APPENDIX

LITERATURE OF ORGANIC CHEMISTRY

A,1. BEILSTEIN'S "HANDBUCH"

THE fourth edition of Beilstein's *Handbuch der organischen Chemie* originally issued by the Deutsche Chemische Gesellschaft * is the largest compilation of information upon organic chemistry. The main series (Hauptwerk) is composed of 27 volumes and covers the literature to January 1, 1910. The first supplement (Erstes Ergänzungswerk), 27 volumes, surveys the literature to 1919. Thus far (1955) some 26 volumes of the second supplement (Zweites Ergänzungswerk), covering the decade to 1929, have been published. In addition there is a comprehensive subject index (Volume XXVIII, Parts I and II) and a formula index (Volume XXIX, Parts I and II) for the main series and first supplement and also for the second supplement: all organic compounds described to 1929 are listed with references to the appropriate volumes of Beilstein.

The system of classification adopted is based upon the premise that every definite compound can be expressed by a structural formula. This leads to the four **divisions** tabulated below. Furthermore, the position of each definite organic compound in the appropriate division is determined by its **stem nucleus**, which is obtained by replacing in the formula of the compound all atoms or groups attached to carbon by the equivalent number of hydrogen atoms except where such replacement would involve the breaking of a cyclic chain. Moreover, whenever a given formula gives rise to stem nuclei of more than one division, the compound will be found in the same main division as the one of its component stem nuclei which comes last in the systematic arrangement: this is sometimes spoken of the "principle of latest position in the system." No cyclic chain of atoms may be broken during the formulation of the stem nucleus: this principle leads to the inclusion of compounds such as the anhydrides and imides of dibasic acids, sulphimides, lactides and lactones of hydroxy-acids, etc. under heterocyclic compounds.

The four main divisions, with examples of stem nuclei, are tabulated below.

Division I. Acyclic compounds (*Acyclic stem nuclei*). The carbon atoms are joined in open chains only.

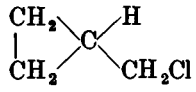
COMPOUND	STEM NUCLEUS
$CH_3CHClCOOH$	$CH_3CH_2CH_3$
$CH_3CH_2OCH_3$	CH_3CH_3 and CH_4
$CH_3CH_2OSO_2OH$	CH_3CH_3
$CH_3CH_2CH_2N_3$	$CH_3CH_2CH_3$

Division II. Acyclic compounds (*Isocyclic stem nuclei*). The carbon

* Julius Springer, Berlin.

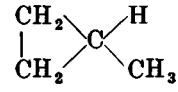
atoms are joined in closed rings which do not include other kinds of atoms as ring components.

COMPOUND

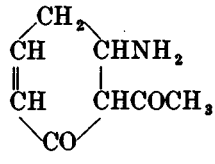


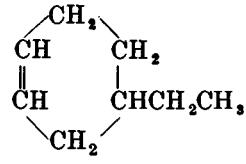
$BrC_6H_4COOCH_2CH_2Cl$

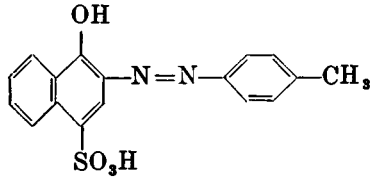
STEM NUCLEUS

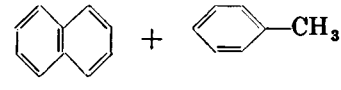


$C_6H_5CH_3$ and CH_3CH_3



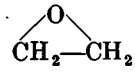


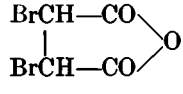


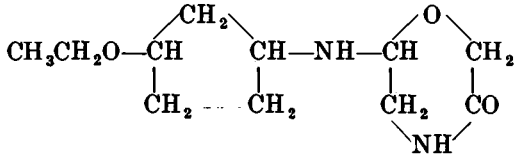


Division III. Heterocyclic compounds (*Heterocyclic stem nuclei*). The carbon atoms are joined in closed rings which include one or more other kinds of atoms as ring components. Anhydrides and imides of dibasic acids, as well as lactones, lactams, etc. are thus included in this division

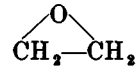
COMPOUND

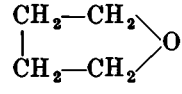


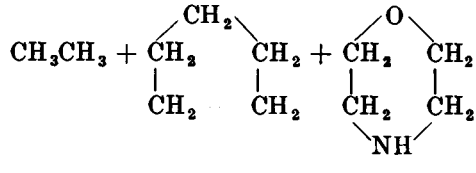




STEM NUCLEUS







The last compound is a good example of the " principle of latest position " ; the stem nuclei are assigned to divisions I, II and III respectively, but the substance is assigned to the " latest " division III.

Division IV. Natural products. These may be compounds of unknown or partially known structure at 1.1.1910 or 1.1.1920 and have not been assigned places in the previous divisions.

