problem will remove all these pathologies, which are in any case absent in the isotherms, and one can conclude that the vdW theory will reproduce the gross observed features to regions far removed from the critical region.

13.3.4 From van der Waals to Wilson via Landau

As already mentioned, *universality* is the most astounding aspect of critical phenomena. Van der Waals was the first to discover a particular form of universality as embodied in the *law of corresponding states*. According to Levelt Sengers [38], van der Waals was also the first to explicitly invoke the concept of a critical exponent, done so in the context of surface tension in a letter of Nov 1893 to Kammerlingh Onnes (who is also credited with the concept of corresponding states). We already saw that the vdW theory correctly accounts for the existence of critical exponents, both for latent heats in fluids, as well as for the more non-trivial case of surface tension. But the values predicted, 0.5 for β instead of the universally observed value closer to 1/3, and 1.5 for the surface tension exponent as against the observed, again universal, value of close to 1.25, are clearly not correct.

Several issues come to one's mind in this connection. We saw that the vdW theory was grossly inaccurate in its prediction of the *critical compressibility* Z_c; its predicted value is 0.375 while the observed value for water is 0.22. Therefore one can ask whether the critical exponents can be improved by choosing a different gas equation, as for example, the *Clausius equation* introduced in eqn.(1.16). Indeed, for carbon dioxide, the Clausius equation agrees very well with the observed critical parameters. The Clausius equation has *three* parameters unlike the vdW equation, which has two. The compressibility ratio is not fixed, but if all the three parameters are *positive*, is constrained by $1/4 < Z_c < 3/8$. The Clausius equation too admits a law of corresponding states. In fact, Planck clearly states in section 30 of his book (1910 edition) [57] that any equation of state that has at most *three* independent parameters always admits a law of corresponding states. But an analysis of critical phenomena for the Clausius equation, in the same way as done for the vdW equation, reveals that the exponents are the *same* as in vdW theory!

Landau's theory of critical phenomena allows one to understand this universalities among universality, in the sense that even *different* reduced equations, each one of which represents infinitely many physical systems, are still governed by the same critical exponents! A notion of great importance in the Landau theory is that of *the order parameter*. This parameter distinguishes the state of the system below T_c from its state above T_c. In water, and also vdW theory, the order parameter is $\mathrm{v_g} - \mathrm{v_l}$. Above T_c, its value is zero, and below T_c it is nonzero. In vdW theory, it behaves like

$\mathrm{t}^{1/2}$ near critical point. In the vdW theory, close to critical point, $\mathrm{v}^2 = 4\mathrm{t}$, and this equation is *symmetric* under $\mathrm{v} \leftrightharpoons -\mathrm{v}$. This is also the symmetry of the *Ising model*. The importance of this remark will be elucidated in the next section.

Now the Landau theory amounts to writing a very general expression for the relevant thermodynamic potentials (F or G), in terms of t and the order parameter. In the order parameter space, for example, the Gibbs potential close to the critical temperature looks like fig.(12.6) with the middle figure representing coexistence. As one approaches criticality, the figure approaches a curve with a single minimum at zero order parameter. It is easy to see then that in the vicinity of the critical point, the order parameter has the Ising symmetry mentioned above, and further that it behaves like $\mathrm{t}^{1/2}$. Thus the value of $\beta = 1/2$ is *generic* to Landau theory. The reader is referred to Landau's book for a very clear exposition of these ideas [34]. The other exponents emerging from the Landau model are:

$$\beta = \frac{1}{2} \quad \alpha = 0 \quad \gamma = 1 \tag{13.34}$$

the same values we found for the vdW theory.

13.3.5 The renormalization group

A great breakthrough in understanding critical phenomena and the observed critical exponents came through the works of Kenneth Wilson, and his idea of *Renormalization Group*. It is beyond the scope of this book to give an adequate account of this great development. We try to give a basic flavor of it, and direct the reader to Wilson's original papers [79] or the review article by Kogut and Wilson [32]. A very elementary, but conceptually accurate account which is also very readable is by Kadanoff and Maris [29]. The basic idea of the renormalization group is that unlike in thermodynamics where the system is *homogeneous* or nearly homogeneous, *fluctuations* about the homogeneous values ought to be taken into account, and in fact these fluctuations become very strong as the critical point is approached. An experimental manifestation of this is the so called *critical opalescence* whereby the liquids near the critical temperature scatter light strongly. The explanation for this originally came from Einstein.

As a result of such strong fluctuations, different parts of the system become *correlated*. The so called *correlation length* signifies the scale over which parts of the system are strongly correlated. The renormalization group theory says that the correlation length *diverges* as the critical temperature is approached. This divergence is characterized by the *correlation length exponent*. A striking consequence is that as the correlation length diverges, all other finite length scales in the problem become irrelevant, and the correlation length sets the only scale. Because of this, all quantities which have dimensions will also scale as the appropriate power of the correlation length. The upshot is that, say, the Gibbs potential instead of being a function of *two* independent variables, becomes a function of a single ratio, and near criticality the dominant part of the potential has the form [34, 3]

$$G \simeq |T-T_c|^{2-\alpha} f\left(\frac{B_e^{1+\frac{1}{\delta}}}{|T-T_c|^{2-\alpha}}\right) \tag{13.35}$$

B_e for the liquid-gas case is $\mathrm{p}-4\mathrm{t}$ [34]. Because of this, one gets relationships between the various exponents i $\alpha, \beta, \gamma, \delta, \beta'$ etc. called the *scaling relations*:

$$\alpha + 2\beta + \gamma = 2 \qquad \gamma = \beta(\delta - 1) \tag{13.36}$$

The exponents of Landau theory, which encompasses vdW theory, clearly satisfy these scaling relations. The Landau and vdW exponents are called *classical* because they ignore fluctuations.

The power of the renormalization group is that according to it the exponents only depend on (i) the dimensionality of space, (ii) the number of different order parameters, also called the *order parameter dimensionality*, and (iii) the symmetries of the order parameter. It is for this reason that the exponents of a liquid-gas system must be, according to renormalization group theory, the same as that of the *three dimensional Ising model*!

The three dimensional Ising model, unlike its two dimensional cousin, has not yet been solved *analytically*. However, a great many techniques are available which have been put to use to 'calculate' the critical exponents of the 3d Ising model. In particular, Le Guillou and Zinn-Justin have reported the exponents [36]

$$\beta = 0.33 \quad \alpha \approx 0.1 \quad \gamma = 1.242 \quad \delta \approx 4.82 \tag{13.37}$$

These too satisfy the scaling relations of eqn.13.36. The surface tension exponent from the 3d Ising model is given by $\beta' = (4-2\alpha)/3 \approx 1.27$. This is remarkably close to the experimentally determined value of 1.256.

13.3.6 Renormalization group inspired thermodynamics

Though the fluctuations are beyond the scope of thermodynamics, one can still use thermodynamics to give a very satisfactory description of, say, the liquid-gas transitions even far away from the critical region. The idea is to use the 'dominant' potential of eqn.(13.35) as the thermodynamic potential for a description in the close vicinity of the critical point, where the various exponents are what a proper renormalization group analysis would give.

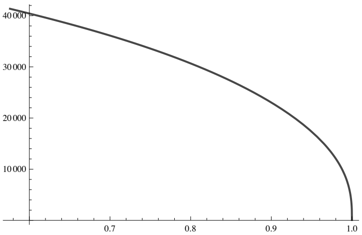

FIGURE 13.6 3d Ising model inspired latent heat.

So, for the water case one would use the values as given by eqn.(13.37), and

$\beta' = 1.27$ for the surface tension analysis. To describe the phenomena far away from the critical point, one adds a power series in t. It is remarkable that the surface tension interpolation formula based on the 3d Ising model exponent along with a single correction term (though in this case as a factor), completely explains the entire data all the way up to the boiling point of water!

In a completely similar spirit Torquato and Stell [73] proposed the following interpolation formula for the latent heat:

$$L(\mathrm{t}) = \mathrm{a}_1\mathrm{t}^{\beta} + \mathrm{a}_2\mathrm{t}^{\beta+\Delta} + \mathrm{a}_3\mathrm{t}^{1-\alpha+\beta} + \sum_{\mathrm{i}=1}^{3} \mathrm{b}_\mathrm{i}\,\mathrm{t}^\mathrm{i} \tag{13.38}$$

where they used an additional exponent coming from the Ising model, i.e $\Delta \approx 0.50$. They found the coefficients a, b through a best fit to the IAPS data. We have shown, in figure 13.6, a plot based on such a formula where the coefficients are very nearly those used by them, and multiplying their formula by 18 to get the molar latent heat. The agreement with actual data, say, from the Dortmund data bank is excellent. The IAPS has implemented such a *renormalization group based thermodynamics* by a much more elaborate formula [77], but the idea is the same as what has been explicitly discussed.

13.4 Problems

Problem 13.1 *Derive the equation for the critical adiabat, i.e an adiabat passing through the critical point, for a vdW system.*

Problem 13.2 Calculate the critical exponents β and β' for the Clausius equation given in eqn.(1.16). Make use of the reduced form of this equation (see problem 12.2).

Problem 13.3 Calculate the specific heat at constant area for a surface whose surface tension has the form given by eqn.(13.3). What is the physical significance of such a specific heat? Does this specific heat remain finite at T_c or diverge? If it diverges, what is the corresponding exponent?

Problem 13.4 Consider a dilute solution made up of a solvent and a solute. Show that the surface tension of the dilute solution σ is related to the surface tension of the pure solvent σ_0 according to

$$\sigma(T) - \sigma_0(T) = -\frac{n_s}{T}A \tag{13.39}$$

where A is the area of the surface and n_s the surface concentration of the solute. Do you see any resemblance between this equation and van't Hoff formula for osmotic pressure?

Problem 13.5 If the surface tension $\sigma(T)$ is a function of temperature only, and if the liquid is described by vdW theory, show that the law of corresponding states asserts that the surface tension of all vdW fluids must be of the form $\sigma(T) = A\,\frac{\mathrm{a}}{\mathrm{b}^{5/3}}\,f(T/T_c)$. Apply this to eqn.(13.3) to show that B in that formula must have the form $B = B_0\,(\mathrm{a}/\mathrm{b}^{5/3})$ where B_0 does not depend on the vdW parameters. Given that B for water is $235.8 \cdot 10^{-3}$ N/m for water, estimate it for Helium using the results of the previous problem, and compute the surface tension of liquid He_4 at 3 K given its $T_c = 5.2K$.

14 Approach to Absolute Zero

We saw in section 3.8 of chapter 3 (Nernst-Planck Theorem) that there are thermodynamic arguments to indicate the difficulty of reaching the absolute zero temperature, i.e 0 K. While it could not really be strictly proven using only the first and second laws, the powerful analysis of Nernst hinted at the desirability of introducing a separate law, usually called the *Third Law* of thermodynamics. In this chapter, we explore, from a purely experimental point of view, the issue as to *how close to absolute zero can one get?* An excellent source for further reading is Lounasmaa's book *Experimental Principles and Methods Below 1 K* [40]. Another excellent source is Frank Pobell's book *Matter and Methods at Low Temperatures* [58]. The reader is also recommended to the extensive, and highly readable articles on this subject by Srinivasan [66, 67, 68, 69], as well as by Per Delsing [12].

It turns out that one can get pretty close. But the still intriguing question is whether any of the fundamental theories of physics pose an *actual* limit as to how far one can go. Certainly quantum theory on its own does not seem to pose any limitation, nor do any of the theories of the elementary particle world. Quantum gravity theories on the other hand, have thrown tantalizing hints at a deeper connection with thermodynamics, that they may well set such a limit. But for the moment all such thoughts are purely speculative, and really far from the true spirit of thermodynamics.

Difficulties, if not outright limitations, in experimentally achieving a temperature arbitrarily close to absolute zero, seem to be manifold. Thermal insulations, for example, have to be nearly perfect. In its broadest sense, this is a problem in ultimate refrigeration. Refrigeration, again, can be broadly characterized as the technique for extracting heat from a body, thereby cooling it. This can not happen *spontaneously* if a conflict with the basic laws of thermodynamics is to be avoided. Specifically, work needs to be done, and the difficulty in reaching this thermodynamic Holy Grail can be thought of as the insurmountable amount of work that one may end up doing. In this chapter, we take a look at some novel refrigeration techniques that have driven the quest of reaching as close to absolute zero as possible. Curiously, the winner of the race, the Bose-Einstein Condensate (BEC), reaching the record limit of 500 *picokelvins* (500 pK or half a nK), does so by essentially exploiting evaporative cooling!

14.1 Standard methods of refrigeration

One of the most common techniques of refrigeration uses the principle of so called *evaporative cooling*. This has been used in ancient Egypt as long ago as 2500 BC and in India even as early as 3000 BC to cool water. In India, even to this day it is popular as a poor man's way of cooling water by as much as 15 degree Celsius! The technique is simplicity personified, and consists of a narrow-necked earthenware pot filled with water. The pot being porous, water oozes out, very much as in a capillary tube, and the hot, dry air outside evaporates the water, taking away the latent heat from the pot and subsequently from the water inside it. The total amount of cooling depends on the total mass of water converted to vapor.

If a breeze of dry air were to be incident on the pot, the *rate* of evaporation is enhanced and so also the cooling rate. This is so, as the breeze continually replenishes the supply of dry air, facilitating the process of evaporation. A familiar day-to-day example of this is the cooling effect produced on our bodies by a breeze on a hot sweaty day.

14.1.1 Cooling power

A way of quantifying the efficiency of a cooling, or equivalently, a refrigerating process, is through the so called *cooling power*. This is the same as the rate of cooling alluded to before, it is $\dot{Q}$, the rate at which heat is removed. This is not a proper thermodynamic concept, because in thermodynamics the concept of time does not make sense. However, what does make thermodynamic sense is the amount of heat removed ΔQ when a certain amount of cooling agent has been utilised. In the context of evaporative cooling, this is the amount of water that has evaporated. Therefore $\frac{\Delta Q}{\Delta m}$ is thermodynamically sensible, and hence *computable* from thermodynamics.

But in a refrigerating device in real life, the design of the refrigerator (pumps, compressors etc.) is such that the *rate* $\dot{m}$ at which a refrigerant evaporates can be specified and this, when combined with the thermodynamics of the device, allows one to compute the cooling power.

In all methods based on evaporative cooling, if δm is the mass of the substance that has evaporated, then the heat extracted is $\delta m \cdot l$ where l is the latent heat of vaporisation per unit mass of the refrigerant. Then $\delta Q = \delta m l$ and $\dot{Q} = \dot{m} \cdot l$. In this, l of course has a thermodynamic meaning, but not $\dot{m}$.

In all cases of refrigeration, the heat extracted will depend (in most cases linearly) on the amount of what may be called the *control parameter*. In evaporative cooling this is clearly the mass of the substance that has evaporated; in *Adiabatic Demagnetization*, discussed later in this chapter, it is the amount of the magnetic field by which a magnetic substance is *demagnetized*; and in the extremely novel *acoustic refrigeration* it is the acoustic power etc.

Cooling power is clearly a good indicator of the preferability of the particular mode of refrigeration. At a given temperature, a method with higher cooling rate will result in *faster* refrigeration. But care should be taken not to confuse cooling power with the *Coefficient of Performance* (COP) of a refrigerator. This latter concept has been discussed earlier.

Is it then meaningful to compare the cooling powers of different refrigerators, from a thermodynamic point of view? In general not, as no meaningful comparisons can be made about different control parameters. With methods of refrigeration involving the *same* substance and consequently the same control parameter, it is indeed thermodynamically sensible to compare the cooling powers.

As an example, consider different methods of refrigeration involving He_3. These could be the Helium-cryostat, dilution refrigeration, or Pomeranchuk cooling (all of these will be discussed later in this chapter). The amount of cooling in all of them depends on the amount of He_3 pumped out of the system. Therefore, a comparison of the efficacy of cooling can indeed be made among these methods by comparing the amount of heat carried away per unit mass of He_3 pumped. Even if the refrigerants are different, as for example is the case for He_3 and He_4 cryostats, a thermodynamically meaningful comparison of cooling powers can be made by comparing the heat extracted per unit mass (or, per mole) of the refrigerant.

But clearly, there is no natural way of comparing the cooling power of a Helium cryostat with the cooling power of an Adiabatic Demagnetization Refrigerator(ADR) where the heat carried away depends on the amount of demagnetization. However, a meaningful comparison can indeed be made between an ADR using paramagnetic salts and an ADR using *nuclear* magnetism. Both these methods will also be discussed in detail later. This can be done by comparing the heat extracted per unit of magnetic field demagnetised.

An implication of the third law is that *all* cooling powers must vanish as absolute zero is approached. We will see clear evidence for it in the various refrigeration methods to be discussed. This is physically achieved in very different manners, and the reader is urged to carefully examine these differences.

In what follows, we shall be mostly interested in refrigeration techniques that have proved useful in, so to say, the *last mile* as far as the journey to absolute zero is concerned. Therefore, we shall not deal with domestic or even industrial or other scientific refrigeration techniques.

