

A New Formation of Diamond.

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Boiling-Point and Melting-Point of Carbon.

On the average the critical point of a substance is 1·5 times its absolute boiling-point. Therefore the critical point of carbon should be about 5800° Ab. But the absolute critical temperature divided by the critical pressure is for all the elements so far examined never less than 2·5; this being about the value Sir James Dewar finds for hydrogen. So that, accepting this, we get the maximum critical pressure as follows, viz., 2320 atmospheres:—

$$\frac{5800^{\circ} \text{ Ab.}}{\text{CrP}} = 2\cdot5, \text{ or CrP} = \frac{5800^{\circ} \text{ Ab.}}{2\cdot5}, \text{ or } 2320 \text{ atmospheres.}$$

Carbon and arsenic are the only two elements that have a melting-point above the boiling-point; and among compounds carbonic acid and fluoride of silicium are the only other bodies with similar properties. Now the melting-point of arsenic is about 1·2 times its absolute boiling-point. With carbonic acid and fluoride of silicium the melting-points are about 1·1 times their boiling-points. Applying these ratios to carbon we find that its melting-point would be about 4400°.

Therefore, assuming the following data,

Boiling-point	3870° Ab.
Melting-point	4400°
Critical temperature	5800°
Critical pressure	2320 Ats.

the Rankine or Van der Waals formula calculated from the boiling-point and critical data would be as follows:—

$$\log P = 10\cdot11 - 39120/T,$$

and this gives for a temperature of 4400° Ab. a pressure of 16·6 Ats. as the melting-point pressure.

The results of the formula are given in the form of a table:—

Temperature	Pressure.
Ab.	Ats.
3870°	1.00 Boiling-point.
4000°	2.14
4200°	6.25
4400°	16.6 Melting-point.
4600°	40.4
4800°	91.2
5000°	193
5200°	386
5400°	735
5600°	1330
5800°	2320 Critical point (15 tons per square inch).

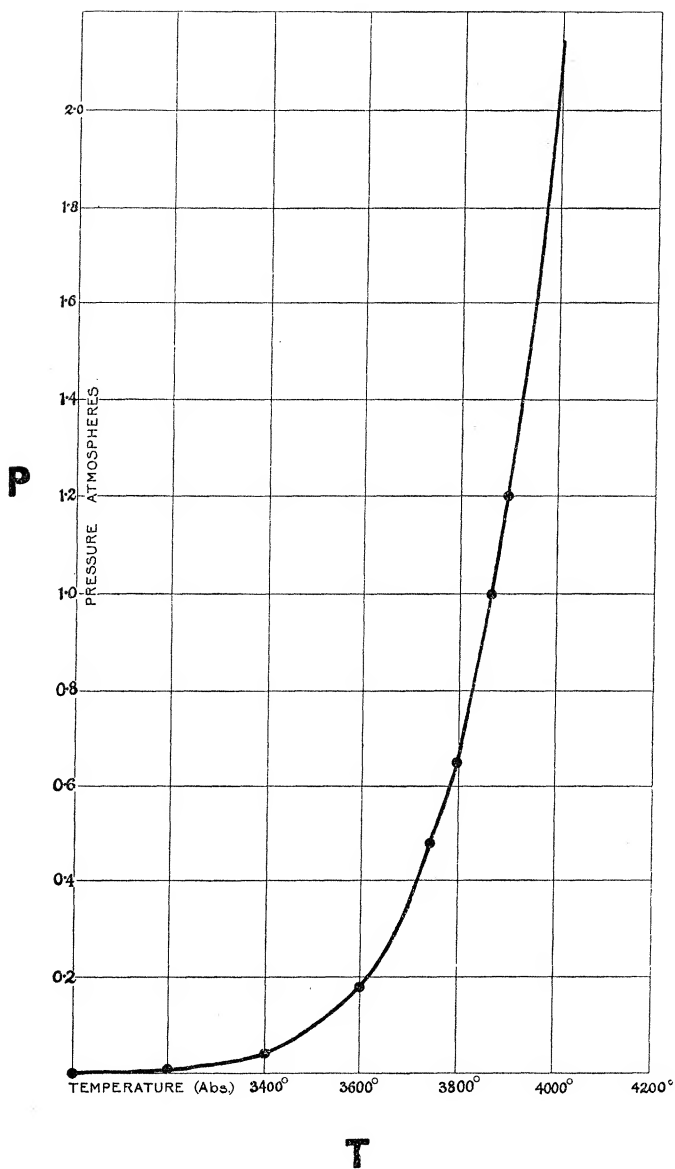
If then we may reason from these rough estimates, above a temperature of 5800° Ab. no amount of pressure will cause carbon vapour to assume liquid form, whilst at 4400° Ab. a pressure of above 17 atmospheres would suffice to liquefy some of it. Between these extremes the curve of vapour pressure is assumed to be logarithmic, as represented in the accompanying diagram. The constant 39120 which occurs in the logarithmic formula enables us to calculate the latent heat of evaporation. If we assume the vapour density to be normal, or the molecule in vapour as C_2 , then the heat of volatilisation of 12 grammes of carbon would be 90,000 calories; or, if the vapour is a condensed molecule like C_6 , then the 12 grammes would need 30,000 calories. In the latter case the evaporation of 1 gramme of carbon would require 2500 calories, whereas a substance like zinc needs only about 400 calories.