Some amplification of the classification of heterocyclic compounds may now be given. The two important hetero atoms are oxygen and nitrogen: in the former class are included S, Se and Te and in the latter class P, As, etc. The sub-division (hetero-classes) of Division III is as follows:

Compounds with one cyclically bound oxygen atom.
Compounds with two cyclically bound oxygen atoms.
Compounds with three cyclically bound oxygen atoms, etc.
Compounds with one cyclically bound nitrogen atom.
Compounds with two cyclically bound nitrogen atoms.
Compounds with three cyclically bound nitrogen atoms, etc.
Compounds with one cyclic nitrogen and one cyclic oxygen atom.
Compounds with one cyclic nitrogen and two cyclic oxygen atoms.
Compounds with one cyclic nitrogen and three cyclic oxygen atoms, etc.
Compounds with two cyclic nitrogen and one cyclic oxygen atom.
Compounds with two cyclic nitrogen and two cyclic oxygen atoms.
Compounds with two cyclic nitrogen and three cyclic oxygen atoms, etc.

The acyclic division, the isocyclic division and all hetero-classes are further divided into 28 main classes, the first of which consists of the stem nuclei (*i.e.*, hydrocarbons in the acyclic and isocyclic divisions), whilst the others depend upon the functional group present. The most important main classes and functional groups are collected below.

Class	Characterising Groups
1. Stem nuclei	—
2. Hydroxy compounds	—OH
3. Carbonyl compounds	—CHO or >C=O
4. Carboxylic acids	—COOH
5. Sulphinic acids	$-SO_2H$
6. Sulphonic acids	$-SO_3H$
7. Selenious and selenic acids	$-SeO_2H$, $-SeO_3H$
8. Amines	$-NH_2$
9. Hydroxylamines	—NHOH
10. Hydrazines	$-NHNH_2$
11. Azo compounds	—N=NH
12–22. Other nitrogen derivatives	
23–28. Compounds in which C is united directly to a metallic element (organo-metallic compounds). The order is according to Periodic Groups 5, 4, 3, 2, 1, 6, 7 and 8. Thus Class 23 consists of compounds in which C is attached to P, As, Sb or Bi.	

Space does not permit the inclusion of a further discussion of the detailed sub-divisions adopted in the Handbuch,* and it may be noted

* The reader is referred to the following for a more comprehensive account:
(1) Beilstein's *Handbuch*, Main Series, Volume I, pp. 1–46 (1918).
(2) Prager, Stern and Ilberg, *System der organischen Verbindungen*, 246 pp. (1929). This volume lists the 4877 "system numbers" and includes the common names with appropriate references to "system numbers" (Julius Springer: Edwards Brothers).
(3) Huntress, *A Brief Introduction to the Use of Beilstein's Handbuch der organischen Chemie*, 44 pp. (1938) (J. Wiley).
(4) Richter and Ilberg, *Kurze Anleitung zur Orientierung in Beilsteins Handbuch der organischen Chemie*, 23 pp. (1936) (Julius Springer).
(5) Soule, *Library Guide for the Chemist*, pp. 127–153 (1938) (McGraw-Hill).
(6) Dyson, *A Short Guide to Chemical Literature*, pp. 68–74 (1951) (Longmans, Green)

that in order to facilitate cross references within the various parts of the classification, the entire subject matter has been divided into 4877 arbitrary units called "**system numbers.**" The general scope of the work will be evident from **Table A,1**, in which is included the page numbers of selected key compounds in the Hauptwerk (Main Series).