14.2 Helium cryostats

The principle behind this class of refrigeration is that when liquids boil at their boiling points (normal or otherwise), latent heat is carried away from the body to be cooled. To reach as low a temperature as possible, one needs to identify liquids with as low a boiling point as possible. As per the Clapeyron equation, the boiling point can be lowered by working under reduced pressures. But with reduced vapor pressures, the density of the vapor goes down. This means the pumping rate must be enhanced correspondingly. As has already been shown in chapter 15, the vapor pressure has an exponentially falling dependence on temperature of the form

$$P(T) = c(T) \cdot e^{-\frac{\Lambda}{RT}} \tag{14.1}$$

where Λ is the *molar* latent heat, and $c(T)$ can in principle have some power law dependence on temperature. $c(T)$ can also depend on the substance. As was seen earlier, in the Debye(Einstein) models of solids, the vapor pressure in the process of *sublimation* is such that $c(T) \approx T^{-\frac{1}{2}}$. But for us, the important point is that vapor pressure drops exponentially. It helps to introduce a characteristic temperature scale $T_v = \frac{\Lambda}{R}$, in terms of which the exponential dependence of vapor pressure can be reexpressed as $e^{-\frac{T_v}{T}}$. The significance of this is that when $T << T_v$ the vapor pressure becomes negligibly small.

If we treat the vapor as an ideal gas, the density of the vapor is given by $\rho = \frac{M}{RT} P(T)$ (M is the molecular weight). The rate at which the vapor is pumped out of the system is then given by

$$\dot{m} = \rho S_p = S_p \frac{M}{RT} P(T) = S_p \frac{M}{RT} c(T) e^{-\frac{T_v}{T}} \tag{14.2}$$

Here S_p is the rate of pumping the vapor, usually expressed in *litres/sec*. The cooling power is, consequently,

$$\dot{Q} = \dot{m}\, l(T) = \rho S_p = S_p \frac{M}{RT} P(T) = S_p \frac{M}{RT} c(T) e^{-\frac{T_v}{T}} l(T) \tag{14.3}$$

Even though the c(T)/T factor is larger at lower temperatures, the exponential fall far outweighs this. Therefore, as one operates at temperatures well below T_v, for a given S_p, the cooling power becomes extremely small. Up to a point, this can be compensated through a corresponding increase in S_p. But beyond a point, that option becomes unfeasible, and then this method of refrigeration has to be given up.

Before discussing specific details, let us again note some generalities. As the absolute zero is approached, the cooling power rapidly vanishes. In this particular case, not only does the vapor pressure go to zero, so does the latent heat. The latter follows from the fact that Nernst-Planck theorem demands that all entropy differences must vanish at absolute zero.

The asymptotic vanishing of the cooling power as absolute zero is approached means that it gets harder and harder to lower the temperature of a body, making the attainment of absolute zero absolutely impossible. Had the cooling power remained *finite* at absolute zero, there would not have been any such impediment.

14.2.1 He4 cryostat

Let us now turn to a discussion of the He4 cryostat. We have already briefly discussed the phase diagram of He4 in chapter 14. What concerns us for the present discussion is that part of the phase diagram in which He4 exists in both the liquid and gaseous phases. The first noteworthy feature is that the vapor phase persists all the way to absolute zero (more precisely, up to an arbitrary neighbourhood of absolute zero).

There is a critical point at 5.19 K, beyond which there is no distinction between the liquid and gas phase. As the temperature is lowered, there is coexistence between the so called He I liquid phase and vapor. As already mentioned before, He4 exists in *two* liquid phases. There is a *continuous* line of critical points separating the liquid He I and liquid He II phases. This is the so called line of λ-transitions. This meets the coexistence line between the vapor and liquid I phases at what is called the λ-point at a temperature of 2.18 K at a pressure of roughly 0.05 Atm. For our discussion it means that up to 2.18 K there is coexistence between the vapor and liquid I phase, and below that a coexistence between vapor and liquid II phase. The liquid II phase is called the *superfluid* phase and is marked by a number of very remarkable properties.

The normal boiling point of liquid He (liquid I, also called the normal liquid) is 4.23 K and the *molar latent heat* of vaporisation is roughly 83 J. Thus the characteristic temperature T_v for this case is around 10 K. Already the normal boiling point itself is low compared to T_v.

Therefore by boiling liquid He4 at atmospheric pressure, one can reduce the temperature of a body placed in a He4 cryostat to 4.23 K. By boiling the liquid at lower pressures (facilitated by pumping), the boiling point can be lowered and so also the temperature to which the body can be cooled. The limitation to this process of cooling, as already explained, comes from the steep fall in vapor pressure with temperature. Already at the λ-point this has fallen by a factor of 20 compared to the normal boiling point. A further lowering of the boiling point by 1 K, that is to a temperature of 1.2 K, is still possible. Beyond that the pumping requirements become prohibitive. Thus this is the lowest temperature that can be practically reached in a He4 cryostat. At this temperature He4 is already in its superfluid state. With a thermal conductivity some million times larger than the normal liquid, the cryostat becomes highly vulnerable to thermal leaks.

14.2.2 He3 cryostat

Now let us turn to the improvement in cryogenics that result by just replacing He4 by its lighter (though much more expensive) isotope He3. At a fundamental level the difference between He3 and He4 could not have been more dramatic. While He4 is what is called a *Bosonic* system, He3 in contrast is *Fermionic*.

We have discussed the phase diagram of He3 also in chapter 14. There we presented two such diagrams for He3. One was a 'low resolution' phase diagram which showed only the liquid, gas and the solid phases. The maximum pressure was about 5 MPa and temperature resolution of about 0.1 K. We also a displayed a high resolution 'modern' phase diagram, which, in addition to these three phases showed two additional *superfluid* phases. While the low resolution picture had no triple points at all, the latter had several. But to see these additional features one had to probe ultra-low temperatures of the order of 0.1 mK but over a comparable range of pressures. For the purposes of this chapter, the low resolution picture suffices.

The features of importance to us are the critical point at 3.35 K, the normal boiling point at 3.19 K, and the molar latent heat of 26 J. The characteristic temperature T_v turns out to be 3.13 K, very close to the normal boiling point itself. Thus at any given temperature (we are now thinking of temperatures of a few K), the vapor pressure of He3 is *significantly* higher. This is shown in figure 14.1 where the top curve is that of He3, and the bottom that of He4. The pressure is in Kpa and temperature in mK. This has been drawn based on the solution to problems 14.2 and 14.3. For a real-life comparison see Pobell [58]. This means one can expect a much larger cooling power with He3 cryostats as compared to their He4 counterparts. Additionally,

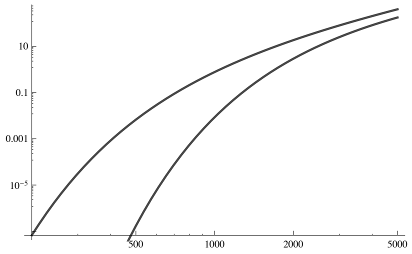

FIGURE 14.1 A comparison of He3 and He4 vapor pressures.

one can go to much lower temperatures where the vapor pressure is still reasonable enough to use pumping effectively.

The lowest temperature reachable is about 0.25 K which is about a fifth of what is reachable with He4. It should be noted that as fractions of the characteristic temperature T_v, the lowest temperatures reachable by both He4 and He3 cryogenics are comparable, about a tenth. The reason for this should be clear; what limits going to lower and lower temperatures is the steep fall of vapor pressure with temperature, and as we have seen, that is controlled essentially by the ratio $\frac{T}{T_v}$.

Though He3 is a lot more effective in reaching lower temperatures, it is also a very expensive option, and should be used only where necessary. In other words, if some desired temperature is reachable through a He4 cryostat, it is wasteful to use He3 to achieve the same temperature. The main reason for why He3 is so expensive is that its natural abundance is only 10^{-7} that of He4.

14.3 Dilution refrigeration

14.3.1 Thermodynamics of He3-He4 mixtures

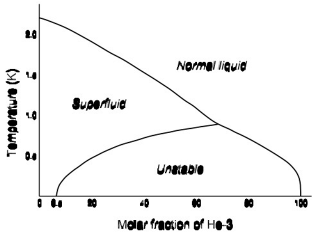

FIGURE 14.2 He3-He4 mixture

The basis for this novel means of refrigeration is in the fascinating thermodynamics of He3-He4 mixtures. This is best understood in terms of the phase diagram for such mixtures, shown in fig.(14.2).The temperature range shown is 0-2.2 K and plotted on the horizontal axis is the *molar fraction* of He3 in the mixture. If N_3 is the number of moles of He3 and N_4 the number of moles of He4, the molar fraction $x = \frac{N_3}{N_3+N_4}$. Let us first examine the region of very low x, which corresponds to the mixture being composed of almost entirely He4. The temperature being so low, He4 is in a liquid state. At $x = 0$, which is pure He4, 2.18 K represents the λ-point, already alluded to before. Above this temperature, we have the *normal* liquid phase and below it the *superfluid* liquid phase. As the concentration of He3 is increased, this normal-superfluid λ-transition persists but the transition temperature shifts. This can be compared to the phase diagram of dilute solutions discussed in chapter 13. Of course, when the concentration of He3 is no longer small, the dilute solution theory is not expected to hold.

But even before going to regions of higher concentration, already there is something very peculiar about this system, at least from a classical point of view (see also Srinivasan [68]). We learned about the *Gibbs paradox* in the context of *entropy of mixing*. In the thermodynamic context, this arose out of the *nonextensivity* of the naive expression for entropy, say, of even the ideal gas. You may recall that this led to the paradoxical situation of an entropy gain by mixing two volumes of the same gas. Since entropy in thermodynamics can only be determined modulo a constant, this could be circumvented by a suitable constant contribution to entropy, but even with that modification, there was always the gain in entropy upon mixing two different substances, signifying the essential irreversibility involved.

Now if we combine this with Nernst-Planck theorem, then classically one has to conclude that there can be no mixtures at absolute zero! This follows on noting that the entropy of *all* substances must vanish at absolute zero. Since the individual components themselves have vanishing entropy, any mixture of them will have non-vanishing entropy, contradicting Nernst-Planck theorem! But the phase diagram indicates the existence of a mixture phase all the way up to absolute zero. Not only that, the limiting concentration of He3 is some 6.5% which is non-negligible! There is no resolution within classical physics for this amazing phenomenon. Only a *quantum statistical mechanical* treatment can explain this. Then it turns out that the mixture at absolute zero indeed has zero entropy. The nonvanishing concentration of He3 very close to absolute zero will be seen to play a crucial role in the working of a dilution refrigerator!

Moving to higher than this 6.5% concentration, one finds the other novel aspect of this system. Not all combinations of temperatures and concentrations are permissible. In fact, there is a whole region of the phase diagram where no stable configuration is possible. As this is a very important aspect of this system, let us look at it step by step. So, when the concentration is just a little over 6.5%, as the temperature is lowered, the system first makes a λ-transition from a normal liquid (not a pure He3 or He4 liquid, but a liquid of mixture) to a superfluid liquid (again of a mixture). For example, starting at a concentration of $x_{ini} = 20\%$, the normal-superfluid transition happens around roughly 1.8 K. On further cooling, it remains a superfluid up to about 0.5 K. Any further cooling at this concentration leads the system into an *unstable composition.*

But eventually it must end up in some *stable* configuration. What exactly is this stable configuration? If we draw a horizontal line at this lower temperature, it intersects the phase diagram in *two* points corresponding to, let us say, the concentrations $x_d(T)$ and $x_c(T)$. Quite clearly, $x_d < x_{ini} < x_c$. In other words, at the lower temperature one has a stable phase that is *rich* in He3 (the one with x_c) and another stable phase that is poorer in He3 as compared to the He3 concentration one started with (x_{ini}). So the system *phase separates* into a He3-rich phase, called the *concentrated phase*, and a He3-poor phase called the *dilute phase* (hence the reason for the subscripts (c,d)). In fact, the fraction f_d of the dilute phase coexisting with the fraction $f_>$ of the concentrated phase is easily calculated:

$$f_d = \frac{x_c - x}{x_c - x_d} \qquad f_c = \frac{x - x_d}{x_c - x_d} \tag{14.4}$$

The dilute and the concentrated phases, being stable phases in coexistence, satisfy the equilibrium condition of equal Gibbs potential per unit mass, i.e $g_d = g_c$.

The phase diagram further indicates that at very low temperatures $x_c \to 1$ and $x_d \to 0.065$. A naive expectation may have been $x_d \to 0$, but this is not so, and as already mentioned this striking result needs quantum mechanics for its understanding. It follows from eqn.(14.4) that a single stable phase at any temperature T is possible only if the concentration x_{ini} is tuned to be such that it is either $x_c(T)$, in which case it is only the concentrated phase ($f_c = 1, f_d = 0$) or $0 \leq x_{ini} \leq x_d(T)$ in which case the stable phase is entirely the dilute phase.

What is of importance to refrigeration by dilution is the difference in entropy between the dilute and concentrated phases. Though many treatments base themselves on considerations of enthalpy also, in the end it is only the entropy difference between the two stable phases that matters. This entropy difference can be computed if one has a knowledge of the specific heats of the two phases. The literature is confusing even on this. Some talk of specific heat per unit mass, some others of molar specific heat, and some even of specific heat per atom (not very sensible in a purely thermodynamic context). In mixtures, number densities and molar concentrations are not straightforwardly related. There is also confusion about the equilibrium condition itself. As can be gathered from our discussions on phase equilibria in chapter 14, the equilibrium condition is that Gibbs potential per unit mass must be the same in the two coexisting phases.

Let us turn to a discussion of the entropy and subsequently the latent heat difference between the two phases. To avoid any confusion, let us first pose the following question: suppose one mole of He3 is converted from a concentrated phase to one mole of He3 in the dilute phase. Then what is the change in the molar entropy of He3? Clearly, for the dilute phase to have exactly one mole of He3, there should be enough superfluid He4 around.

Strictly speaking, it is the entropy difference between the dilute and concentrated phases that we should be seeking. But below 0.5 K the He4 is in the so called *Bose Condensed* state, and carries *zero entropy*. Consequently the specific heat also vanishes. Therefore, as far as latent heat (or equivalently) entropy considerations are concerned, the He4 part, both in the dilute phase as well as the concentrated phase at nonzero K, simply acts like a silent spectator. However, as we shall see, He4 does influence the enthalpy. But the equilibrium condition gives the enthalpy difference to be directly related to the entropy difference.

In the dilute phase, the He3 can be treated as a so called *Ideal Fermi Gas*. It is beyond the scope of this book to give a proper account of it. We shall simply give the formula for the *molar specific heat* of He3, when its molar concentration is x

$$C_d = a_{gas} f(x) \cdot T \tag{14.5}$$

Putting all the relevant factors, one gets

$$C_d(x = .065) = 106 T J/mole \tag{14.6}$$

The specific heat of He3 in the concentrated phase is a lot more complicated. In that phase, He3 is in a liquid state and it is not easy to give an analytical expression. But according to the legendary Russian physicist, Lev Landau, though He3 is a so called *Fermi Liquid*, it behaves like an *Ideal Fermi Gas* not of He3 atoms, but of some fictitious helium-like atoms, so that the *very low temperature* specific heat of He3, even in the liquid state, is given by

$$C_c = a_{liq} f(x) \cdot T \tag{14.7}$$

What distinguishes a_{gas} from a_{liq} in these is the differing values of the so called *effective mass* of Landau theory of Fermi liquids. It is remarkable that even in the liquid state, the dependence of the specific heat on molar concentration as well as temperature is *exactly the same* as in the ideal Fermi gas description of the dilute phase! Lounasmaa [41] on the other hand, uses the experimental data in the 40 mK range to come up with an empirical fit for the molar specific heat in the concentrated (liquid) phase:

$$C_c = 25T J/mole \tag{14.8}$$

Another estimate which is commonly used is

$$C_c = 22T J/mole \tag{14.9}$$

It should be noted that this too can be thought of as having the same functional form of eqn.(14.7) with an emprically determined a_{emp} playing the role of a_{liq}. We can generically denote this parameter by a and write the generic expression for He3 specific heat as $a f(x) T J/mole$.

If the equilibrium condition (equality of Gibbs potential per unit mass) were to be applied separately to He3, one would expect

$$H_c^{(3)} - TS_c^{(3)} = H_d^{(3)} - TS_d^{(3)} \tag{14.10}$$

The superscript (3) serves as a reminder that only quantities pertaining to He3 are to be used. The above mentioned linear temperature dependences can be assumed to hold all the way to absolute zero. The enthalpy and entropy can be obtained by integrating $C(T), C(T)/T$ respectively:

$$S(T) = \int_0^T \frac{C(T)}{T} dT \qquad H(T) - H(0) = \int_0^T C(T) dT \tag{14.11}$$

While S(0) has been set equal to zero in accordance with third law, there is no such requirement regarding H(0). The integrals above exist and the behaviour of specific heat near absolute zero is indeed in conformity with third law. We will be applying all these considerations to very low temperatures where we can take $x_c = 1$ and $x_d = .065$. However, since the functional forms of $x_c(T), x_d(T)$ are known, in principle one can integrate the expressions in eqn.(14.11). The generic expression for the enthalpy and entropy can now be written down as

$$S(a,x,T) = a f(x) T \qquad H(a,x,T) = H(a,x,0) + \frac{a}{2} f(x) T^2 \tag{14.12}$$

with x taking the appropriate temperature-independent values. Using these expressions we can recast the equilibrium condition of eqn.(14.10) as

$$H(a_{liq}, x = 1, 0) - \frac{a_{liq}}{2} f(1) T^2 = H(a_{gas}, x = .065, 0) - \frac{a_{gas}}{2} f(.065) T^2 \tag{14.13}$$

This can never be satisfied for different T no matter what H(a,x,0) is. Hence the equilibrium condition should not be applied to the He3 part alone. On the other hand, if the condition is applied to both the He4 and He3 parts, there is no contradiction. Thus the temperature-dependent enthalpy of He4 is crucial for the equilibrium.