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I have long speculated as to the possibility of obtaining artificially such pressures and temperatures as would fulfil the above conditions. In their researches on the gases from fired gunpowder and cordite, Sir Frederick Abel and Sir Andrew Noble obtained in closed steel cylinders pressures as great as 95 tons to the square inch, and temperatures as high as 4000° C. According to a paper recently communicated to the Royal Society, Sir Andrew Noble, exploding cordite in closed vessels, has obtained a pressure of 8000 atmospheres, or 50 tons per square inch, with a temperature reaching in all probability 5400° Ab.

Here, then, we have conditions favourable for the liquefaction of carbon, and were the time of explosion sufficient to allow the reactions to take place, we should certainly expect to get the liquid carbon to solidify in the crystalline state.*

* Sir James Dewar, in a Friday Evening Discourse at the Royal Institution, 1880,



showed an experiment proving that the temperature of the interior of a carbon tube heated by an outside electric arc was higher than that of the oxy-hydrogen flame. He placed a few small crystals of diamond in the carbon tube, and, maintaining a current of hydrogen to prevent oxidation, raised the temperature of the tube in an electric furnace to that of the arc. In a few minutes the diamond was transformed into graphite. At first sight this would seem to show that diamond cannot be formed at temperatures above that of the arc. It is probable, however, for reasons given above, that at exceedingly high pressures the result would be different.

By the kindness of Sir Andrew Noble I have been enabled to work upon some of the residues obtained in closed vessels after explosions, and I have submitted them to the same treatment that Moissan's granulated iron had gone through.* After weeks of patient toil I removed the amorphous carbon, the graphite, the silica,† and other constituents of the ash of cordite, and obtained a residue among which, under the microscope, crystalline particles could be distinguished. Some of these particles, from their crystalline appearance and double refraction, were silicon carbide; others were probably diamonds. The whole residue was dried and fused at a good red heat in an excess of potassium bifluoride, to which was added during fusion 5 per cent. of nitre. (Previous experiments had shown me that this mixture readily attacked and dissolved silicon carbide; unfortunately it also attacks diamond to a slight degree.) The residue, after thorough washing and then heating in fuming sulphuric acid, was washed, dried, and the largest crystalline particles picked out and mounted. All the operations of washing and acid treatment were performed in a large platinum crucible by decantation (except the preliminary attack with nitric acid and potassium chlorate, when a hard glass vessel was used); the final result was washed into a shallow watch-glass and the selection made under the microscope.

From the treatment these crystals have undergone, chemists will agree with me that diamonds only could stand such an ordeal; on submitting them to skilled crystallographic authorities my opinion is confirmed. Speaking of one crystal (303), Professor Bonney calls it "a diamond showing octahedral planes with dark boundaries due to high refracting index." After careful examination, Professor Miers writes of the same crystal diamond:—"I think one may safely say that the position and angles of its faces, *and of its cleavages*, the absence of birefringence, and the high refractive index, are all compatible with the properties of the diamond crystallising in the form of an octahedron. Others of the remaining crystals, which show a similar high refractive index, appeared to me to present the same features."

It would have been more conclusive had I been able to get further evidence as to the density and hardness of the crystals; but I am still working at the subject, and hope to add these confirmatory tests. From what I have already said I think there is no doubt that in these closed-vessel explosions we have another method of producing the diamond artificially.

* 'Chemical News,' vol. 76, p. 14, July 9, 1897.

† The silica was in the form of spheres, perfectly shaped and transparent, mostly colourless, but among them several of a ruby colour. When 5 per cent. of silica was added to cordite, the residue of the closed-vessel explosion contained a much larger quantity of these spheres.