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
		ACYCLIC DIVISION	
I	1918	1–151	*Hydrocarbons.* Methane, 56. Ethane, 80. Ethylene, 180. Acetylene, 228. *Hydroxy Compounds: Alcohols and Derivatives.* Methyl alcohol, 273. Ethyl alcohol, 292. Ethyl ether, 314. Glycerol, 502. *Carbonyl Compounds: Aldehydes, Ketones, Ketenes and Derivatives.* Formaldehyde, 558. Acetaldehyde, 635. Acetone, 635. Ketene, 724. *Hydroxy-Carbonyl Compounds: Aldehyde-Alcohols, Ketone-Alcohols, Monosaccharides and Derivatives.* Glycolaldehyde, 817. Aldol, 824. Pentoses, 858. Hexoses, 878.
I, 1st Supplement	1928	1–151	
I, 2nd Supplement	1941	1–151	
II	1920	152–194	*Carboxylic Acids: Salts and Derivatives.* Formic acid, 8. Acetic acid, 96. Oxalic acid, 502. Succinic acid, 601. Fumaric acid, 737
II, 1st Supplement	1929	152–194	
II, 2nd Supplement	1942	152–194	
III	1921	195–322	*Carboxylic Acids: Polyfunctional and Derivatives.* Hydroxy-carboxylic acids: Carbonic acid, 3. Glycollic acid, 228. Lactic acid, 261. Tartaric acid, 481. Citric acid, 556. Urea, 42. Cyanamide, 74. Thiocyanic acid, 140. Carbonyl-carboxylic acids: Glyoxalic acid, 594. Acetoacetic acid, 630. Hydroxy-carbonyl carboxylic acids: Glycuronic acid, 883.
III, 1st Supplement (combined with Volume IV)	1929	195–449	
III, 2nd Supplement (combined with Volume IV)	1942	195–449	
IV	1922	323–449	*Sulphonic Acids.* Hydroxy, 13. Carbonyl, 21. *Amines.* Methylamine. Hydroxy-amines: Aminoethyl alcohol, 274. Carbonyl-amines: Aminoacetaldehyde, 307. Aminoacetone, 314. Hydroxy-carbonyl amines: Glucosamine, 328. Aminocarboxylic acids: Glycine, 333. *Hydroxylamines*, 534. *Hydrazines*, 546. *Azo Compounds*, 562. *Organo-metallic Compounds*, 580.
IV, 1st Supplement	1929	195–449	
IV, 2nd Supplement	1942	195–449	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
		ISOCYCLIC DIVISION	
V	1922	450–498	*Hydrocarbons.* *cyclo*Propane, 15. Benzene, 179. Toluene, 280. Xylene, 362. Naphthalene, 531. Diphenyl, 576. Anthracene, 657. Triphenylmethane, 698.
V, 1st Supplement	1930	450–498	
V, 2nd Supplement	1943	450–498	
VI	1923	499–608	*Hydroxy Compounds.* Phenols, Aromatic Alcohols, Phenol-Alcohols: Menthol, 28. Phenol, 110. Cresol, 349. Benzyl alcohol, 428. Naphthol, 596. Resorcinol, 796. Pyrogallol, 1071.
VI, 1st Supplement	1931	499–608	
VI, 2nd Supplement	1946	499–608	
VII	1925	609–736	*Carbonyl Compounds.* Aldehydes, Ketones, Ketenes, Quinones: Camphor, 101. Benzaldehyde, 174. Acetophenone, 271. Benzophenone, 410. Benzoquinone, 600. Benzil, 747. Anthraquinone, 781.
VII, 1st Supplement (combined with Volume VIII)	1931	609–890	
VII, 2nd Supplement	1948	609-736	
VIII	1925	737–890	*Hydroxy-Carbonyl Compounds.* Salicylaldehyde, 31. Benzoin, 166. Vanillin, 247. Aurin, 361. Rosolic acid, 365. Alizarin, 439.
VIII, 1st Supplement	1931	609–890	
VIII, 2nd Supplement	1948	737–890	
IX	1926	891–1050	*Carboxylic Acids.* Benzoic acid, 92. Cinnamic acid, 572. Phthalic acid, 791.
IX, 1st Supplement	1932	891–1050	
IX, 2nd Supplement	1949	891–1050	
X	1927	1051–1504	*Hydroxy-Carboxylic Acids.* Salicylic acid, 43. Mandelic acid, 194. Gallic acid, 470. Carbonyl carboxylic acids, 594. Hydroxy-carbonyl carboxylic acids, 943.
X, 1st Supplement	1932	1051–1504	
X, 2nd Supplement	1949	1051–1504	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
		ISOCYCLIC DIVISION (*continued*)	
XI	1928	1505–1591	*Other Acids.* Sulphinic acids: Benzenesulphinic acid, 2. Sulphonic acids: Benzenesulphonic acid, 26. *p*-Toluenesulphonic acid, 97. Naphthalene-sulphonic acid, 155. Hydroxy-sulphonic acids: Phenol-sulphonic acid, 234. Naphthol-sulphonic acid, 269. Hydroxy-carbonyl sulphonic acids: Camphor-sulphonic acid, 345. Carboxylic-sulphonic acids, 368. Se and Te acids, 422.
XI, 1st Supplement (combined with Volume XII)	1933	1505–1739	
XI, 2nd Supplement	1950	1505–1591a	
XII	1929	1592–1739	*Monoamines.* Aniline, 59. Toluidine, 772. Benzylamine, 1013. Naphthylamine, 1212.
XII, 1st Supplement	1933	1505–1739	
XII, 2nd Supplement	1950	1592–1739	
XIII	1930	1740–1871	*Polyamines.* Diamines: *o*-Phenylenediamine, 6. Benzidine, 314. Triamines, 294. Hydroxy-amines: *o*-Aminophenol, 354. Pararosaniline, 750.
XIII, 1st Supplement (combined with Volume XIV)	1933	1740–1928	
XIII, 2nd Supplement	1950	1740–1871	
XIV	1931	1872–1928	*Carbonyl-Amines.* Aminobenzaldehyde, 21. Aminoacetophenone, 41. Aminobenzophenone, 76. Aminoanthraquinone, 177. Hydroxy-carbonyl amines, 233. Amino-carboxylic acids: Anthranilic acid (*o*-aminobenzoic acid). 310. Amino-hydroxy-carboxylic acids, 577. Amino-sulphonic acids: Sulphanilic acid, 695.