Thus at very low temperatures, the molar entropy difference between the dilute and concentrated phases is

$$S_d - S_c = \frac{L}{T} = 81\,T\,J/K \tag{14.14}$$

leading to a latent heat for conversion from concentrated to dilute phase of $81\,T^2 J/mole$. Comparing this to the latent heat of vaporization, one sees that the concentrated phase is akin to the liquid phase and the dilute phase to the vapor phase (but keep in kind that both the concentrated and dilute phases are actually liquids in this case). Continuing that analogy, one can conclude that if one mole of He3 in concentrated phase passes to one mole of He3 in the dilute phase, there will be cooling very much like the evaporative cooling in the liquid-vapor system.

14.3.2 Cooling power of dilution refrigerators

It is clear that if $\dot{n}_3$ is the rate in moles per sec at which He3 is made to cross the phase-coexistence surface between the dilute and concentrated phases, the rate of cooling, i.e the cooling power, is given by

$$\dot{Q} = \dot{n}_3\,81\,T^2 \tag{14.15}$$

As emphasized before, this cooling power also vanishes at absolute zero, as Nernst-Planck theorem would demand. But in order to see how fast the cooling power vanishes, we need to examine the possible limitations on $\dot{n}_3$, as after all in the case of the cryostats, it was this factor that vanished exponentially at lower temperatures. This is where the nonzero molar fraction of He3 in the dilute phase, even at absolute zero, makes a dramatic difference. If He3 is being pumped to achieve cooling, the factor $\dot{n}_3$ is *temperature independent*!

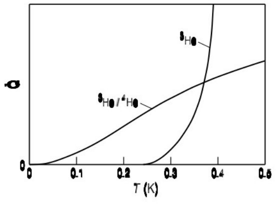

FIGURE 14.3 Comparison of cooling powers of He3 cryostats and dilution refrigerators.
Source: Modified from fig. 3.7, p.31, of O.V. Lounasmaa [40].

Hence the cooling power of dilution refrigerators goes down only *quadratically* with temperature. In the cryostat, the latent heat was practically insensitive to temperature, whereas in the dilution case it is $\dot{n}_3$ that is insensitive. A comparison of the cooling rates for the *same*, but otherwise arbitrary, He3 pumping rate is shown in figure 14.3.

As can easily be gathered from this, dilution refrigeration is far superrior to even the He3 cryostat. The latter, as already remarked, becomes totally inefficient below about 0.2 K. The dilution refrigeration, on the other hand, can cool objects to a few mK. In the next section, we consider a few salient features of this novel means of refrigeration.

14.3.3 The dilution refrigerator

So the idea is to convert He3 in the concentrated phase into He3 in the dilute phase. To make the analysis simpler, let us assume that we are close to the temperatures where $x_c \approx 1.0$ and $x_d \approx .065$. A more general analysis is not much more difficult, it is just that it suffices to bring out the essence of the method to work at temperatures where the molar fractions have these values.

The most important part of the refrigerator is the so called *mixing chamber* where the mixing and consequently also the cooling takes place. Imagine mixing N_3 moles of He3 with N_4 moles of He4 at some low enough temperature. After phase separation, let N_3^c be the number of moles of He3 in the concentrated phase and N_3^d be the corresponding number of moles in the dilute phase. Since x_c is very close to unity, hardly any He4 will be in the concentrated phase, and we can take the circumstances to be such that all N_4 moles of He4 are in the dilute phase so $N_4^d = N_4$. The conservation of the amount of He3 gives:

$$N_3 = N_3^c + N_3^d \tag{14.16}$$

But N_3^d and N_4^d (which in this case is the same as N_4) are related by $N_3^d = \frac{0.065}{0.935} N_4^d$, since $\frac{N_3^d}{N_3^d + N_4^d} = x_d = 0.065$. Hence it follows that $N_3^c = N_3 - \frac{0.065}{0.935} N_4$. This means that the number of moles of He3 that have passed from pure He3 phase to the dilute phase is $\Delta N_3 = \frac{0.065}{0.935} N_4$. The amount of cooling is therefore $\Delta Q = 81 \Delta N_3 \cdot T^2 J$. The ratio of N_3 to N_4 can not be arbitrary (or else the assumption that all N_4 moles of the initial He4 pass to the dilute phase will be wrong). In fact $N_3 - \frac{0.065}{0.935} N_4 \geq 0$. The optimal situation is when $N_3 = \frac{0.065}{0.935} N_4$, which happens when the initial concentration is exactly $x_d = 0.065$. In that case all of the initial He3 and He4 pass entirely into the dilute phase, and maximum cooling takes place.

Actual laboratory designs are of course too elaborate for discussion here. But the schematics of the main design elements for a dilution refrigerator will be given next. For more details, the reader is referred to [41, 68].

14.3.4 Dilution refrigeration: skeletal designs

Before discussing even the schematics of a dilution refrigerator, it is worth clarifying the meaning of $\dot{n}_3$ in the cooling power formula. This is the number of moles of He3 that *crosses the phase boundary*. If phase equilibrium is disturbed, such a movement of He3 will restore the phase equilibrium.

In fact this is exactly analogous to the liquid-vapor case. Suppose in a container there is liquid coexisting with its vapor at some temperature. If some amount of vapor is pumped out, the phase equilibrium is momentarily disturbed. But it is restored by the requisite amount of liquid vaporizing, leading to cooling in the process. So a certain amount of vapor has crossed the phase boundary.

Coming back to the helium mixture case, if the molar concentration of the dilute phase is altered, phase equilibrium will be disturbed. Depending on how exactly it is disturbed, a certain amount of He3 will cross the phase boundary one way or the other. If the He3 molar concentration is *decreased*, say by removing a certain amount of He3 from the dilute phase, then some amount of He3 from the concentrated phase will move into the dilute phase, thereby leading to cooling.

On the other hand, if the molar concentration of He3 in the dilute phase is decreased by *increasing* the amount of He4, then too phase equilibrium is disturbed in the same way and again He3 will move from the concentrated to the dilute phase, and again lead to cooling.

Therefore to effect a Δn_3 across the phase boundary, and hence to effect a cooling, it does not matter whether we do it through physical movement of He4 or He3. The fact that the dilute phase has a molar fraction 0.065 of He3 at all temperatures of operation is important for both of them. In the case of explicit extraction of He3, it matters as it controls the amount of He3 available for extraction. In the case of manipulation through He4 it matters because the amount of He3 that will actually cross the phase boundary due to the change in amount of He4 is also directly proportional to x_d.

The problem with extracting He3 from the dilute phase is that in the chamber in which phase coexistence happens, the dilute phase, being more dense because of dominant presence of the more dense He4, settles at the bottom! Nevertheless, with ingenuity this can indeed be achieved as will be briefly discussed now. Because of these issues, there are essentially two different designs, one in which He3 is circulated, and the other in which He4 is circulated. The circulations, achieved through pumps and heat exchangers, make the operation *continuous*. This allows one to achieve very low temperatures even when the cooling powers are very modest. Let us first look at the so called *Leiden design* in which only He4 is circulated.

At its bare essentials, this design consists of two chambers, called respectively the *demixing chamber* and the *mixing chamber*. The demixing chamber is held at some low enough temperature by a He3 cryostat (this means the temperature of the demixing chamber can not be lower than about 0.3 K). The demixing chamber has an inlet through which liquid He3 and liquid He4 can be introduced. The first step is indeed this filling of the demixing chamber. This immediately leads to phase separation with the lighter He3 liquid on the top, and the denser dilute phase at the bottom.

The demixing chamber is connected to the mixing chamber by a tube in which *simultaneously* the lighter He3 can raise to the mixing chamber from the demixing

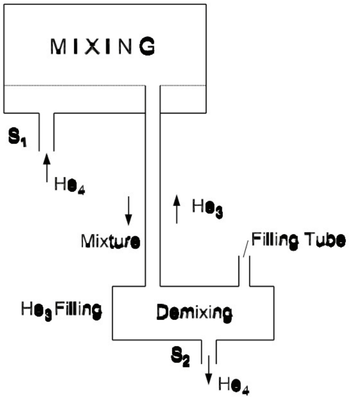

FIGURE 14.4 A dilution refrigerator with He4 circulation

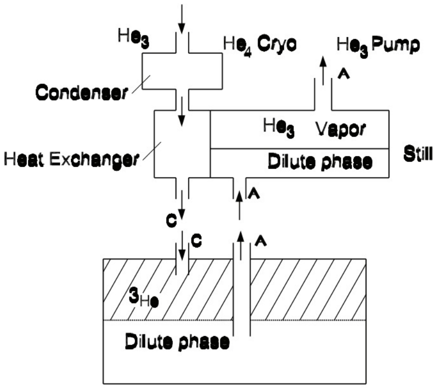

FIGURE 14.5 One with He3 circulation

chamber, and the heavier dilute phase, to be formed in the mixing chamber during the next step, can descend to the demixing chamber.

As a result of the first step, the concentrated phase rises to the mixing chamber and partially fills it. The next step is to fill the mixing chamber with liquid He4. This is done through a so called *superleak*, placed at the bottom of the demixing chamber. The superleak is essentially a tube filled with some powder through which only the superfluid He4, with vanishing *viscosity*, can penetrate. This He4 liquid mixes with the liquid He3 already present, leading to phase separation and cooling.

Now the heavier dilute phase which occupies the *bottom* of the mixing chamber descends into the demixing chamber. The demixing chamber, in addition to the inlet, has a *superleak outlet* at its bottom. Through this superleak, He4 can be taken *out* of the chamber, leading to an increase in the molar concentration of He3 in the dense phase, which is why this chamber is called a *demixing* chamber. This, of course, leads to heating and this heat is carried away by the He3 cryostat cooling this chamber.

The He4 extracted is further cooled and pumped back to the mixing chamber through its superleak. Thus the dilution refrigeration can be realised as a continuous process. Note that only He4 has been circulated in this design.

Now we discuss the other design, again very schematically, where He3 is extracted from the dilute phase and circulated to achieve continuous operation. Here too there are two chambers, one of which, like the Leiden design, is the mixing chamber. The other is called the *still* and in it, the He3 of the dilute phase is allowed to vaporize. It is then removed from this still through He3 pumps. As the first step, He3 is input and liquefied with the help of a He4 cryostat at about 1.1 K. This liquid He3 is eventually fed into the mixing chamber where it mixes with liquid He4 and phase separation takes place. The dilute phase is then fed into the still. Here, of course, both He4 and He3 vaporize. But the vapor pressure of He4 is extremely small compared to that of He3, and this allows for an easy pumping of He3 vapor out of the still. This He3 vapor is pumped back to the mixing chamber after liquefaction, exactly as in the first step. The process can be repeated in a cycle leading to continuous operation.

With dilution refrigeration, cooling to about 2 mK can be achieved. This is a significant improvement over both He3 and He4 cryostats in the march towards absolute zero.

14.4 Magnetic cooling

We now discuss yet another novel cooling technique called *Adiabatic Demagnetization* that can also result in cooling to a few mK level. This is totally different in its physics and thermodynamics from the previous sections in that it exploits the thermodynamics of magnetic systems, extensively discussed in chapter 8, to achieve cooling. It also goes by the name *magneto-caloric effect.* This method has, however, been available since the mid-1930's, some three decades before dilution refrigeration came on the scene. With the nuclear version, it has again come back as a desirable means of reaching very very low temperatures.

In terms of our earlier terminology the control parameter is the *magnetic field.* We first discuss some generalities of *adiabatic cooling* as adiabatic demagnetization happens to be one particular manifestation of these principles.

14.4.1 Principles of adiabatic cooling

The phenomenon of adiabatic cooling is nothing new to us now as we already encountered it in *free expansion* of an ideal gas. As the name suggests, we should be examining processes that are adiabatic, or more explicitly, *isentropic.* This in particular will mean that entropy S will be one of the quantities entering the description. Since we are also seeking a way to cool objects, temperature T must also enter. Finally, the control parameter should be there too and we shall keep it very general and call it x! So what's a very general equation we can think of involving S,T and some x? Clearly, the *triple product* of thermodynamic partial derivatives

$$\left(\frac{\partial S}{\partial x}\right)_T \left(\frac{\partial x}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_x = -1 \tag{14.17}$$

Of the three factors, $\left(\frac{\partial x}{\partial T}\right)_S$ is what will quantify the adiabatic cooling upon the change in the control parameter. This equation can consequently be rewritten as

$$\left(\frac{\partial T}{\partial x}\right)_S = -\left(\frac{\partial S}{\partial x}\right)_T \left(\frac{\partial T}{\partial S}\right)_x \tag{14.18}$$

The second factor on the rhs is the inverse specific heat when the control parameter is held fixed. This is expected to be finite and even positive. Thus as long as all specific heats exist, and entropy can be changed *isothermally* by changing some control parameter (x in this case, so $\left(\frac{\partial S}{\partial x}\right)_T$ is nonzero), one can achieve adiabatic cooling by appropriately changing the control parameter. It is as general as that. One does not even have to assume that the specific heat is positive.

To understand this better, let us in fact take all specific heats to be positive (if they are not, cooling and heating conditions will get interchanged), and let the entropy, say, decrease when x is increased isothermally. Then $\left(\frac{\partial S}{\partial x}\right)_T$ is negative. Consequently, $\left(\frac{\partial T}{\partial x}\right)_S$ will be positive, which means temperatures can be lowered by adiabatically reducing x.

14.4.2 Adiabatic demagnetization

These considerations can immediately be applied to cooling by adiabatic demagnetization. Then the idea will be to first reduce the entropy of a magnetic substance by isothermally magnetizing it and then adiabatically demagnetize it to lower its temperature. Let us again look at some generalities first.

There are two distinct types to be discussed, the first of which uses *paramagnetic salts*, while the second uses the very weak *nuclear magnetization*. In both cases, it is a very good approximation to treat the systems as being *linearly magnetizable* in the sense of what has been described in chapter 10. This means, the magnetization (total) has the linear dependence $\mathscr{M} = V\chi(T,P)B_e$ on the magnetic field. Specializing the general considerations of the previous subsection to the magnetic case, i.e identifying x with the (external) magnetic field B_e, one gets

$$\left(\frac{\partial T}{\partial B_e}\right)_S = -\left(\frac{\partial S}{\partial B_e}\right)_T \left(\frac{\partial S}{\partial T}\right)_{B_e}^{-1} = -\frac{1}{C_{B_e}}\left(\frac{\partial S}{\partial B_e}\right)_T \tag{14.19}$$

where C_{B_e} stands for the specific heat of the magnetic system at constant external field. Without specifying any further details on the susceptibility, we first make use of eqn.(38) of chapter 10:

$$\left(\frac{\partial S}{\partial B_e}\right)_T = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{B_e} = B_e V\left(\frac{\partial \chi(T,P)}{\partial T}\right)_P \tag{14.20}$$

Combining these two equations we obtain what may be called a fundamental identity for magnetic cooling:

$$\left(\frac{\partial T}{\partial B_e}\right)_S = -\frac{1}{C_{B_e}} B_e V \left(\frac{\partial \chi(T,P)}{\partial T}\right)_P \tag{14.21}$$

So far things have been very general except for the restriction to linear systems. Actually, the latter can easily be relaxed to find the equivalent relations. Let us see what type of restrictions arise due to the Nernst-Planck theorem. The lhs of the above equation effectively determines the cooling power and this must vanish as absolute zero is approached. Also, C_{B_e} must also approach zero as absolute zero is approached as Nernst-Planck theorem demands that *all* specific heats must vanish in that limit. Consequently $\left(\frac{\partial \chi}{\partial T}\right)_P$ must also vanish as absolute zero is approached.

After having spelled out all these generalities, we now restrict ourselves to cases where the susceptibility obeys the Curie law $\chi = \frac{a}{T}$ (see chapter 8 for a fuller discussion). As shown there, all expressions can be explicitly worked out, and in particular

$$S(B_e,T) = S(0,T) - \frac{1}{2}Va\frac{B_e^2}{T^2} \tag{14.22}$$

The important consequence of this is that for paramagnetic substances, for which $a > 0$, entropy *decreases* as the magnetic field is increased. From our general considerations it then follows that cooling results upon adiabatic *demagnetization*. Before discussing the magnitude of the various effects, let us note that another consequence of the above equation is that for the specific heat C_{B_e}:

$$C_{B_e}(T) = C_0(T) + \frac{VaB_e^2}{T^2} \tag{14.23}$$

Here $C_0(T)$ is the specific heat (taken to be at constant pressure) of the paramagnetic system in the absence of any external field.

So what are the sequence of steps required? First, a paramagnetic salt is isothermally magnetized. Let us say this initial temperature is T_i and let the initial field be B_i (we drop the subscript to denote the field is external). The next step is adiabatic demagnetization, and to make the effect as large as possible, let us consider *complete* demagnetization so that the final field $B_f = 0$. Since this step is adiabatic, and hence no change of entropy, the entropy before demagnetization, $S(B_i,T_i)$ must equal the entropy after complete demagnetization, $S(0,T_f)$. The final temperature T_f will of course be lower.

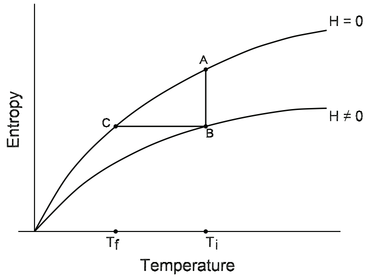

FIGURE 14.6 Adiabatic demagnetization.

In figure 14.6, the point A represents the start at an intial temperature of T_i with no magnetic field. The entropy of the system is $S_A = S(T_i,0)$. After magnetizing the system isothermally to field value B_i, we reach the point B where the entropy $S_B = S(T_i,B_i)$ is *lower* than S_A. A complete demagnetization of the system adiabatically takes it to C where the magnetic field is again zero and $S_C = S(T_f,0) = S_B < S(T_i,0)$. If we had continued the two curves all the way to absolute zero, they would have to converge as by Nernst-Planck theorem $S(0,0) = S(0,B) = 0$ for all values of B. It is then clear that by suitable choice of T_i and B_i we can get lower and lower values of T_f, but never $T_f = 0$.