XIV, 1st Supplement	1933	1740–1928	
XIV, 2nd Supplement	1951	1872–1928	
XV	1932	1929–2084	*Hydroxylamines.* β-Phenylhydroxylamine, 2. *Hydrazines.* Phenylhydrazine, 67. Acetaldehyde phenylhydrazone, 127. 2 : D4-initrophenylhydrazine, 489.
XV, 1st Supplement (combined with Volume XVI)	1934	1929–2358	
XV, 2nd Supplement	1951	1929–2084	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
		ISOCYCLIC DIVISION (*continued*)	
XVI	1933	2085–2358	*Azo Compounds.* Azobenzene, 8. Azotoluene, 60. Azophenol, 90. Azocresol, 130. *Diazo Compounds.* Diazobenzene, 428. *Azoxy Compounds.* Azoxybenzene, 621. *Nitramines and Nitroso-hydroxylamines.* Phenylnitramine, 661. *Triazines.* Diazoaminobenzene, 687. *Phosphorus Compounds.* Triphenylphosphine, 759. *Arsenic Compounds.* Triphenylarsine, 828. Phenylarsonic acid, 868. *Antimony Compounds*, 891. Bi, Si, Sn, Pb, B, Tl, Mg, Ca, Hg, Na, Pt.
XVI, 1st Supplement	1934	1929–2358	
XVI, 2nd Supplement	1951	2085–2358	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
		HETEROCYCLIC DIVISION	
XVII	1933	2359–2503	*One Cyclic Oxygen* (*S, Se or Te*). Stem nuclei: Furan, 27. Thiophene, 29. Hydroxy compounds: Furfuryl alcohol, 112. Carbonyl compounds: Butyrolactone, 234. Furfural, 272. 2-Acetyl-thiophene, 287. Xanthone, 355. Succinic anhydride, 404. Phthalic anhydride, 469.
XVII, 1st Supplement (combined with Volumes XVIII and XIX)	1934	2359–3031	
XVII, 2nd Supplement	1952	2359–2503	
XVIII	1934	2504–2665	*One Cyclic Oxygen* (continued). Carbonyl compounds (*continued*): Phenolphthalein, 143. Quercetin, 242. Carboxylic acids: Furoic acid, 272. Furfuracrylic acid, 300. Sulphonic acids, 567. Amines, 583. Hydroxylamines, 637. Hydrazines, 639. Azo compounds, 643. Diazo compounds, 651. Carbon-metal compounds, 653.
XVIII, 1st Supplement	1934	2359–3031	
XVIII, 2nd Supplement	1952	2504–2665	
XIX	1934	2666–3031	*Two Cyclic Oxygens.* Stem nuclei: Dioxan, 1. Thianthrene, 45. Hydroxy compounds, 63. Carbonyl compounds: Ethylene carbonate, 100. Piperonal, 115. Thioindigo, 177. Fluorescein, 222. Carboxylic acids: Piperonylic acid, 269. Amines, 328. *Three Cyclic Oxygens*, 381. *Four Cyclic Oxygens*, 433. *Five Cyclic Oxygens*, 459. . . .
XIX, 1st Supplement	1934	2359–3031	
XIX, 2nd Supplement	1952	2666–3031	
XX	1935	3032–3102	*One Cyclic Nitrogen.* Piperidine, 6. Pyrrole, 159. Pyridine, 181. Indole, 304. Quinoline, 339. Isoquinoline, 380. Carbazole, 433. Acridine, 459.
XX, 1st Supplement (combined with Volumes XXI and XXII)	1935	3032–3457	
XX, 2nd Supplement	1953	3032–3102	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
HETEROCYCLIC DIVISION (*continued*)			
XXI	1935	3103–3241	*One Cyclic Nitrogen* (continued). Hydroxy compounds: Atropine, 27. Hydroxy-pyridine, 43. Indoxyl, 69. Hydroxyquinoline, 77. Papaverine, 220. Carbonyl compounds: α-Pyrrolidone, 236. Tropinone, 259. Succinimide, 369. Isatin, 432. Phthalimide, 458.
XXI, 1st Supplement	1935	3032–3457	
XXI, 2nd Supplement	1953	3103–3241	
XXII	1935	3242–3457	*One Cyclic Nitrogen* (continued). Carboxylic acids: Nicotinic acid, 38. Quinoline carboxylic acid, 74. Cinchomeronic acid, 155. Hydroxy-carboxylic acids, 190: Indoxylic acid, 226. Carbonyl-carboxylic acids, 284. Sulphonic acids, 386: Quinoline sulphonic acid, 390. Amines, 419: 2-Aminopyridine, 428. Amino-carboxylic acids, 541: Tryptophane, 545. Hydrazines, 563. Azo compounds, 572. Diazo compounds, 590.
XXII, 1st Supplement	1935	3032–3457	
XXII, 2nd Supplement	1953	3242–3457	
XXIII	1936	3458–3554	*Two Cyclic Nitrogens.* Stem nuclei: Piperazine, 4. Diazomethane, 25. Pyrimidine, 89. Pyrazine, 91. Nicotine, 110. Dipyridyl, 199. Phenanthroline, 227. Hydroxy compounds, 348: Cinchonine, 424. Quinine, 511. Indigo white, 538.
XXIII, 1st Supplement (combined with Volumes XXIV and XXV)	1936	3458–3793	
XXIII, 2nd Supplement	1954	3458–3554	
XXIV	1936	3555–3633	*Two Cyclic Nitrogens* (continued). Carbonyl compounds: Antipyrin, 27. Picrolonic acid, 51. Hydantoin, 242. Uracil, 312. Indigo, 416. Barbituric acid, 467. Alloxan, 500.
XXIV, 1st Supplement	1936	3458–3793	
XXIV, 2nd Supplement	1954	3555–3663	
XXV	1936	3634–3793	*Two Cyclic Nitrogens* (continued). Hydroxy-carbonyl compounds, 1: Hydroxy-indanthrene, 102. Carboxylic acids: Diazoacetic acid, 109. Sulphonic acids: Indigo-disulphonic acid (indigocarmine), 304. Amines, 308. Keto-amines: Pyramidone, 452. Allantoin, 474. Murexide, 499. Amino-carboxylic acids: Histidine, 513. Hydrazines, 531. Azo compounds, 535.
XXV, 1st Supplement	1936	3458–3793	
XXV, 2nd Supplement	1955	3634–3793	

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
			HETEROCYCLIC DIVISION (*continued*)
XXVI	1937	3794–4187	*Three Cyclic Nitrogens to Eight Cyclic Nitrogens.*
XXVI, 1st Supplement (combined with Volume XXVII)	1938	3794–4720	Aldehyde-ammonia, 6. Triazole, 11. Hydroxy compounds, 103. Carbonyl compounds: Cyanuric acid, 231. Carboxylic acids, 276: Benzotriazole-carboxylic acid, 291.
Supplement XXVI, 2nd	1955	3794–4187	Four cyclic nitrogens, 321: Xanthine, 447. Caffeine, 461. Uric acid, 513.
XXVII	1937	4199–4720	*One Cyclic Oxygen and One Cyclic Nitrogen.*
XXVII, 1st Supplement	1938	3794–4720	Stem nuclei. Morpholine, 5. Hydroxy compounds: Scopolamine, 99. Carbonyl compounds, 135: Saccharin, 169. Carboxylic acids, 313. Sulphonic acids, 355. Amines, 361: Meldola's blue, 383. Methylene blue, 395. *Two to Four Cyclic Oxygens and One Cyclic Nitrogen.* *One Cyclic Oxygen and Two Cyclic Nitrogens.* *Two to Six Cyclic Oxygens and Two Cyclic Nitrogens.*
			GENERAL INDEXES TO VOLUMES I–XXVII OF MAIN SERIES AND FIRST SUPPLEMENT AND ALSO TO SECOND SUPPLEMENT
XXVIII			*Subject Index.*
	1938		Part I. A–G.
	1939		Part II. H–Z.
	1955		Part I. A–G.
	1956		Part II. H–Z.
XXIX			*Formula Index.*
	1939		Part I. C_1–C_{13}.
	1940		Part II. C_{14}–C_{195}.
	1956		Part I. C_1–C_{11}.
	1956		Part II. C_{12}–C_{17}.