Let us first work out the magnitude of the cooling effects at room temperatures and easily achievable fields of a few Tesla. Then all the magnetic field induced terms, both in the entropy as well as in the specific heats, are small. In fact the zero field specific heats C_0 are large. Writing down the adiabatic condition explicitly

$$S(B_i,T_i) = S(0,T_f) \to S(0,T_i) - \frac{1}{2}Va\frac{B_i^2}{T^2} = S(0,T_f) \qquad (14.24)$$

But $S(0,T_i) - S(0,T_f) \approx (T_i - T_f)C_0(T_i)$. Therefore, the amount by which the initial temperature gets lowered upon adiabatic demagnetization is

$$T_i - T_f = \frac{VaB_i^2}{2C_0T_i} \qquad (14.25)$$

For a typical paramagnetic salt at room temperature, a demagnetization by a Tesla results in a temperature drop of less than a mK and the effect is really negligible.

But as one goes to very low starting temperatures there is a dramatic improvement in the cooling efficiency of adiabatic demagnetization, essentially due to two reasons. The low temperature specific heats are much smaller than their room temperature counterparts. This is as required by Nernst-Planck theorem. They typically vanish as $aT + bT^3$. This enhances the effect which is inversely proportional to the specific heat. Secondly, the effect itself is inversely proportional to the initial temperature. Therefore in going from room temperature to even 1K, there is nearly a factor of 300 improvement.

In fact, at such low temperatures the field dependent $\frac{VaB^2}{T^2}$ dominates over the C_0 term, and the effects can be very large. In fact, from eqn.(14.21) and Curie law, one gets

$$\left(\frac{\partial T}{\partial B_e}\right)_S = B_e\frac{T}{C_{B_e}}\frac{Va}{T^2} \approx \frac{T}{B_e} \qquad (14.26)$$

where use has been made of eqn.(14.23) as well as the approximation that C_0 is negligible. What eqn.(14.26) says is that

$$\frac{T_i}{B_i} = \frac{T_f}{B_f} \qquad (14.27)$$

which is dramatic. By demagnetizing the field from a Tesla to a Gauss, the final temperature can be 10^{-4} the starting temperature.

Of course, some important caveats should be made clear. The Curie law, which usually holds only as a high temperature approximation, must hold at the low T_i. This requires finding paramagnetic salts for which Curie law is valid at very low temperatures. A naive extrapolation of the above result would give the erroneous impression that complete demagnetization would result in absolute zero! But our general considerations, even for magnetic systems, have already disposed of that possibility. The reasons are the caveats mentioned, like breakdown of Curie law and of other approximations made in deriving the above.

Example 14.1: Field dependences of entropy and third law

What are some of the restrictions imposed by the third law on the possible magnetic field dependences of entropy?

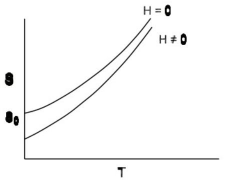

FIGURE 14.7 Violating the third law.

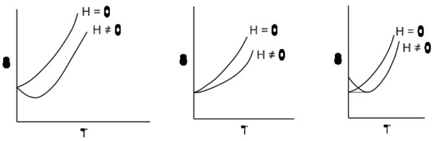

FIGURE 14.8 More on violating the third law...

Let us consider some field dependences of entropy as depicted in figs.(14.7,14.8). First consider the figure 14.7. We have seen, on rather general grounds, that the effect of magnetization at any temperature is to lower the entropy from its zero field value. Therefore one possibility is that at all temperatures, including 0 K, this is so. This case is what is shown in the first figure.

Now, the essential content of the third law is that there should exist no horizontal path, i.e an adiabatic process that would take some point on the $B_e \neq 0$ curve to the 0 K point on the field zero entropy curve. But this is clearly violated by fig.(14.7)! Hence such field dependences will violate the third law. It is easy to check that as long as the 0 K point on the non-zero field curve lies lower than the corresponding point on the zero field curve, third law violations are possible.

Let us see what happens if the 0 K point on the $B_e \neq 0$ curve is higher than the one on the curve with zero field, as shown in the last of the figures in fig.(14.8). Since eventually the magnetized curve has to come lower, the only possibility is as shown, i.e the nonzero field entropy must have a minimum somewhere. If the minimum lies at S_0 or lower, we can again reach absolute zero in one single step, violating the third law. If the minimum lies above S_0, nothing can be said in this context.

Lastly, when the 0 K points on the two curves coincide, as in the first two figures, third law can be violated, leaving only the case presented in the middle figure as one consistent with third law.

14.4.3 Electronic demagnetization: some results

Consider the cooling by adiabatic demagnetization of *paramagnetic* salts. We shall not go into the details of the actual experimental designs. A very important practical issue is the choice of the paramagnetic salt. The desirable features are that i) it must be such that Curie law holds to as *low* a temperature as possible, and ii) its magnetic susceptibility is as *high* as possible. For example, it has been found that in some magnetic clusters Curie law is valid even at as low a temperature as 1K [70]. The first criterion is important as one can cool to a lower temperature if the starting temperature itself is as low as possible. The second point is important as a higher susceptibility means *lower* magnetic fields can achieve the same results.

There are in fact a few more very important criteria when it comes to choosing the magnetic material. One has to do with the extent to which entropy can be lowered upon complete magnetization. Microscopically, this has to do with the *spin* content.

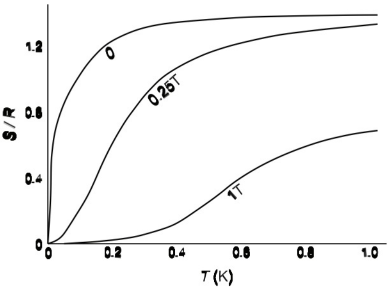

FIGURE 14.9 Paramagnetic adiabatic demagnetization.

The higher the spin the better is the material for use in adiabatic demagnetization cooling.

The last point also addresses the limit to which a paramagnetic salt can be cooled by this process. This is one of the factors that limits the approach to absolute zero. The point is, as the magnetic system is cooled, its own magnetic properties may undergo important changes. This is in fact what happens to most paramagnetic substances. At low enough temperatures they become *ferromagnetic* (or *antiferromagnetic*), which are completely *magnetically ordered*. In fact this order is *spontaneous* which means it does not require any external field to lower the entropy. Consequently, there can not be further cooling due to adiabatic demagnetization. The temperature at which this spontaneous ordering occurs is called the *ordering temperature*.

Therefore a desirable paramagnetic substance should have as low an ordering temperature as possible, as one can not achieve temperatures below the ordering temperature by adiabatic demagnetization techniques.

Cerium Magnesium Nitrate (CMN) is a popular choice for many reasons. It can be cooled with a Helium bath around 1K and modest magnetic fields of a few Tesla can achieve very low temperatures. It has been found that Curie law is valid even at 6 mK and its ordering temperature is 1.9 mK. The lowest temperature achieved witn CMN as the paramagnetic salt in adiabatic demagnetization devices has been around 2 mK. The entropy of the most magnetically disordered state is $S = R\ln 2$.

Some other paramagnetic salts that are frequently used are: Magnesium Ammonium Sulphate (MAS) with an ordering temperature of 170 mK and maximum spin entropy of $R\ln 6$, Ferric Ammonium Alum (FAA) with an ordering temperature of 26 mK and spin entropy of $R\ln 6$, Chromium Potassium Alum (CPA) with an ordering temperature of 9 mK and spin entropy of $R\ln 4$.

A lower ordering temperature results when the magnetic interactions are weaker. Many of the paramagnetic salts have *water of crystallization* which actually help in bringing this about. In figure 14.9, a typical entropy vs temperature plot encountered with paramagnetic salts is given. In this example, a sample at 1K is isothermally magnetized to 1 Tesla and completely demagnetized to yield a final temperature of 25 mK. The spin entropy for this example is $R\ln 4$. The curves are just plots of the entropy $S/R = \ln 2\cosh x - x\tanh x$, where $x = \mu B/kT(\mu$ is the magnetic moment of the paramagnetic atom).

14.4.4 Nuclear demagnetization: some results

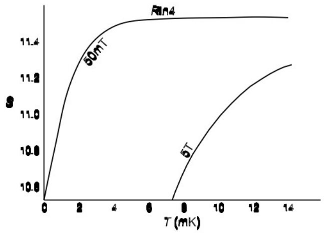

FIGURE 14.10 Nuclear adiabatic demagnetization.

The principle of *nuclear demagnetization* is exactly the same as the electronic demagnetization discussed in the context of paramagnetic salts. What is different, however, is the scale of things. Nuclear magnetism is a *thousand* times weaker than electronic magnetism. The susceptibilities are a *million* times smaller. The ordering temperatures are also much smaller, typically 0.1 μK! This means one can hope to cool samples to these low temperatures which are at least a thousand times smaller than what was possible with paramagnetic salts.

A typical material used for nuclear demagnetization is Copper. A price has to be paid for the advantages of nuclear demagnetization. One has to work with much higher magnetic fields. In the case of copper, the spin entropy is $R\ln 4$. The decrease in entropy upon magnetization should be as high a fraction of this as possible. But even with 8T of magnetic field at an initial temperature of 10 mK, the reduction in entropy is only about 10%, whereas in the case of paramagnetic salts at 1K with a field of 1T, one could get as high as 50% reduction.

The first succesful implementation of nuclear demagnetization was by Kurti in 1956, nearly a decade before dilution refrigeration came on the scene. The coldest achieved temperature achieved then was about $1\mu K$ (careful distinction should be made between this magnetic cooling and the cooling of the lattice. Kurti could not lower the lattice temperature below about mK. It took Lounasmaa another decade to achieve lattice cooling also to microkelvin range). Because of the very low temperatures of operation, all the standard problems of cryogenics like thermal insulation etc become really severe in implementing nuclear demagnetization.

In figure 14.10, nuclear demagnetization with copper is shown very schematically. It is the same function that was plotted in figure 14.9, but for the much smaller nuclear moments. The important points to notice, as already emphasized before, are the much higher magnetic fields required and the comparatively lower degree of magnetic ordering achieved. This can be quantified by the fraction of the entropy of the completely magnetically disordered state, $R\ln 4$ for copper, that can be lowered by the isothermal magnetization step.

14.4.5 Cascade nuclear demagnetization

The race to the proximity of absolute zero is really like a relay race. For example, in the case of paramagnetic adiabatic demagnetization one first used a helium bath to cool to 1.2 K, which at one time was the lowest temperature achievable, and then achieve mK temperature ranges.

Extending this concept, Knuuttila and coworkers [16] of the μKI (microkelvin investigations) group of the Lounasmaa lab at Helsinki, reached the lowest temperature ever in a Rhodium sample. In the first stage they used dilution refrigeration to reach 3 mK range. Then in the next stage they used adiabatic nuclear demagnetization to reach 50 μK. In the last stage, they again used adiabatic nuclear demagnetization with the rhodium sample to reach the record of 100 picokelvin (pK) which is 10^{-10} K!

14.4.6 Further lows!

In a completely new and novel technique for cooling Medley and coworkers [45], in Ketterle's lab, have reached temperatures even lower than the rhodium record. They have reached temperatures of 50 pK, but these are *spin temperatures* only. Their method, called *gradient demagnetization* is a generalization of adiabatic demagnetization where it is the field, not its gradient, that is demagnetized. They can use this to cool rubidium atoms to 350 pK.

14.5 Pomeranchuk cooling

Let us recall the discussion of the phase diagram of He3 from chapter 14; following the theoretical suggestion of Pomeranchuk and its subsequent experimental vindication, it was found that below 0.3 K, the phase coexistence line between solid He3 and liquid He3 had an *anomalous slope*, while beyond this temperature it was *normal*. Let us display only that part of the larger phase diagram of He3 that highlights this feature. This is shown in the figure above.

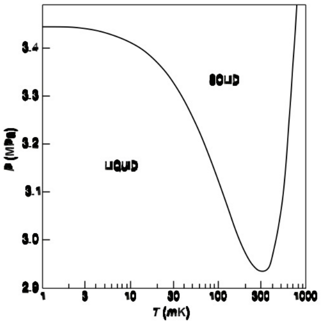

FIGURE 14.11 Phase Diagram of He3 showing the Pomeranchuk point.

As already discussed there, the anomalous P(T) curve for He3 has a totally different origin than the familiar anomalous coexistence curve for water. In the case of water, the solid phase (ice) had a *lower* density than the liquid (water) phase at the coexistence temperature. But the solid phase had lower entropy than the liquid phase as is evident from the fact that heat (latent) has to be *supplied* to ice to turn it into water. Equivalently, the solid phase was *more ordered* than the liquid phase.

It is clear from the Clapeyron equation that in order to have an anomalous slope one of $s_s - s_l, v_s - v_l$ must be negative. In He3, the solid and liquid phases behave normally as far as density or specific volume is concerned; the liquid phase is lighter and hence $v_l > v_s$ (for ice this was opposite). Hence the specific entropy of the liquid must be *lower* than the specific entropy of the solid He3 below 0.3 K i.e $s_l < s_s$! It is the liquid which is more ordered than the solid, which is rather unexpected.

It is instructive to go over Pomeranchuk's reasonings and the estimate for the temperature where the phase diagram has a dip. Though in chapter 14 we had said that it would involve microscopic details beyond pure thermodynamics, after our detailed discussions of dilution refrigeration and adiabatic refrigeration, those *microscopic* details can easily be motivated. Basically, the solid He3 behaves like a *paramagnet* but the only thing is that the source of this magnetism is *nuclear*.

As we already saw in our discussion of nuclear demagnetization, the ordering temperature for nuclear magnetism is $\simeq \mu K$ and at temperatures higher than this, the nuclear spins are totally disordered. In terms of entropy, this means that the magnetic entropy would have saturated at $R\ln(2J+1)$ where J is the spin content. For He3, this is $J = \frac{1}{2}$.

On the other hand, as we saw from eqn.(14.9), the entropy of the liquid phase of He3 can be taken to be linear in T when temperatures are around 50 mK. Let us see what would happen if we blindly extrapolated this linear temperature dependence of entropy all the way to 300 mK or so. For the case where the nuclear spins are $J = 1/2$, the high temperature solid entropy is mostly dominated by the *magnetic entropy*, and will have a value $R\ln 2$.

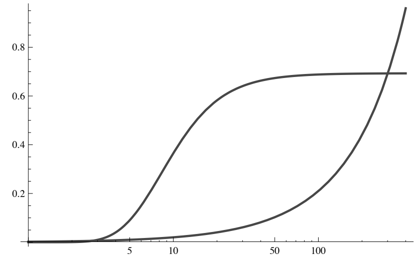

FIGURE 14.12 Entropy vs temperature for He3 around T_P.

Clearly, the linearly rising curve for the liquid will intersect the solid entropy curve at some temperature T_P such that $22T_P = R\ln 2$; putting in the numbers one gets $T_P = 260mK$! It is also clear from this simple picture that for $T < T_P$, the solid has a higher entropy than the liquid! The experimentally observed transition point (i.e transition from anomalous to normal behaviour) is at 300 mK, which is close to the rough estimate. One of the reasons for the deviation is that the entropy of the liquid phase can not really be approximated by a linear behaviour beyond 50 mK or so. Realistic behaviours are more like what is shown in figure 14.12, where the upper curve for the solid entropy has been obtained by some type of scaling of the curve in figure 14.9, and the lower curve for the liquid entropy was chosen to be of the form $aT + bT^2$. The real-life curve (see fig. 4.1 of [40]) does not look very different from this. The solid entropy mimicked has the correct high T limit of $\ln 2$, and vanishes at low T as required by third law.

The real-life situation in the case of He3 is rather involved. The relevant magnetic entropy is not the one we encountered in the paramagnetic case (there is no applied magnetic field here). The nuclear spins effectively experience a magnetic interaction of the Heisenberg-type. Pomeranchuk had originally thought this to be due to the direct dipole-dipole interaction. But this is very weak with an ordering temperature of about $1\mu K$. In He3 the exchange interaction is much stronger leading to an *anti-ferromagnetic* interaction with an ordering temperature of about 1 mK [58].

14.5.1 The principle of cooling

The principle of *Pomeranchuk cooling* is very much like the evaporative cooling. In that case, a liquid with lower entropy passing to a vapor with higher entropy, must draw an amount of heat equal to the latent heat of vaporisation. Now imagine a certain mass of liquid He3 *solidifying* into solid He3 at temperatures below 0.3 K. Now, it is the liquid which is the lower entropy system and the solid the higher entropy system. Again there will be cooling. This is indeed the principle behind Pomeranchuk cooling. Liquid He3 at these temperatures freezes upon heating. A typical cooling process can again be understood in terms of the figure 14.12: when the liquid at, say, temperature of 25 mK, is *isentropically* frozen to a solid, represented by a *horizontal move*, the temperature is indeed lowered to only a few degree K. Alternately, the cooling can be thought of as an *isothermal* process where a certain mass of liquid at T freezes to a solid by absorbing $T(s_s - s_l)m$ of heat. In that case, the transformation is along a vertical line on the same figure.