TABLE A,1. MODIFIED KEY TO BEILSTEIN'S HANDBUCH DER ORGANISCHEN CHEMIE, 4TH EDITION (*continued*)

VOLUME	YEAR OF PUBLICATION	"SYSTEM NUMBERS"	BRIEF LIST OF CONTENTS
NATURALLY OCCURRING COMPOUNDS			
XXX	1938	4723–4723a	*Rubber*, 1. *Guttapercha and Balata*, 64. *Carotenoids*, 81.
XXXI	1938	4746–4767a	*Carbohydrates, Part I.* Arabinose, 32. Glucose, 83. Arbutin, 210. Fructose, 321. Maltose, 386. Lactose, 407. Sucrose, 424. Raffinose, 462.

Each entry in " Beilstein " includes, where available, the information listed below with the references to the important original articles.

Name, formula and structure.
Important historical notes.
Occurrence, formation, preparation.
Properties : colour, crystallography, physical constants, etc.
Chemical changes : action of heat, light, electricity, inorganic reagents and organic reagents.
Physiological properties.
Technical applications.
Analysis.
Addition compounds and salts.
Conversion products of unknown structure.

The space devoted to any one compound varies from one line to several pages according to its importance.

A,2. ORIGINAL SOURCES OF CHEMICAL INFORMATION

All new information on chemical matters or original presentations and discussions of known material are published in scientific journals. The most important of these dealing with organic compounds are (the abbreviated names are given in parentheses) :

Journal of the Chemical Society (*J. Chem. Soc.*).
American Chemical Journal (merged with the Journal of the American Chemical Society in 1913) (*Amer. Chem. J.*).
Journal of the American Chemical Society (*J. Amer. Chem. Soc.*).
Journal of Organic Chemistry (*J. Org. Chem.*).
Annalen der Chemie or Liebig's Annalen (*Annalen*).
Berichte der deutschen chemischen Gesellschaft (*Ber.*).
Bulletin de la Société chimique de France (*Bull. Soc. chim.*).
Bulletin de la Société chimique de Belgique (*Bull. Soc. chim. Belg.*).
Recueil des Travaux chimiques des Pays-Bas (*Rec. Trav. chim.*).
Helvetica Chimica Acta (*Helv. Chim. Acta*).
Monatshefte für Chemie (*Monatsh.*).
Journal für praktische Chemie (*J. pr. Chem.*).
Zhurnal Obschei Khimii *or* Journal of General Chemistry, U.S.S.R. (*J. Gen. Chem., U.S.S.R.*).
Gazzetta Chimica Italiana (*Gazzetta*).

Periodical summaries of recent knowledge are to be found in the Annual Reports on the Progress of Chemistry (issued annually by the Chemical Society, London), Quarterly Reviews (issued quarterly by the Chemical Society, London), and in Chemical Reviews.

A,3. SECONDARY SOURCES OF CHEMICAL INFORMATION. ABSTRACTING JOURNALS

Abstracting journals are publications giving contemporaneous, concise summaries of the various original communications and other contributions to knowledge. Each abstract usually supplies the title of the original contribution abstracted, name(s) of author(s), original reference (*i.e.*, name of journal or other source of information, year, series volume, page) and generally a brief summary of the original source. The value of the abstract, in the first instance, will depend upon how detailed the summary is. It must be emphasised, however, that the reader should never be satisfied with the account to be found in the abstract : he should, as far as possible, consult the original work and abstract it.

The three most important abstracting journals for organic chemistry are :

1. **British Chemical Abstracts.** These were commenced in the year 1871 and were included in the Journal of the Chemical Society. In 1926 the abstracting was taken over by the Bureau of Chemical Abstracts ; abstracts were then published in two parts : Part A " Pure Chemistry " (formerly issued by the Chemical Society) and Part B "Applied Chemistry "

(formerly issued by the Society of Chemical Industry). The Collective Indexes (1873–1882; 1883–1892; 1893–1902; 1903–1912; 1913–1922; 1923–1932; 1933–1937) provide an excellent means for following abstracts in the English language from 1871. Publication of the abstracts in "Pure Chemistry" was discontinued in January 1954.

2. **Chemical Abstracts.** These were commenced by the American Chemical Society in 1907. The abstracts are very comprehensive (particularly in recent years) from the standpoint of subject matter and journals covered. Four decennial indexes have appeared—1917, 1927, 1937 and 1947—and these are widely used for locating information published during the period 1907–1947. The annual indexes cover the period 1948 to date.

3. **Chemisches Zentrallblatt.** This periodical, published by the Deutsche Chemische Gesellschaft to 1945, originated in 1830 as the Pharmaceutisches Zentrallblatt, the name was changed in 1850 to Chemisches-Pharmaceutisches Centrallblatt, again in 1856 to Chemisches Centrallblatt, and in 1907 to Chemisches Zentrallblatt. Collective indexes are available from 1870. The abstracts, particularly for organic chemistry, are very detailed to 1939.

A,4. LOCATING AN ORGANIC COMPOUND

A problem that frequently arises in the organic laboratory is to obtain more information concerning a particular compound than is found in the ordinary text-book, or whether such a compound is known. Formerly Richter's *Lexicon der Kohlenstoff-Verbindungen* (covering all the organic compounds known to December 31, 1909) and Stelzner's *Literatur Register der organischen Chemie* (1910–1922) were first consulted, but since the publication of the General Indexes to Beilstein's *Handbuch* (Volumes I–XXVII of the Main Series and First Supplement), this is no longer necessary. The two General Indexes (Subject Index and Formula Index) to Beilstein's *Handbuch* include all organic compounds known to 1919: the references are to the appropriate volume of "Beilstein." After 1919, it is necessary to consult the Collective Indexes of the various journals (compare Section A,3); of these the Decennial Indexes to 1947 of Chemical Abstracts (including the Collective Formula, 1920–1946) and the subsequent annual indexes to Chemical Abstracts will be found the most satisfactory.