We now discuss the *cooling power* of this cooling process. It is clearly given by

$$\dot{Q}_{pom} = \dot{n}_{sol} T(S_s - S_l) \tag{14.28}$$

By referring to the figure fig.(14.12) we see that even around 50 mK, the entropy of the liquid can be neglected and the entropy of the solid well approximated by the saturation value $R\ln 2$, giving rise to the approximate cooling rate $\dot{Q}_{pom} \approx \dot{n}_{sol}RT\ln 2$. The cooling power of dilution refrigeration went as $\simeq T^2$ whereas we see from above that the cooling power of Pomeranchuk cooling only vanishes as T. Since $T << 1$, the cooling power of Pomeranchuk cooling far exceeds that of dilution refrigeration. The cooling powers in arbitrary units (actually determined by the rate of He3 involved) of the two processes are compared in fig.(14.13). The improved cooling characteristics of Pomeranchuk cooling are clearly seen.

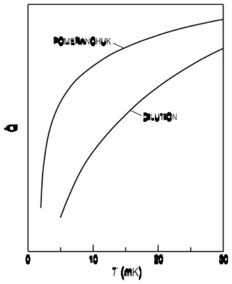

FIGURE 14.13 Pomeranchuk vs dilution cooling.
Source: Modified from fig. 4.5, p.67, of O.V. Lounasmaa [40].

14.5.2 Ends or means?

The real objective of most low temperature laboratories is to develop techniques to create conditions where new physics can be investigated. It is these techniques that allowed, for example, the extension of the phase diagram of He3 to its modern version as described in chapter 10. They have also shown that at low enough temperatures even paramagnetic salts become ferromagnetic etc. In this fashion, Lithium was seen to become a *superconductor* at 0.4 mK.

One of the most spectacular outcomes of low temperature physics has been the realization of *Bose Einstein Condensates*. This is a purely quantum mechanical phenomenon which can manifest under conditions of very low density and extremely low temperatures. First achieved in 1995 by Eric Cornell and Carl Weimann, it consisted in cooling Rubidium atoms to 170 nK. The atoms then condensed into what has been termed a *new state of matter*. Such a state of matter was predicted by S.N. Bose and Albert Einstein way back, in the earliest stages of the development of Quantum Theory. As the ambient temperature of the universe is 2.7 K, much hotter than these temperatures, this state can not occur naturally ever, and has to be only created in a laboratory! By allowing this condensate to undergo evaporative cooling, temperatures of 20 nK, the lowest ever achieved temperature then, could be reached. Similar techniques have been used to reach condensate temperatures lower than 500 pK in 2003.

14.6 Problems

Problem 14.1 It was pointed out, following eqn.(14.13), that the equilibrium condition should be applied not just to He3, but to both He3 and He4, and that the enthalpy of He4 is crucial. Determine the necessary enthalpy of He4.

Problem 14.2 The temperature dependence of vapor pressures is, to a good accuracy, of the form $P(T) = \mathrm{c}T^{\mathrm{b}}e^{-L/RT}$, where b,c are constants and L is the molar latent heat of vaporization. For He4, $L \simeq 83J$ and the boiling point is at $T_B = 4.2$ K. If additionally it is given that the vapor pressure at 2.48 K is 0.1 atm, determine b,c.

Problem 14.3 The molar latent heat of vaporization of He3 is roughly 26 J and the boiling point is at 3.2 K. If it is given that at 1.2 K, the vapor pressure of He3 is 35 times the vapor pressure of He4, determine the constants b,c of the previous problem for the case of He3.

Problem 14.4 If the lowest feasible vapor pressure to work with for cryogenics is 100 Pa, determine the lowest temperature one can hope to get to with a) He4 cryostat, and b) a He3 cryostat.

Problem 14.5 It was stated that the third law requires all cooling rates to vanish as 0 K is approached, and a consequence of this for cooling by adiabatic demagnetization was that susceptibilities should also vanish in this limit. Examine this for a) systems obeying Curie law for magnetization, and b) for systems whose magnetization is given by the Langevin function of problem 8.5.

Problem 14.6 Determine the crossover temperature at which Pomeranchuk cooling starts to become more efficient than dilution refrigeration. For a given pumping rate, how much more efficient is the former, compared to the latter, at 1 mK.

15 Entropy Constants

We saw earlier that the entropy at absolute zero for all systems can be taken to be zero. This is Nernst-Planck theorem or the third law of thermodynamics. As entropy enters all thermodynamic relations only as its differential dS, and never on its own (unlike temperature, for example), an addition of a constant, independent of the thermodynamic degrees of freedom of the system, does not affect any of these relations. This would imply that entropy in itself is ambiguous up to an additive constant. Third law can be taken to be a normalising condition for entropy.

Let us recall that for a reversible path connecting two states A,B of a system, the change in entropy is given by

$$\int_A^B \frac{đQ}{T} = S(B) - S(A) \tag{15.1}$$

If we take A to be the state of the system at 0 K, and use third law so that $S(A) = 0$, we get

$$\int_0^B \frac{đQ}{T} = S(B) \tag{15.2}$$

Since this integral can be evaluated, at least in principle, along an arbitrary path, there can no more be a freedom to add any constant to S.

Let us now look at the entropy of a mole of an ideal gas that thermodynamics had given us earlier:

$$S = R\ln V + \frac{R}{\gamma - 1}\ln T + S_0 \tag{15.3}$$

where $\gamma = C_P/C_V$ is the ratio of the specific heats, and S_0 a possible constant that thermodynamics is unable to fix.

Clearly at $T = 0$ no value of S_0 is going to realise the third law. The attitude usually taken is that no physical substance remains an ideal gas (most do not even remain gases!) at absolute zero, and that the above equation should only be used at high enough temperatures.

Because of the third law, S_0 is no longer arbitrary. However, if we are only dealing with one particular system, all thermodynamic changes of state involve only changes in entropy of this system, and knowledge of S_0 is *irrelevant*. But when many systems are in thermal equilibrium with each other as a result of transformations of one system to another, we will see that knowledge of entropy constants becomes essential. Third law can then be probed empirically and will no longer be a purely academic criterion.

This is quite evident if one considers the Helmholtz free energy $F = U - TS$; while an unknown constant in U results in an unknown constant in F, an unknown constant in S leads to a *temperature dependent* contribution to F. When there is only a system, with no distinction made between different *phases* of the system, only the equilibrium temperature enters the discussion and again the knowledge of S_0 becomes irrelevant.

15.1 Gaseous reactions

Let us discuss a situation where both the internal energy and entropy constants are physically relevant. This is the phenomenon of gaseous reactions, a prime example of which is the reaction

$$2\,H_2\,O \rightleftharpoons 2H_2 + O_2 \tag{15.4}$$

For any given temperature and pressure, a state of equilibrium is reached when the amounts of various constituents remain the same. Let us consider a general reaction of this kind

$$n_1A_1 + n_2A_2 + \ldots + n_rA_r \rightleftharpoons m_1B_1 + m_2B_2 + \ldots + m_sB_s \tag{15.5}$$

The concentrations are denoted by $[X]$. The *law of mass action* states that the quantity

$$\frac{[A_1]^{n_1} \cdot [A_2]^{n_2} \ldots [A_r]^{n_r}}{[B_1]^{m_1} \cdot [B_2]^{m_2} \ldots [B_s]^{m_s}} = K(T) \tag{15.6}$$

is a function of T only. We shall assume that every constituent gas obeys ideal gas law. The Helmholtz free energy per mole of the constituent X is given by

$$F(X) = U(X) - TS(X) = C_V^X\, T + W^X - T(C_V^X\, \ln T - R\ln[X] + a_X) \tag{15.7}$$

where W^X is a possible constant in $U(X)$ and a_X is the entropy constant for X. On noting that the number of moles of X is given by $V \cdot [X]$, the partial free energy of X is given by

$$V \cdot [X]\{C_V^X\, T + W^X - T(C_V^X\, \ln T - R\ln[X] + a_X)\} \tag{15.8}$$

and the total free energy at any time, where all the constituents $\{A_i, B_j\}$ are present is

$$\begin{aligned} F &= \sum_{i=1}^{r} V \cdot [A_i]\{C_V^{A_i}\, T + W^{A_i} - T(C_V^{A_i}\, \ln T - R\ln[A_i] + a_{A_i)}\} \\ &+ \sum_{j=1}^{s} V \cdot [B_j]\{C_V^{B_j}\, T + W^{B_j} - T(C_V^{B_j}\, \ln T - R\ln[B_j] + a_{B_j})\} \end{aligned} \tag{15.9}$$

Equilibrium condition is obtained by requiring that F is stationary with respect to changes in $[A_i], [B_j]$. Furthermore, the changes in $[A_i]$ are obviously proportional to n_i, and if $[A_i]$ decrease, $[B_j]$ increase etc. Thus, under $\delta[A_i] = -\varepsilon \quad n_i, \delta[B_j] = \varepsilon \quad m_j$ the change in F, given by,

$$\begin{aligned} \delta F &= -\varepsilon \cdot V[\sum_i n_i\{C_V^{A_i}T + W^{A_i} - T(C_V^{A_i}\ln T - R\ln[A_i] + a_i) + RT\} \\ &- \sum_j m_j\{C_V^{B_j}T + W^{B_j} - T(C_V^{B_j}\ln T - R\ln[B_j] + b_j) + RT\}] \end{aligned} \tag{15.10}$$

This can be rewritten as

$$\delta\, F = -V\, RT\, \varepsilon\, \ln[K(T) \cdot D(T)] \tag{15.11}$$

where

$$\begin{aligned}\ln D(T) &= -\frac{1}{R}\{\sum_j (R+C_V^{B_j}-b_j)m_j - \sum_i (R+C_V^{A_i}-a_i)n_i\}\\ &+ \frac{1}{R}\{\sum_j C_V^{B_j}\, m_j - \sum_i C_V^{A_i}\, n_i\}\cdot \ln T\\ &- \frac{1}{RT}\{\sum_j W^{B_j}\, m_j - \sum_i W^{A_i}\, n_i\}\end{aligned} \qquad (15.12)$$

The condition for equilibrium is that $\delta F = 0$ i.e $K(T) = D^{-1}(T)$. Thus we see that the function occurring on the lhs of eqn.(15.6) is indeed a function of T only. Furthermore, the T-independent term of eqn.(15.12) indeed depends on the entropy constants $\{a_i, b_j\}$ and hence these are measurable [17]. An important quantity characterizing such reactions is the *Heat of reaction*. Denoting this by $\tilde{H}$ (to distinguish it from the enthalpy H), we have in this particular case

$$\tilde{H} = \{\sum_i C_V^{A_i}\, n_i - \sum_j C_V^{B_j}\, m_j\}T + \{\sum_i W^{A_i}\, n_i - \sum_j W^{B_j}\, m_j\} \qquad (15.13)$$

and one gets the very important relation

$$\frac{d\log K(T)}{dT} = \frac{\tilde{H}}{RT^2} \qquad (15.14)$$

Thus we see that purely thermodynamic considerations can not give the T-independent constant of proportionality in $K(T)$. As emphasized before, the entropy constants are becoming physically relevant in this case because there are transformations from one system to another.

In some cases the quantity $W = \sum_j m_j W^{B_j} - \sum_i n_i W^{A_i}$ is of interest. For example, in the ionisation of a gas, say, sodium, i.e $Na \leftrightharpoons Na^+ + e$, W is nothing but the energy required to completely ionise the sodium gas.

It is instructive to display the differing temperature dependences in K(T) explicitly. If we write

$$K(T) = K_0 T^\alpha e^{\frac{W}{RT}} \qquad (15.15)$$

where K_0 is the temperature independent, constant factor in K(T). (Sometimes K(T) itself is referred to as the *law of mass action constant*. This is obviously a misnomer.) By explicit comparison we can write down the expressions for α and K_0:

$$\begin{aligned}\alpha &= \frac{1}{R}\left\{\sum_i n_i C_V^{A_i} - \sum_j m_j C_V^{B_j}\right\}\\ \ln K_0 &= \sum_j m_j(R-b_j) - \sum_i n_i(R-a_i) - \alpha\end{aligned} \qquad (15.16)$$

We see that the entropy constants $\{a_i, b_j\}$ are crucial for a determination of K_0, which is certainly measurable experimentally. It should be emphasized that this representation is valid only when all the C_V's are constants. But it is easy to generalize these considerations to more realistic cases of T-dependent specific heats.

At this point, it is instructive to enquire whether these entropy constants can be determined theoretically at all. At this point, rather surprisingly at first, Quantum Mechanics makes its entry! Even though no known physical system remains a gas at absolute zero and is described by ideal gas behaviour, as a theoretical exercise this system can be treated within quantum mechanics (this, of course, will not be done here) and one finds the following interesting features directly relevant to the contents of this chapter, and the one on the third law of thermodynamics: a) the specific heat is not constant and in fact decreases with T, vanishing at absolute zero (contrary to the heuristic picture that there is always zero point motion in quantum mechanics!); b) this, as discussed before, and again to be discussed later in this chapter, *determines* the entropy constant. As shown independently by Sackur and Tetrode, the ensuing entropy constant for *monoatomic* ideal gases is

$$a = R\ln\frac{(2\pi\, M\, R)^{3/2}\, e^{5/2}}{h^3\, {N_A}^4} + R\,\ln\omega \tag{15.17}$$

where N_A, h, M are, respectively, the *Avogadros number*, Planck's constant, and the Atomic weight, and ω is the so called *quantum degeneracy* of the ground state, and is of order unity. It is worth remarking that in all the relationships encountered in thermodynamics, a *kinematic* property like *mass* never made an appearance. This is so in classical statistical mechanics too. It is quantum mechanics that first brings it into a thermodynamic discussion. It is also worth pondering over the appearance of the Planck's constant in what is clearly a classical context! Another interesting feature of eq.(15.17) is the appearance of the Avogadro number, which is a hallmark of the atomic nature of matter.

When $\omega \neq 1$, there will be a violation of Nernst-Planck theorem. In practical calculations, it is important to use the correct value of ω. It is important to stress that the violation of Nernst-Planck theorem whenever $\omega \neq 1$ does not invalidate the significance, or usefulness of, the entropy constants discussed here. This is because the degeneracy term adds a well defined, not an arbitrary, constant to the entropy defined by Nernst-Planck normalisation, thereby adding the same constant to the entropy constants. In the examples discussed later, it is equivalent to starting with a system very close to absolute zero, but with entropy $R\ln\,\omega$ instead of zero.

15.2 Entropy constants for solids

As another illustration of how Nernst-Planck theorem fixes the entropy constants, we now consider the case of solids. Specifically, let us look at the behaviour of specific heats of solids as a function of temperature. In the classical theory this is given by the *Dulong-Petit law* according to which the molar specific heat of solids is constant, with value $3R$. This clearly violates Nernst-Planck theorem. But quantum theory makes a dramatic difference. We shall illustrate this with two theories for specific heats that were developed by Einstein and Debye, respectively. What is amazing is that both these were developed long before quantum theory was fully developed. Einstein's theory of solids was developed in 1906, barely after Planck formulated his blackbody theory, and Debye theory came out in 1912, just around the time the Bohr atomic theory was getting formulated.

As we have already given a detailed account of these epoch-making developments in section 5.5 of chapter 5, we shall only use them to address their impact on the issue of entropy constants, and their extreme importance in understanding specific phenomena like the vapor pressure of solids.

Even though the Debye theory came later, and was in fact a technical improvement over Einstein's theory, let us first consider the Debye theory. According to this theory, the specific heats of solids is given by

$$C_D(T) = 3RD(\frac{T}{\Theta}) \tag{15.18}$$

where Θ is a temperature scale called the *Debye temperature*, which depends on the material, and with the function $D(\xi)$ given by

$$D(\xi) = 12\xi^3 \int_0^{1/\xi} dx \frac{x^3}{e^x - 1} - \frac{3/\xi}{e^{1/\xi} - 1} \tag{15.19}$$

At high temperatures, $\xi \to \infty$ and $D(\infty) \to 1$. Therefore, at high temperatures the specific heat approaches the classical value of $3R$. But at low temperatures where $\xi \to 0$, the specific heat vanishes as

$$C(T) \to \frac{12\pi^4}{5} \frac{R}{\Theta^3} T^3 + \dots \tag{15.20}$$

This is indeed compatible with the Nernst-Planck theorem as the entropy at low temperatures vanishes as

$$S(T) \to \frac{4\pi^4}{15} \frac{R}{\Theta^3} T^3 + \dots \tag{15.21}$$

Using eqns. (15.18) and (15.19), along with the Nernst-Planck definition of entropy,

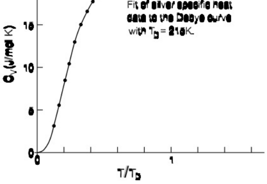

FIGURE 15.1 Debye model for silver
Source: Data from the table *Thermodynamic Functions of Copper, Silver, Gold* on p. D74 of *Handbook of Chemistry and Physics (1973-74)*, 54th Edition, Ed. Weast, CRC Press.

it is easy to see that entropy at all temperatures, according to Debye theory, is given by

$$S(T) = 3R\{4\frac{T^3}{\Theta^3}\int_0^{\frac{\Theta}{T}} dx\,\frac{x^3}{e^x-1} \quad -\ln(1-e^{-\frac{\Theta}{T}})\} \tag{15.22}$$

It is straightforward to work out the high temperature behaviour of the Debye entropy now:

$$S(T) \to 3R\ln T + 4R - 3R\ln\Theta \tag{15.23}$$

This explicit example clearly demonstrates how the Nernst-Planck theorem, namely the requirement of vanishing entropy at absolute zero, fixes the entropy constant.

In figure 15.1, a comparison is made between the specific heat of solid silver as predicted by the Debye theory and experimental data for silver. Clearly, the agreement is very good.

Now we carry out a similar analysis with Einstein's theory for the specific heat of solids. The purpose is again to demonstrate how third law fixes the entropy constants at high temperature. We will not go into the details of the Einstein theory again, as the relevant details can be found in section 5.5.

The specific heat predicted by Einstein's theory is

$$C_E(T) = 3R(\frac{T_E}{T})^2\,\frac{e^{T_E/T}}{(e^{T_E/T}-1)^2} \tag{15.24}$$

where T_E is a scale of temperature in the Einstein theory. We shall relate T_E to Θ shortly. This too approaches the classical value of $3R$ at high temperatures. However, at very low temperatures, the specific heat in this theory behaves as

$$C(T) \to 3R(\frac{T_E}{T})^2\,e^{-T_E/T} \tag{15.25}$$

Though this is in conformity with Nernst-Planck theorem, this is too rapid a fall. The Debye theory explains the low temperature data better.

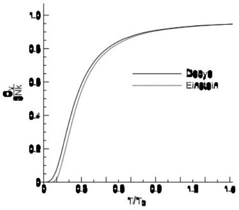

FIGURE 15.2 Einstein vs Debye

In figure 15.2, a comparison is made between the two theories. One subtlety has to be faced before the two theories can be compared; one has to relate the two different temperature scales appearing in them. We simply mention that relationship without going into details: $T_E = \Theta\,(\frac{\pi}{6})^{1/3}$. Once again, the entropy of a solid in Einstein's theory can be calculated at all temperatures on noting the indefinite integral

$$\int_x^\infty dx\,\frac{x}{(Sinhx)^2} = xCothx - \ln Sinhx \tag{15.26}$$

The resulting expression for entropy is

$$S(T) = 3R\,[\frac{T_E}{T}\,Coth\,\frac{T_E}{T} - \ln Sinh\,\frac{T_E}{T}] \tag{15.27}$$

The low temperature behaviour of $S(T)$ in Einstein theory is, then,

$$S(T) \rightarrow 6R\,\frac{T_E}{T}\,e^{-2\frac{T_E}{T}} \tag{15.28}$$

On the other hand, the high temperature behaviour of the entropy is

$$S(T) \rightarrow 3R + 3R\ln\frac{T}{T_E} \tag{15.29}$$

Expressing this in terms of the Debye temperature scale, one gets

$$S(T) \rightarrow 3R + 3R\ln\frac{T}{\Theta} + R\ln(\frac{6}{\pi}) \tag{15.30}$$

Thus one sees that the entropy constant in Einstein theory is $0.33R$ lower than the corresponding constant in Debye theory. Though the high temperature limits of specific heats is in both cases the Dulong-Petit value $3R$ there is a 10% difference in the entropy constants at high temperature. In addition to the phenomenon of gas dissociation, where we saw the observable impact of the entropy constants, we shall soon present other observable consequences of these constants. In particular, we shall present some nice experimental verifications of the Sackur-Tetrode formula.

Following Fermi, we shall now discuss how the entropy constants affect another common phenomenon, namely, the vaporization of a solid. In this, a solid passes to a gaseous phase, taken to be described by an ideal monoatomic gas. As expected, this will involve an interplay between the entropy constants for monoatomic ideal gas as given by the Sackur-Tetrode formula on the one hand, and by the entropy constant for a solid as given by Debye theory on the other. We shall also illustrate what happens if one uses Einstein theory for solids instead.

Let us consider the molar entropy difference between the solid and the gas, coexisting at temperature T:

$$S_{vap}(T) - S_{solid}(T) = \frac{\Lambda}{T} \tag{15.31}$$

where Λ is the molar heat of vaporization. Substituting the expression for S_{solid} from Debye theory, and the expression for S_{gas}, the entropy of an ideal monoatomic gas as completed by the Sackur-Tetrode relation, one finds,

$$\begin{aligned}\frac{\Lambda}{T} &= \frac{3R}{2}\ln T + R\ln V + a - 3R\ln\frac{T}{\Theta} - 4R\\ &= \frac{5R}{2}\ln T - R\ln P + (a + R\ln R) - 3R\ln\frac{T}{\Theta} - 4R\end{aligned} \tag{15.32}$$

Note that in passing from an expression for entropy in terms of (V,T) to one in terms of (P,T), the coefficient of $\ln T$ changes from $C_V = \frac{3R}{2}$ to $C_P = \frac{5R}{2}$, *and*, the entropy constant given earlier by a, changes to $a + R\ln R$. It is straightforward to put everything together and arrive at

$$P_{Debye} = \frac{(2\pi M)^{3/2} R^{5/2} \Theta^3 \omega}{e^{5/2} h^3 N_A^4} \frac{1}{\sqrt{T}} e^{-\frac{\Lambda}{RT}} \tag{15.33}$$

A similar equation emerges for Einstein theory, albeit with different constants owing to the different entropy constants, as expressed in eqn.(15.30):

$$P_{Ein} = (\frac{e\pi}{6}) \cdot \frac{(2\pi M)^{3/2} R^{5/2} \Theta^3 \omega}{e^{5/2} h^3 N_A^4} \frac{1}{\sqrt{T}} e^{-\frac{\Lambda}{RT}} \tag{15.34}$$

The numerical factor $\frac{e\pi}{6}$ is about 1.4, which is remarkably close to $\sqrt{2}$! Thus, in absolute terms, the Einstein theory of solids predicts a vapor pressure that is 1.4 times higher than what the Debye theory predicts, and it ought to be possible to tell the difference experimentally. Several comments are in order, as pointed out by Fermi, regarding eqn.(15.33):

- There are no *undetermined* constants in the vapor pressure equation. Note, however, that the power law corrections (in T) to the exponential behaviour here are quite different from the power law corrections to the vapor pressure formulae in the case of liquid-vapor transitions as found in problems 14.1 and 14.2. The expressions for the vapor pressures, both in Debye as well as Einstein theories, should be contrasted with the purely thermodynamic derivation of this important equation based on the *Clapeyron equation*

  $$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)} \tag{15.35}$$

  where p, T, λ, v_2, v_1 are, respectively, pressure per gm, temperature, heat of vaporisation per gm, specific volume of vapor, and specific volume of solid. As $v_2 >> v_1$, using ideal gas law for the vapor can be used to convert the Clapeyron equation to

  $$\frac{dp}{dT} = \frac{\lambda M}{RT^2} p \tag{15.36}$$

  If λ is approximated by a constant, this can be integrated to yield

  $$P = const.e^{-\frac{\Lambda}{RT}} \tag{15.37}$$

  on using $\Lambda = \lambda M$. Comparing this with eqn.(15.33), the thermodynamic derivation is unable to fix the constant. This, of course, is due to the inability of thermodynamics to fix the entropy constants.

- The comparison also reveals an additional factor of $T^{-1/2}$ that is absent in the thermodynamic derivation. As Fermi has remarked, this difference has to do with the possible variations of the vapor pressure with temperature. The derivation based on entropy correctly takes this into account.
  The two can be reconciled if the λ in the Clapeyron equation is replaced by an effective temperature-dependent λ_{eff}:

  $$\lambda_{eff}(T) = \lambda - \frac{RT}{2M} \tag{15.38}$$

  For the liquid to vapor transition in water, the first term is 2260 J/gm at the boiling point of water, while at that temperature, the second term is roughly 80 J/gm. Hence the difference is small. It may appear that at low temperatures the difference may become substantial, but then the high temperature expansions used may not be justified.
- The constant in the vapor pressure equation can indeed be measured experimentally, pointing to a way of experimentally verifying the Sackur-Tetrode formula. Instead, we shall discuss other ways of doing this as that would further exemplify the importance of the entropy constants.

15.3 Two experimental verifications of the Sackur-Tetrode formula

We now discuss two experimental vindications of the Sackur-Tetrode formula for the entropy constants of monoatomic gases.

Example 15.1: Vaporization of mercury

The first one is what Fermi has himself discussed in his book [17]. This is the liquid to vapor transition in Mercury, with $M = 200.6$. While in the vapor phase the Sackur-Tetrode formula can be used, the liquid phase is much more complicated, and certainly the Debye theory will not apply. Following Fermi, we first compute the entropy of the mercury vapor at the boiling point of mercury at 630 K, at 1 atmosphere. An immediate issue that arises in trying to evaluate the entropy, as a function of P,T is that of the units to be used for pressure and temperature.

The rule is to use T in degrees Kelvin, P in C.G.S units, and use the C.G.S units for all other dimensionful quantities including the gas constant R. Let us explicitly carry out this computation. Use will be made of the explicit evaluation of the constant a as given by Fermi:

$$\begin{aligned} a &= R \ln \frac{(2\pi MR)^{3/2}\, e^{5/2}\, \omega}{h^3 N_A^4} \\ &= R(-5.65 + \frac{3}{2}\ln M + \ln \omega) \end{aligned} \tag{15.39}$$

The pressure in this case is 1 atm., which is $1.013 \cdot 10^6$ C.G.S units. Therefore $\frac{5}{2}\ln T = 2.5 \cdot \ln 630 = 16.118$, $\ln P = \ln 10^6 = 13.816$, $\frac{3}{2}\ln 200.6 = 7.952$; the entropy constant after adding $R\ln R$ to it because of the change to (P,T) as independent variables is $20.54R$, yielding an entropy $S_{gas} = 22.838R = 189.88 \cdot 10^7$, after taking $\omega = 1$(Fermi's value is $191.0 \cdot 10^7$).

A comparison of this is made with entropy evaluated using Nernst-Planck theorem. Starting with solid mercury at absolute zero with zero entropy, the entropy of solid mercury at the melting point of 243 K can be calculated by integrating $\frac{C_P}{T}$ from 0 K to 243 K. Using experimental values one gets $S_{solid}(233K) = 59.9 \cdot 10^7$.

At this point a conceptual point may be worrisome. According to the zeroth law, absolute zero can never be achieved, and hence no specific heat data can be obtained at that point. Then how can one integrate the entropy integral from zero? Let us explain this on the basis of Debye theory. Let us, for argument sake, assume that experimentally only 1 K is reachable. The entropy of the solid at 1 K can be found by using the low temperature behaviour of the entropy given in eqn.(15.21) to be only 150. Therefore even if we cut off the lower end of the integral at 1 K, which is actually pretty high from the point of view of modern day cryogenics, a negligible error is made. If the lower limit is cut off at even lower temperatures, the remaining contribution to total entropy becomes even more negligible.

At this point, we could have even used Debye theory to actually calculate the entropy of solid mercury at 243 K. The Debye temperature of mercury is 100 K. The answer, using the high temperature expansion of eqn.(15.23) is $55.8 \cdot 10^7$ which is already quite close to the experimentally determined value! As the melting temperature is only 2.43 times higher than the Debye temperature, there will be corrections to the high temperature expansion.

Now this solid mercury melts at 243 K to liquid mercury by reversibly absorbing 2330 Joules per mole of heat of fusion. This increases the entropy by $9.9 \cdot 10^7$. The liquid mercury at the melting point of 243 K has now to be heated at constant atmospheric pressure to liquid mercury at the boiling temperature of 630 K . The entropy change here can not be computed using Debye theory as it is not applicable to liquids. But once again experimental data on C_P of liquid mercury can be used to compute the change of entropy as before, and the result is $26.2 \cdot 10^7$.

Finally, the liquid at the boiling temperature reversibly absorbs the heat of vaporisation of 59,300 J/mole. This increases the entropy by a further amount of $94 \cdot 10^7$. Adding up all the entropy changes, starting at zero entropy, one gets $(59.9 + 9.9 + 26.2 + 94.0 = 190) \cdot 10^7$, which is remarkably close to the prediction of $191 \cdot 10^7$ by the Sackur-Tetrode theory! It is instructive to display the various entropies that are involved in this problem:

$$\begin{aligned}
S_{solid}(0) &= 0 \cdot 10^7 \\
S_{solid}(T_m = 243) &= 59.9 \cdot 10^7 \\
S_{liq}(T_m = 243) &= 69.8 \cdot 10^7 \\
S_{liq}(T_b = 630) &= 96.0 \cdot 10^7 \\
S_{gas}(T_b = 630) &= 190.0 \cdot 10^7 \\
S_{gas}(T_B = 630)^{calc} &= 189.88 \cdot 10^7 \qquad (15.40)
\end{aligned}$$

Example 15.2: Solid Neon to its vapor via a liquid phase

As our next example we consider Neon with an atomic weight of $M = 20.18$. Neon is a rare earth element and these are very interesting elements. Neon is a solid below its melting point of $T_m = 24.6K$. At this temperature, and 1 atm. of pressure, it turns into a liquid but does not stay a liquid very long. Just a few degrees higher, at $T_b = 27.2K$ and again at one atmospheric pressure, it turns into Neon gas. Firstly both the melting and boiling points are at rather low temperatures. Secondly, the Debye temperature of solid Neon is $63K$! The reader should try to understand what it means for a substance to have a Debye temperature at which it is not a solid at all! We therefore have here an example that complements that of Mercury in the sense that in its solid phase it is the low temperature expansion of the Debye theory that is more relevant.

Other relevant data about Neon are its latent heat of melting, which is 335 Joules/mole at T_m, and its latent heat of vaporisation of 1761 J/mole at T_b.

We can go through the same steps as was done in the example of Mercury. As the method should be clear from the previous example, only the results are quoted here. The entropy of Neon gas at its boiling point, as calculated from the Sackur-Tetrode relation is $96.45 \cdot 10^7$ where once again we substitute 27.2 for T and 1 atm in C.G.S units for P. The entropy of solid Neon at the melting point 24.6 K calculated by using data on C_P comes to $14.29 \cdot 10^7$.

This part of the entropy can also be calculated theoretically from Debye theory by using eqn.(15.20). The result is $13.2 \cdot 10^7$, which is again quite close to the experimentally determined value.

At the melting point, the reversible transition from solid to liquid phase increases the entropy by $13.62 \cdot 10^7$. The entropy increase in heating the liquid from the melting to boiling point comes out to be $3.85 \cdot 10^7$, and finally the reversible liquid-gas transition increases the entropy further by $64.74 \cdot 10^7$. Adding everything together, the entropy of Neon gas at its boiling point, as calculated from data, is $(14.29 + 13.62 + 3.85 + 64.74 = 96.5) \cdot 10^7$ which is in excellent agreement with the value of $96.45 \cdot 10^7$ calculated from the Sackur-Tetrode formula!

15.4 The entropy constants for diatomic gases

It is clear that under the simultaneous scalings of T, R according to $T' = \lambda\, T, R' = \frac{R}{\lambda}$ should not have any significance, amounting merely to a change of units. Therefore, entropy, a physical quantity, must also satisfy $\frac{S'}{R'} = \frac{S}{R}$. Applying this to eqn.(15.3), one concludes

$$\frac{S_0'}{R'} = \frac{S_0}{R} - \frac{\ln \lambda}{\gamma - 1} \tag{15.41}$$

In thermodynamics and classical statistical mechanics, where entropy constants are *arbitrary*, this scaling principle is of no consequence. But in quantum theory, where entropy constants are fixed, this scaling principle becomes necessary. It can be explicitly verified that the entropy constant given by Sackur and Tetrode in eqn.(15.17) indeed satisfies eqn.(15.41) with $\gamma = 5/3$ for a monoatomic gas.

It is clear that when $\gamma \neq 5/3$, which is the case for polyatomic gases in general, the entropy constant given in eqn.(15.17) has to be modified. We show in this section how they are modified for *diatomic* gases. In such gases, the molecules have other degrees of freedom in additional to the *translational* degrees of freedom, which are the only degrees of freedom in the monoatomic gases. For diatomic molecules we have in addition the *rotational* and *vibrational* degrees of freedom. Each of them make contributions to specific heats and entropy. At high temperatures, described well classically, their contributions to specific heats are, R each, respectively and accordingly their contributions to entropy at high temperatures, modulo the entropy constants, are also $R\ln T$. To determine the contributions to the entropy constants, one needs to investigate the entropies that quantum theory would give. We shall simply cite the results for the high and low temperature behaviours. More details can be found in many sources on *Quantum Statistical Mechanics.*

First, let us look at the rotational degrees of freedom. Their contribution to low temperature molar specific heats and entropies are

$$C_{rot}^{low} = 12R\frac{\Theta_R^2}{T^2}e^{-\frac{2\Theta_R}{T}} \qquad S_{rot}^{low} = 6R\frac{\Theta_R}{T}e^{-\frac{2\Theta_R}{T}} \tag{15.42}$$

Clearly the specific heat vanishes as $T \to 0$ and so does the entropy, as required by Nernst-Planck theorem. The high temperature behaviours are

$$C_{rot}^{high} = R \qquad S_{rot}^{high} = R\ln\frac{Te}{\sigma\Theta_R} \tag{15.43}$$

In these formulae, Θ_R is a new scale of temperature generated by quantum theory, and σ is a symmetry factor which is 1 if the molecule is made of different atoms, and 2 if it is made of the same atoms, as for example H_2. We see that rotational specific heats an additional $R\ln(\frac{e}{\sigma\Theta_R})$ to the entropy constant.

The treatment of the vibrational degrees of freedom is analogous. The relevant formulae are, for low temperatures,

$$C_{vib}^{low} = R\frac{\Theta_V^2}{T^2}e^{-\frac{\Theta_V}{T}} \qquad S_{vib}^{low} = Re^{-\frac{\Theta_V}{T}} \tag{15.44}$$

and for high temperatures

$$C_{vib}^{high} = R \qquad S_{vib}^{high} = R\ln\frac{Te}{\Theta_V} \tag{15.45}$$

Θ_V is yet another intrinsic temperature scale brought forth by quantum theory. Again, the low temperature specific heat and entropy are in conformity with Nernst-Planck theorem. This is in fact, a central feature of quantum theory. It may be said in hind sight that a careful experimental establishment of the entropy constants might have heralded quantum mechanics independently of the historical path via the blackbody radiation! The high temperature behaviour of the vibrational specific heat adds a further $R\ln\frac{e}{\Theta_V}$ to the entropy constant of a diatomic gas.