A,5. SELECTED REFERENCE WORKS ON ORGANIC CHEMISTRY

Apart from a complete set of Beilstein's *Handbuch* and as many scientific journals with indexes as the Institution can afford, the following selected volumes are suggested as forming the nucleus of a small library for use in connexion with work in the organic chemistry laboratory.

Heilbron and Bunbury, *Dictionary of Organic Compounds*, Revised Edition, Four Volumes, 1953 (Eyre and Spottiswoode).

Mulliken, *Identification of Pure Organic Compounds*, Volumes I–IV, 1904–1922 (J. Wiley).

Huntress-Mulliken, *Identification of Pure Organic Compounds*, Order I, 1941 ; Huntress, *Organic Chlorine Compounds*, Order III, 1948 (J. Wiley : Chapman and Hall).

Organic Syntheses, Volumes 1–35, 1921–1955 (J. Wiley: Chapman and Hall).

Organic Syntheses, Collective Volume I, Second Edition, 1941.

Organic Syntheses, Collective Volume II, 1943.

Organic Syntheses, Collective Volume III, 1955.

Adams, *Organic Reactions*, Volumes I–VIII, 1942–1954 (J. Wiley : Chapman and Hall).

Houben-Weyl, *Die Methoden der organischen Chemie*, Third Edition, Four Volumes, 1925–1941 ; Fourth Edition, Volume VIII, 1952 : Volume II, 1953 and subsequent volumes (G. Thieme, Stuttgart).

Richter-Anschütz, *Chemie der Kohlenstoffverbindungen*, Twelfth Edition, 3 Volumes in 4, 1928–1935 (Akad. Verlag, Leipzig). An English translation under the title Richter's *Organic Chemistry* is available (Elsevier Publishing Co., 1934–1947).

Rodd (Editor), *Chemistry of Carbon Compounds*, Five Volumes, each in two parts, 1951– (Elsevier Press : Cleaver-Hume Press).

Radt (Editor), *Elsevier's Encyclopaedia of Organic Chemistry*, Eleven Volumes, 1940–1954 ; First Supplement, Three Volumes, 1951–1955 (Elsevier Press : Cleaver-Hume Press).

This reference work differs from Beilstein in that it is based upon structural formulae and compounds are grouped according to the carbon skeleton rather than the functional group ; the latter system has the advantage that closely related compounds are grouped together. The volumes are not published in numerical order but rather on the basis of fields of current interest. They are a valuable supplement to Beilstein. The volumes which have been published to date (1955) are :

XII A	Bicyclic condensed compounds except naphthalene. (1948.)
XII B (i)	Naphthalene : hydrocarbons : halogen compounds. (1948.)
XII B (ii)	Naphthalene : nitrogen compounds. (1949.)
XII B (iii)	Naphthalene : hydroxy compounds. (1950.)
XII B (iv)	Naphthalene : oxo-compounds except quinones. (1950.)
XII B (v)	Naphthalene : quinones. (1952.)
XII B (vi)	Naphthalene : carboxylic acids with CO_2H in the side chain. (1953.)
XII B (vii)	Naphthoic acids and their halogen, nitrogen and hydroxyl derivatives. (1953.)
XII B (viii)	Naphthoic acids: CO_2 in the nucleus: oxo-acids, poly-acids. (1954.)
XIII	Tricyclic condensed compounds. (1946.)
XIV	Tetracyclic and higher condensed compounds. (1940.)
XIV Supp. (i)	Tetra- and higher cyclic compounds except steroids and triterpenes. (1951.)
XIV Supp. (ii)	Triterpenes. (1952.)
XIV Supp. (iii)	Steroids : hydrocarbon, halogen, nitrogen and hydroxyl derivatives. (1955.)

Theilheimer, *Synthetic Methods of Organic Chemistry*, Volumes I–VIII, 1947–1954 (S. Karger, Basel).
Gilman, *Organic Chemistry*, Four Volumes, 1943–1953 (J. Wiley : Chapman and Hall).
Elderfield, *Heterocyclic Compounds*, Volumes I–IV, 1951–1954 (J. Wiley : Chapman and Hall).
Wagner - Zook, *Synthetic Organic Chemistry*, 1953 (J. Wiley : Chapman and Hall).
Raphael, *Acetylenic Compounds in Organic Synthesis*, 1955 (Butterworths).
Whitmore, *Organic Chemistry*, Second Edition, 1951 (Van Nostrand).
Turner and Harris, *Organic Chemistry*, 1952 (Longmans, Green).
Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell U.P. : G. Bell).
Wheeler and Gowan, *Name Index of Organic Reactions*, 1953 (Society of Chemical Industry).
Surrey, *Name Reactions in Organic Chemistry*, 1954 (Academic Press).
Mitchell, *British Chemical Nomenclature*, 1948 (Arnold).
Weissberger (Editor), *Technique of Organic Chemistry*, Volumes 1–8, 1949–1955 (Interscience).
Siggia, *Quantitative Organic Analysis via Functional Groups*, Second Edition, 1954 (J. Wiley : Chapman and Hall).
Organic Analysis, Volumes I and II, 1953–1954 (Interscience).
Biochemical Preparations, Volumes I–IV, 1949–1955 (J. Wiley ; Chapman and Hall).
Inorganic Syntheses, Volumes I–IV, 1939–1953 (McGraw-Hill).
Lange, *Handbook of Chemistry*, Eighth Edition, 1952 (Handbook Publishers, Sandusky, Ohio).