Putting everything together, we arrive at the Sackur-Tetrode formula for the entropy of a diatomic gas at high enough temperatures to have excited both the rotational and vibrational degrees of freedom:

$$S = R\ln V + \frac{7}{2}R\ln T + R\ln\frac{(2\pi\, M\, R)^{3/2}\, e^{9/2}}{h^3\, {N_A}^4\sigma\,\Theta_R\,\Theta_V} + R\,\ln\omega \tag{15.46}$$

Now under the scaling considered, the intrinsic quantum temperature scales Θ_R, Θ_V should also be scaled according to $\Theta_R \to \lambda\,\Theta_R$, $\Theta_V \to \lambda\,\Theta_V$; then we see that the entropy of diatomic gases of eqn.(15.46), with $\gamma = 9/7$ is such that the new entropy constant indeed satisfies the scaling requirement of eqn.(15.41)!

15.5 Problems

Problem 15.1 Determine the entropy constants for polyatomic ideal gases, and verify the scaling property of eqn.(15.41).

Problem 15.2 Determine the vapor pressure of a diatomic solid along the same lines as eqns.(15.33,15.34). Under identical thermodynamical conditions, which will have a bigger vapor pressure, a monatomic solid or a diatomic solid? Clearly separate the effects of the entropy constants in this discussion.

Problem 15.3 Consider a gaseous reaction of the type $n_1M_1 + n_2M_2 + m_1D_1 \leftrightharpoons n_3M_3 + m_4D_4$, where M's are monoatomic and D's are diatomic. Assuming all of them to behave like ideal gases, determine the quantities K_0 and α in the law of mass action.

Problem 15.4 Consider the double ionization of calcium, i.e $Ca \rightleftharpoons Ca^{++} + 2e$. Determine the degree of ionization as a function of T and the energy required for complete double ionization of Ca.

Problem 15.5 Repeat the previous problem for the ionization of NaCl.

Problem 15.6 In thermionic emission, i.e ejection of electrons upon the heating of a metal, it is of importance to determine the density of an electron gas that is in equilibrium with the hot surface of a metal. Determine this by minimizing the free energy of an electron gas by treating the latter as an ideal monatomic gas. Express the result in terms of T and W, the work function of the metal.

16 Some Mathematical Aspects of Thermodynamics

16.1 Introduction

In this chapter we discuss some mathematical aspects of thermodynamics. This is not going to be an extensive account of the foundations and applications of a mathematical theory of thermodynamics. It is instead intended in the first place as a guide to the mathematics that has already been extensively used so far in the book like the properties and uses of the *partial derivatives*, *integrability conditions* etc. Therefore, the first parts of this chapter will explain, in as straightforward a manner as possible, these aspects. Readers who were unfamiliar with these concepts and could not therefore fully appreciate the scope of this book (and others of this nature) are urged to gain full familiarity with these parts. They are absolutely essential for a proper understanding of the full powers of thermodynamics.

A logical next step to the introduction of partial derivatives is the so called *Pfaffians*, a short name for *Pffafian form of differential equations*. An important issue in this context is the solvability of these differential equations which leads to the notion of *integrability conditions*. Again, this is crucial for a proper appreciation of thermodynamics. Many of these properties have already been widely used in the book and the reader is urged to use the material in the text as examples of these concepts. Most of the properties of thermodynamic potentials including the Maxwell relations are particular applications of these concepts.

After this, we shall explore interesting structures like *Jacobian matrices* and their determinants called *Jacobians*. There is an intimate relationship between partial derivatives and Jacobians, which will be explained in reasonable detail. We shall then introduce what we call *half-Jacobians*. Though this is a purely formal device, it has amazing applications in thermodynamics. Examples will be given of their use in getting Maxwell relations as well as their use in getting various properties of the thermodynamic potentials. As an application we shall show how Jacobians provide compact and elegant means of proving some results that were shown using the properties of partial derivatives.

Then we shall introduce the powerful notions of *differential forms* and their properties. These provide extremely compact codifications of the various laws of thermodynamics. We shall again provide examples of their use in thermodynamics. It should be emphasized that while all these mathematical techniques enable one to derive results known earlier in compact, succinct and elegant ways, they do not really add anything significant towards a deeper physical understanding of thermodynamics. Nevertheless, they offer very powerful techniques which should be part of the 'armory' of any serious student of thermodynamics.

16.2 Differentials and derivatives

This section must be well known to most readers, but it is still included for the sake of completeness, and also to help the few who are not familiar with it. If we have a function f(x) of a single variable x, the differential df(x) of f(x) is

$$df = f(x+dx) - f(x) \tag{16.1}$$

The derivative of f(x) with respect to x is defined as $(f(x+dx) - f(x))/dx$ in the limit in which $dx \to 0$:

$$\frac{d}{dx}f(x) = \frac{df}{dx}\ as\ dx \to 0 \tag{16.2}$$

This allows df to be written, to first order, as

$$df = \frac{d}{dx}f(x)\cdot dx \tag{16.3}$$

Now the first derivative is a function of x and one can construct its derivative which is the second derivative $\frac{d^2}{dx^2}f(x)$ of f(x) and so on.

16.2.1 Partial derivatives

Suppose we have a function of two variables, f(x,y); then the above considerations can be generalized. To first order we expect $df = adx + bdy$. Now there is a new circumstance that we can ask how f(x,y) changes when, say, x is changed to x+dx, but not changing y. Then df = a dx allowing a new type of derivative to be identified with a. It is denoted by $\left(\frac{\partial f}{\partial x}\right)_y$ and is called a *partial derivative* of f(x,y) with respect to x. Likewise we can have the partial derivative $\left(\frac{\partial f}{\partial y}\right)_x$ and the relation, to first order,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{16.4}$$

Now the partial derivatives are themselves functions of (x,y) and one can construct various second derivatives of f(x,y). Consistency requires

$$\frac{d^2}{dxdy}f(x,y) = \frac{d^2}{dydx}f(x,y) \tag{16.5}$$

leading to the important consequence

$$\frac{\partial}{\partial x}(\left(\frac{\partial f}{\partial y}\right)_x)|_y = \frac{\partial}{\partial y}(\left(\frac{\partial f}{\partial x}\right)_y)|_x \tag{16.6}$$

Here $..|_x$ means the quantity evaluated while x is held fixed etc.

Example

Let $f(x,y) = 2xy^2 + 7x^2y + x^2 + 3xy + 6y^2 + 2x + 4y + 5$. Let us evaluate the partial derivative $\left(\frac{\partial f}{\partial x}\right)_y$. This means we must find the derivative of f(x,y) with respect to x, while keeping y fixed. In other words, as far as x-dependence is concerned y will act like a constant whose derivative wrt x is zero. Then, $\left(\frac{\partial f}{\partial x}\right)_y = 2y^2 + 14xy + 2x + 3y + 2$. Likewise, $\left(\frac{\partial f}{\partial y}\right)_x = 4xy + 7x^2 + 3x + 12y + 4$. The partial derivative of $\left(\frac{\partial f}{\partial x}\right)_y$ with respect to y, keeping x fixed, is therefore 14x+3, while the partial derivative of $\left(\frac{\partial f}{\partial y}\right)_x$ wrt x, keeping y fixed is also 14x+3. This is the meaning of eqn.(16.6).

Example from thermodynamics

Consider the specific heat C_V. Its physical meaning is that while keeping the volume of the system fixed, say by enclosing a gas in a rigid container, the amount of heat that must be added to increase the temperature by dT is $C_V dT$. As we have seen, partial derivatives abound in thermodynamics.

16.2.2 Important properties of partial derivatives

Let us consider a quantity u that changes by du when another quantity v is changed by dv, while a third quantity w is held fixed. By our previous considerations $\left(\frac{\partial u}{\partial v}\right)_w = du/dv$ in the limit both du and dv tend to zero. On the other hand, $\left(\frac{\partial v}{\partial u}\right)_w$ is dv/du in the same limit. Therefore, it must follow that

$$\left(\frac{\partial u}{\partial v}\right)_w = \left(\frac{\partial v}{\partial u}\right)_w^{-1} \tag{16.7}$$

So far we talked about partial derivatives as derivative wrt one independent variable, say x in the above example, while another independent variable, y in the above example, was held fixed. But things can be more general and we can talk about partial derivatives when some function of the two variables is held fixed. To illustrate this, consider a function f(x,y) of two independent variables (x,y), so that

$$df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{16.8}$$

which always holds. Now consider varying x and y in such a way that f(x,y) is fixed, i.e df=0. The ratio dy/dx in the limit both dx,dy tend to zero while keeping f fixed is by definition $\left(\frac{\partial y}{\partial x}\right)_f$ and one gets

$$0 = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_f \rightarrow \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1 \tag{16.9}$$

which is the *triple product rule* for partial derivatives used extensively in the book. In arriving at its final form in eqn.(16.9), note that we have made use of eqn.(16.7) twice.

What many beginners find intriguing about this rule is that a 'chain rule' for derivatives ends up with a negative sign! But the above derivation is so transparent that this should not be bothersome any more. Another fact that intrigues them is that the partial derivative $\left(\frac{\partial y}{\partial x}\right)_f$ is non-vanishing even though x and y were declared to be independent. The resolution is that this partial derivative is evaluated keeping the f(x,y) fixed which makes the variations dx and dy no longer independent.

16.2.3 Pfaffian forms

Consider k independent variables $x_1, x_2 \ldots x_k$ and an equation of the form

$$df(\{x_i\}) = f_1(\{x_i\})dx_1 + f_2(\{x_i\})dx_2 + \ldots + f_k(\{x_i\})dx_k \qquad (16.10)$$

where we have used the short hand notation $\{x_i\}$ to denote possible dependence on all the independent variables. This is called a *Pfaffian form* or *Pfaffian form of differential equation*. An important question is the conditions the coefficient functions f_i must obey in order that this differential equation can be solved (or 'integrated') to give a function F. Let us, for the sake of clarity, consider only two independent variables x_1, x_2, and consider a Pfaffian differential equation

$$df(x_1, x_2) = N(x_1, x_2)dx_1 + M(x_1, x_2)dx_2 \qquad (16.11)$$

It is obvious from previous definitions that $N = \left(\frac{\partial f}{\partial x_1}\right)_{x_2}$ and $M = \left(\frac{\partial f}{\partial x_2}\right)_{x_1}$, and by eqn.(16.7), one must have $\left(\frac{\partial N}{\partial x_2}\right)_{x_1} = \left(\frac{\partial M}{\partial x_1}\right)_{x_2}$. Therefore, unless the coefficient functions M, N in the Pfaffian form of eqn.(16.11) satisfy this *integrability condition*, there will be no solutions to the Pfaffian differential equation. This has been the basis of the many thermodynamic identities that were discussed in the book. In fact, all the Maxwell relations are integrability conditions of this type. To clarify the issues raised here, let us consider a famous example where a Pfaffian-looking form is actually not integrable!

The first law

Let us consider the first law for an ideal gas with constant C_V(these considerations are generally valid, not just for this example), i.e $đQ = C_V dT + PdV$. This superficially looks like a Pfaffian form. It would have been a Pfaffian form if instead of $đQ$ we had dQ. Now $C_V dT = d(C_V T)$ so integrability of this equation would have been possible only if PdV could also have been written as a df for all V and T. But a moment's inspection shows that that would have been possible only if P were a function of V alone, which it certainly is not. The integrability condition $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T = 0$ would also have demanded the same. Of course, the physical significance of the failure to integrate this equation is that heat Q is not a state function and is instead path-dependent. Hence the convention to denote changes in Q by $\bar{d}Q$ and not dQ. This is also equivalent to the notions of exact and inexact differentials introduced earlier in the book.

16.3 Jacobian matrices and Jacobians

Let us illustrate the relevant ideas for a case with two independent variables, say, x_1, x_2. Generalization to several variables is straightforward. Now suppose we want to work with another set of independent variables, say, x'_1, x'_2, which are functions of the older independent variables. In the thermodynamic context, an example would be working with P,T instead of P,V. In that simple example one of the variables, i.e P, does not change but the other, say, T is changed to V but by equation of state $V = V(T,P)$.

The first question that arises is about the check for the independence of the new variables, as after all not every pair of functions of the old variables can form independent variables. This is answered through the properties of the *Jacobian Matrix* J_{ij}, defined as

$$J_{ij} = \left(\frac{\partial x'_i}{\partial x_j}\right)_{..} \tag{16.12}$$

where .. stands for keeping fixed all independent variables other than x_j. For the specific example of the two variable case, the Jacobian matrix is given by

$$J_{11} = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2} \quad J_{12} = \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1} \quad J_{21} = \left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \quad J_{22} = \left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} \tag{16.13}$$

The *Jacobian* J is the determinant of this Jacobian matrix:

$$J = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2}\left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} - \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1}\left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \tag{16.14}$$

In answer to the question about the independence of (x'_1, x'_2), the answer is that they will be independent only if $J \neq 0$, i.e if the Jacobian matrix is *non-singular*. There are many notations used for the Jacobian. We shall use the notation $J = \frac{\partial(x'_1, x'_2)}{\partial(x_1, x_2)}$ i.e.

$$J = \frac{\partial(x'_1, x'_2)}{\partial(x_1, x_2)} = \left(\frac{\partial x'_1}{\partial x_1}\right)_{x_2}\left(\frac{\partial x'_2}{\partial x_2}\right)_{x_1} - \left(\frac{\partial x'_1}{\partial x_2}\right)_{x_1}\left(\frac{\partial x'_2}{\partial x_1}\right)_{x_2} \tag{16.15}$$

16.3.1 Some important properties of Jacobians

It is immediately obvious that Jacobians satisfy

$$\frac{\partial(x,y)}{\partial(a,b)} = -\frac{\partial(y,x)}{\partial(a,b)} \rightarrow \frac{\partial(x,x)}{\partial(a,b)} = 0 \tag{16.16}$$

A non-trivial property of the Jacobians is their *composition law*

$$\frac{\partial(x,y)}{\partial(a,b)} \cdot \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(x,y)}{\partial(c,d)} \tag{16.17}$$

It is difficult to establish this directly from the definition of the Jacobian given above. If the independent variables are thought of as *coordinates* of a two-dimensional manifold, the invariant area element is given by $dA = \sqrt{\mathrm{g}}\,dxdy$ where g is the determinant of the *inverse metric* on the manifold. Under changes of coordinates from (x,y) to, say (a,b), this changes according to

$$\mathrm{g}(x,y) = \left\{ \frac{\partial(x,y)}{\partial(a,b)} \right\}^{-2} \mathrm{g}'(a,b) \tag{16.18}$$

The area dA being a geometrical quantity does not depend on the choice of coordinates and one gets the important relation

$$dxdy = \frac{\partial(x,y)}{\partial(a,b)} \cdot dadb \tag{16.19}$$

Considering the sequence of transformations $(x,y) \to (a,b) \to (c,d)$ and directly comparing to the transformation $(x,y) \to (c,d)$, and making use of eqn.(16.19) at every step leads to eqn.(16.17).

Yet another important property of Jacobians is that every partial derivative can itself be expressed as a Jacobian:

$$\frac{\partial(x,z)}{\partial(y,z)} = \left(\frac{\partial x}{\partial y}\right)_z \tag{16.20}$$

This can easily be shown from the definition of the Jacobian itself.

16.3.2 Half-Jacobians!

Let us first introduce a convenient shorthand for Jacobians [59]:

$$\frac{[x,y]}{[a,b]} = \frac{\partial(x,y)}{\partial(a,b)} \tag{16.21}$$

Then the composition law of eqn.(16.17) can be recast as

$$\frac{[x,y]}{[a,b]} \cdot \frac{[a,b]}{[c,d]} = \frac{[x,y]}{[c,d]} \tag{16.22}$$

Now consider the independent variables (c,d) to be arbitrary, in principle specifiable, but never specified in practice. Furthermore, introduce yet another notation via

$$\{x,y\} = \frac{\partial(x,y)}{\partial(c,d)} \tag{16.23}$$

We can call objects like $\{x,y\}$ *half-Jacobians* as only half the information required to compute the Jacobian is explicitly available, i.e (x,y). But it must be kept in mind that [x,y] takes on definite value once (c,d) is specified. As a Jacobian, it never vanishes.

This will turn out to be very important. Because of this, eqn.(16.17), or equivalently eqn.(16.22) can be recast in terms of half-Jacobians as

$$\frac{\partial(x,y)}{\partial(a,b)} = \frac{\{x,y\}}{\{a,b\}} \tag{16.24}$$

Let us consider an interesting application of half-Jacobians by rewriting eqn.(16.8) with the help of eqn.(16.20) and eqn.(16.24) as

$$df = \frac{\{f,y\}}{\{x,y\}}dx + \frac{\{f,x\}}{\{y,x\}}dx \tag{16.25}$$

which, on using $\{x,y\} = -\{y,x\}$, can be written as

$$\{x,y\}df + \{f,x\}dy + \{y,f\}dx = 0 \tag{16.26}$$

16.3.3 Maxwell relations and Jacobians

Now we illustrate the powerfulness of Jacobians by showing the equivalence of the four Maxwell relations to a *single* Jacobian condition. Consider the Maxwell relation $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ and rewrite it in terms of half-Jacobians as

$$\frac{\{V,P\}}{\{S,P\}} = \frac{\{T,S\}}{\{P,S\}} \rightarrow \{T,S\} = \{P,V\} \tag{16.27}$$

In other words this Maxwell relation is equivalent to the statement that the transformation (T,S) to (P,V) is *area preserving*, i.e the corresponding Jacobian is unity. This is the familiar result that the Carnot cycle represented in (P,V) or (S,T) coordinates has the same area! Now it can be shown that $\{T,S\} = \{P,V\}$ also reproduces the other three Maxwell relations. We show one of them explicitly:

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{\{S,T\}}{\{P,T\}} = -\frac{\{P,V\}}{\{P,T\}} = -\left(\frac{\partial V}{\partial T}\right)_P \tag{16.28}$$

16.3.4 Thermodynamic potentials and Jacobians

As a prelude, let us consider the Pfaffian $dz = M(x,y)dx + N(x,y)dy$, from which it follows that, for some other choice of independent variables (a,b)

$$\left(\frac{\partial z}{\partial a}\right)_b = M(x,y)\left(\frac{\partial x}{\partial a}\right)_b + N(x,y)\left(\frac{\partial x}{\partial a}\right)_b \rightarrow \{z,b\} = M\{x,b\} + N\{y,b\} \tag{16.29}$$

This holds for arbitrary choice of b and can be used to efficiently generate a number of identities. Of course, N and M must satisfy the integrability conditions characterstic of the Pfaffian forms.

This result can be readily applied when z can be taken to be any of the thermodynamic potentials. Let us illustrate by taking z to be U,H,F and G respectively, yielding

$$\begin{aligned} dU &= TdS - PdV \rightarrow \quad \{U,X\} = T\{S,X\} - P\{V,X\} && (16.30)\\ dH &= TdS + VdP \rightarrow \quad \{H,X\} = T\{S,X\} + V\{P,X\} && (16.31)\\ dF &= -SdT - PdV \rightarrow \quad \{F,X\} = -S\{T,X\} - P\{P,X\} && (16.32)\\ dG &= -SdT + VdP \rightarrow \quad \{G,X\} = -S\{T,X\} + V\{P,X\} && (16.33) \end{aligned}$$

X can be taken to be any independent variable, and these can yield a host of identities.

16.3.5 Another application to thermodynamics

We close this discussion with another application to thermodynamics. Following Rao [59] we apply the method of Jacobians to derive eqn.(3.49) from chapter 3. Let us first recall that equation:

$$TdS = C_V dT + \frac{T\alpha}{\kappa_T} dV \tag{16.34}$$

From our earlier discussion, it is easy to see that

$$dS = \frac{\{S,V\}}{\{T,V\}} dT + \frac{\{S,T\}}{\{V,T\}} dV \tag{16.35}$$

The specific heat at constant volume C_V, the coefficient of expansion α, and the isothermal compressibility κ_T can be expressed in terms of Jacobians as follows:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\{S,V\}}{\{T,V\}} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{\{V,P\}}{\{T,P\}} \quad \kappa_T = -\frac{1}{V}\frac{\{V,T\}}{\{P,T\}} \tag{16.36}$$

On using $\{S,T\} = \{V,P\}$, it is easy to see that eqn.(16.35) and eqn.16.36) are indeed the same.

16.4 Differential forms in thermodynamics

Now we very briefly present the uses of *differential forms* in thermodynamics. As structures, differential forms are even more formal than Jacobians, and a full discussion of all their nuances is beyond the scope of this book. Let us begin with some definitions. All functions f are said to be *0-forms*. Their differentials, df, are said to be *1-forms*. There is an operation, called the *exterior derivative*, denoted by **d** which acts on all forms and increases their rank by one. For example, acting on functions, which are 0-forms, exterior derivative yields the 1-form df i.e $\mathbf{d}f = df$. At this level, and only at this level, the exterior derivative coincides with the differential. If ω is a p-form, $\mathbf{d}\omega$ is a p+1-form.

A crucial property of exterior derivatives is that $\mathbf{d}(\mathbf{d}(anything)) = 0$. In this respect **d** differs fundamentally from differentials, and this is a frequent source of confusion in this subject. The next structure of importance is the so called *wedge product* of differential forms. If ω is a p-form, and η is a q-form, $\omega \wedge \eta = (-1)^{pq}\eta \wedge \omega$ is a p+q-form.

A very important rule to remember is for the exterior derivative of wedge products. If ω is a p-form, and η is a q-form, the rule is

$$\mathbf{d}(\omega \wedge \eta) = \mathbf{d}\omega \wedge \eta + (-1)^p \omega \wedge \mathbf{d}\eta \tag{16.37}$$

Let us pause and consider a few examples. Let us consider two functions f and g; as per our earlier discussion, both are 0-forms, and their wedge product should also be a 0-form. Indeed, the product function fg is a 0-form, being another function. Next consider the wedge product of f with dg, the latter being a one form. This gives the 1-form fdg. If we apply eqn.(16.37) to the product fg, we get $d(fg) = df \cdot g + f \cdot dg$, which is again familiar. But let us apply it to fdg:

$$\mathbf{d}(fdg) = df \wedge dg \tag{16.38}$$

as $\mathbf{d}^2 g = 0$. This is a 2-form.

16.4.1 Some applications to thermodynamics

Consider the 1-form $dU = TdS - PdV$, which is nothing but the first law. Applying the exterior derivative to this

$$\begin{aligned}
\mathbf{d}(\mathbf{d}U) &= 0 = dT \wedge dS - dP \wedge dV \\
&= (\left(\frac{\partial T}{\partial V}\right)_S dV + \left(\frac{\partial T}{\partial S}\right)_V dS) \wedge dS - (\left(\frac{\partial P}{\partial S}\right)_V dS + \left(\frac{\partial P}{\partial V}\right)_S dV) \wedge dV \\
&= (\left(\frac{\partial T}{\partial V}\right)_S + \left(\frac{\partial P}{\partial S}\right)_V) dV \wedge dS
\end{aligned} \tag{16.39}$$

This is nothing but the Maxwell relation M.1!

As yet another example, consider the same first law but written as $dS = (dU + PdV)/T$, and consider $0 = \mathbf{d}(dS)$ i.e

$$\begin{aligned}
0 &= \mathbf{d}(\frac{dU}{T} + \frac{P}{T}dV) \\
&= -\frac{1}{T^2}dT \wedge dU + \frac{1}{T}dP \wedge dV - \frac{P}{T^2}dT \wedge dV \\
&= -\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T dT \wedge dV + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V dT \wedge dV - \frac{P}{T^2}dT \wedge dV \\
&= \left\{-\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T^2}\right\} dT \wedge dV
\end{aligned} \tag{16.40}$$

This is nothing but the fundamental equation encountered earlier in eqns.(3.7,3.9, 3.41):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{16.41}$$

As a last application of the differential forms we now consider the relationship of the wedge products and Jacobians. Let us restrict ourselves to the case of two independent variables. In particular, let us consider the transformation taking two independent variables (x,y) to two other independent variables (a,b). Let us start with the 2-form $dx \wedge dy$:

$$\begin{aligned} dx \wedge dy &= (\left(\frac{\partial x}{\partial a}\right)_b da + \left(\frac{\partial x}{\partial b}\right)_a db) \wedge (\left(\frac{\partial y}{\partial a}\right)_b da + \left(\frac{\partial y}{\partial b}\right)_a db) \\ &= (\left(\frac{\partial x}{\partial a}\right)_b \left(\frac{\partial y}{\partial b}\right)_a - \left(\frac{\partial x}{\partial b}\right)_a \left(\frac{\partial y}{\partial a}\right)_b) da \wedge db \\ &= \frac{\partial(x,y)}{\partial(a,b)} \cdot da \wedge db \end{aligned} \tag{16.42}$$

From this we can easily deduce the composition law of Jacobians of eqns.(16.17, 16.22). For that, consider the sequence of transformations $(x,y) \to (a,b) \to (p,q)$ and we have

$$dx \wedge dy = \frac{\partial(x,y)}{\partial(a,b)} \cdot da \wedge db = \frac{\partial(x,y)}{\partial(a,b)} \frac{\partial(a,b)}{\partial(p,q)} \cdot dp \wedge dq = \frac{\partial(x,y)}{\partial(p,q)} \cdot dp \wedge dq \tag{16.43}$$

The composition law then follows.

Suggested Reading

1. Rao, Y.V.C, *Engineering Thermodynamics*, Universities Press, Hyderabad, pp.366-379.
2. Salamon, P., Andresen, B., Nulton, James, and Konopka, A.K., *The mathematical structure of thermodynamics*. in A.K. Konopka (ed.): Handbook of systems biology (CRC Press Boca Raton, 2007)

References

1. C.J. Giunta. *http://web.lemoyne.edu/∼giunta/gaygas.html.*
2. F. Cajori. Did Davy melt ice by friction in vacuum? *Nature*, 117, 1926.
3. H.B. Callen. *Thermodynamics and An Introduction to Thermostatistics.* John Wiley and Sons, 1985.
4. C. Carathéodory. *Math. Ann.*, 67:355, 1909.
5. N.-L.-Sadi Carnot. *Rëflexions sur la Puissance Motrice du Feu.* Gauthier-Villars, Paris, 1824.
6. E. Clapeyron. Mëmoire sur la puissance motrice de chaleur. *J. de l'Ecole Pol.*, xiv, 1834.
7. R. Clausius. *Annalen der Physik*, 79:368,500, 1850.
8. R. Clausius. On the moving force of heat and the laws of heat which may be deduced therefrom. *Philosophical Magazine*, 2(4):1–21,102–19, 1850.
9. R. Clausius. *Philosophical Magazine*, 12(4):81, 1856.
10. Humphrey Davy. In *Collected Works*, volume 2, pages 11–12. 1829.
11. A. de la Rive and F. Marcet. *Ann. Chim. Phys.*, 75:113, 1840.
12. P. Delsing. Refrigeration below 1k. *http://fy.chalmers.se/ delsing/LowTemp/LectureNotes/LectureNotes16.PDF.*
13. P. Dulong and A.T. Petit. *Ann. Chim. Phys*, page 395, 1819.
14. A. Einstein. *AdP*, 17:132, 1905.
15. A. Einstein. *AdP*, 22:180, 1907.
16. T. Knuuttila et al. World record in low temperatures. *http://ltl.tkk.fi/wiki/LTL*, 2000.
17. Enrico Fermi. *Thermodynamics.* Dover Publications, 1936.
18. R.H. Fowler and E.A. Guggenheim. *Statistical Thermodynamics.* University Press, 1939.
19. J.W. Gibbs. Equilibrium of heterogeneous substances. *Transactions of the Connecticut Academy*, 1875-77.
20. J.W. Gibbs. *Elementary Principles in Statistical Mechanics.* Yale University Press, 1902.
21. C.J. Gorter and H. Casimir. On supraconductivity. *Physica.*
22. E. Guha. *Basic Thermodynamics.* Narosa Publishing House, 2000.
23. N.D. Hari Dass. A critique of Sadi Carnot's work and a mathematical theory of the caloric. arxiv:1306. 1939 (Phys. hist-ph), 2013
24. N.D. Hari Dass. Does the first part of second law also imply its second part? arxiv:1306. 1937 (Phys. hist-ph), 2013.
25. E.P. Harris and D.E. Mapother. *Physical Review*, 165(2):522, 1968.
26. K. Huang. *Statistical Mechanics.* John Wiley and Sons, 2008.
27. IAPS. Release on surface tension of water substance issued by the International Association for Properties of Steam, 1975, Howard J. White Jr, Executive Secretary, National Bureau of Standards, Washington, D.C.
28. E.T. Jaynes. The Gibbs paradox. In *Maximum Entropy and Bayesian Methods*, Ed. Smith, C.R et al, pages 1–22. Kluwer Academic, 1992.
29. L. Kadanoff and H. Maris. *Am. J. Phys.*, 46(6):652, 1978.
30. W.H. Keesom and P.H. van Laer. *Physica V*, (3):193, 1938.
31. J. Kestin. *A Course in Thermodynamics.* Blaisdell Publishing Company, 1966.
32. J. Kogut and K. Wilson. *Phys. Reports.*, 12C:75, 1974.

33. D. Kondepudi and I. Prigogine. *Modern Thermodynamics*. John Wiley and Sons, 1998.
34. L. Landau and E.M. Lifshitz. *Statistical Physics*. Elsevier, 1980.
35. P.S. Laplace. Sound velocity. In *Oeuvres Complëtes*, volume 14, page 329. Paris, 1912.
36. J.C. Le Guillou and J. Zinn-Justin. *Physical Review B*, 21:3976, 1980.
37. Harvey S. Leff. Teaching the photon gas in introductory physics. *American Journal of Physics*, 70(8):792, 2002.
38. J.M.H. Levelt Sengers. Critical exponents at the turn of the century. *Physica*, 82A:319, 1976.
39. J.M.H. Levelt Sengers. et al. Thermodynamic properties of steam. *J. Phys. Chem. Ref. Data*, 12(1):1, 1983.
40. O.V. Lounasmaa. *Experimental Principles and Methods Below 1 K*. Academic Press, 1974.
41. O.V. Lounasmaa. Dilution refrigeration. *Sci. Instrum.*, 12:668, 1979.
42. J.J. MacIntosh. **Robert Boyle**. *Stanford Encyclopedia of Philosophy*, 2010.
43. J.C. Maxwell. 10. *Nature*, page 407, 1874.
44. J.C. Maxwell. 11. *Nature*, page 418, 1875.
45. P. Medley. et al. Spin gradient demagnetization cooling of ultra cold atoms. *arXiv:1006.467414[cond-mat., quant-gas.]*, 2010.
46. E. Mendoza. Delaroche and Berard, and experimental error. *The British Journal for the History of Science*, 23(78):285, 1990.
47. Ingo Müller. *A History of Thermodynamics*. Springer-Verlag, 2007.
48. W. Nernst. *Gött. Nachr.*, 1906:1.
49. W. Nernst. *PAW*, page 933, 1906.
50. W. Nernst. *The New Heat Theorem*. Dover, 1969.
51. L. Onsager. *Del Nuovo Cimento*, VI(Serie IX):2, 1949.
52. A. Pais. *Subtle is the Lord*. Oxford University Press, 1982.
53. Wolfgang Pauli. *Thermodynamics and Kinetic Theory of Gases*. Dover, 1958.
54. A.B. Pippard. *The Elements of Classical Thermodynamics*. Cambridge University Press, 1961.
55. M. Planck. *Verh. Deutsch. Phys. Ges.*, 2:202, 1900.
56. M. Planck. *Verh. Deutsch. Phys. Ges.*, 2:237, 1900.
57. Max Planck. *Treatise on Thermodynamics*. Dover, 1910.
58. F. Pobell. *Matter and Methods at Low Temperatures*. Springer, 2007.
59. Y.V.C. Rao. *Engineering Thermodynamics Through Examples*. Universities Press, 2002.
60. H.V. Regnault. *Memoires de l'Academie des Sciences de l'Institut de France, Paris*, 21:1–748, 1847.
61. R. Resnick, D. Halliday, and K.S. Krane. *Physics, Volume I*. John Wiley and Sons, 2000.
62. J.S. Rowlinson. Translation of 'the thermodynamic theory of capillarity'. *J. Statistical Physics*, 20(2):197, 1979.
63. M.N. Saha and B.N. Srivastava. *A Treatise on Heat*. The Indian Press, 1958.
64. Arnold Sommerfeld. *Thermodynamics and Statistical Mechanics*. Levant Books, Kolkata, 2005.
65. J. Srinivasan. Sadi Carnot and the second law of thermodynamics. *Resonance*, 6(November):42, 2001.
66. R. Srinivasan. Approach to absolute zero-i. *Resonance*, 1(December):6, 1996.
67. R. Srinivasan. Approach to absolute zero-ii. *Resonance*, 2(February):8, 1997.
68. R. Srinivasan. Approach to absolute zero-iii. *Resonance*, 2(June):6, 1997.
69. R. Srinivasan. Approach to absolute zero-iv. *Resonance*, 2(October):8, 1997.

70. S. Takemura, R. Kobayashi, and Y. Fukumoto. A possible origin of the low temperature Curie law of the spin doughnut $mo_{75}v_{20}$. *Journal of Physics*, Conference Series(145):012081, 2009.
71. W. Thomson. Account of Carnot's Theory. *Transactions of the Edinburgh Royal Society*, page xiv, 1849.
72. W. Thomson. On a mechanical theory of thermoelectric currents. *Proceedings of Royal Society of Edinburgh*, 1851.
73. S. Torquato and G. Stell. *The Journal of Physical Chemistry*, 85(21):3029, 1981.
74. J.D. van der Waals. *Z. Physik u. Chem.*, 13:42, 1894.
75. N.B. Vargaftik, B.N. Volkov, and L.D. Voljak. International tables of surface tension of water. *J. Phys. Chem. Ref. Data*, 12(3):817, 1983.
76. G. Venkataraman. *Journey into Light*. Indian Academy of Sciences, 1988.
77. W. Wagner and A. Pruss. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data*, 31:387–535, 2002.
78. H.F. Weber. *Philosophical Magazine*, ser.4 49(324):161, 1875.
79. K. Wilson. *Phys. Rev. B*, 4:3174, 1971.

Thermodynamics

Unshaken by the revolutionary developments of quantum theory, the foundations of thermodynamics have demonstrated great resilience. The impact of thermodynamics on scientific thought as well as its practical impact have been unmatched by any other field of science. Its applications range over physics, chemistry, physical chemistry, engineering, and, more recently, biology and even black holes. **The Principles of Thermodynamics** offers a fresh perspective on classical thermodynamics, highlighting its elegance, power, and conceptual economy. The book demonstrates how much of natural phenomena can be understood through thermodynamics.

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