A,6. LABORATORY ACCIDENTS AND FIRST AID *

In case of accidents, always call or notify the demonstrator or teacher as soon as possible.

A First Aid Box or Cupboard should be kept in a readily accessible position in the laboratory and should contain the following articles clearly labelled :

* A valuable report, containing many references to cognate literature, is given in *The Origins and Prevention of Laboratory Accidents*, 1949 (Royal Institute of Chemistry, London, W.C. 1). See also *Guide for Safety in the Chemical Laboratory*, 1955 (Van Nostrand ; Macmillan).

Bandages (several sizes), gauze, lint, cotton wool, adhesive plaster, " Elastoplast " or equivalent, and a sling.
Delicate forceps, needles, thread, scissors, and safety pins.
Fine glass dropper.
Two eye glasses.
Vaseline, Castor oil, Olive oil, Sal volatile, Boracic acid powder, Sodium bicarbonate powder, Chloramine-T powder, Sulpha-pyridine powder, Butesin picrate ointment.
Acriflavine jelly or emulsion (*e.g.*, " Burnol ").
Tannic acid jelly (*e.g.*, " Tannafax ").
One fireproof blanket—this is best stored in a special container just outside the First Aid Cupboard.

Bottles containing :
One per cent. acetic acid.
One per cent. boric acid.
Saturated sodium bicarbonate solution.
One per cent. sodium bicarbonate solution.
Rectified spirit.
Glycerine.
Light petroleum, b.p. 80–100°.
A disinfectant, *e.g.*, " Dettol " or " T.C.P."

A " Laboratory Emergency Chart," which should be hung in a prominent position near the First Aid Box, is obtainable from the Fisher Scientific Company.

BURNS

Burns caused by dry heat (*e.g.*, by flames, hot objects, etc.). For slight burns in which the skin is not broken, apply tannic acid jelly (" Tannafax "), acriflavine jelly (" Burnol ") or butesin picrate ointment (butesin is *n*-butyl *p*-aminobenzoate).

For larger burns, or burns in which the skin is reddened or blistered, apply one per cent. sodium bicarbonate solution without delay, and call for medical aid at once.

Acids on the skin. Wash immediately and thoroughly with a liberal quantity of water, then with saturated sodium bicarbonate solution, and finally with water. For a serious acid burn, follow this by applying a disinfectant, drying the skin and covering with acriflavine jelly.

Alkalis on the skin. Wash immediately with a large volume of water, then with 1 per cent. acetic acid, and finally with water. For a serious burn, follow this treatment by applying a disinfectant, drying the skin and covering with acriflavine jelly.

Bromine on the skin. Wash the affected part immediately with a liberal supply of light petroleum, b.p. 80–100°, and then rub glycerine well into the skin. After a little time remove the superficial glycerine and apply acriflavine jelly or butesin picrate ointment.

Sodium on the skin. If a small solidified fragment of sodium can still be seen, remove it carefully with forceps. Wash thoroughly with water, then with 1 per cent. acetic acid, and finally cover with gauze soaked in olive oil or acriflavine jelly.

Phosphorus on the skin. Wash well with cold water and treat with 1 per cent. silver nitrate solution.

Methyl sulphate on the skin. Wash immediately and liberally with concentrated ammonia solution, and then rub *gently* with wads of cotton wool soaked in concentrated ammonia solution.

Organic substances on the skin. Wash freely with rectified spirit, then with soap and warm water.

CUTS

If the cut is only a minor one, allow it to bleed for a few seconds, see that no glass remains, apply a disinfectant (rectified spirit, " Dettol," 1 per cent aqueous chloramine-T solution, or sulpha-pyridine powder) and bandage.

For serious cuts, send for a doctor at once : meanwhile wash with a disinfectant and endeavour to check bleeding by applying pressure immediately above the cut. Continuous pressure should not be maintained for more than five minutes.

EYE ACCIDENTS

In all cases the patient should see a doctor. If the accident appears serious, medical aid should be summoned immediately *while* first aid is applied.

Acid in the eye. If the acid is dilute, wash the eye repeatedly with 1 per cent. sodium bicarbonate solution in the eye cup. If the acid is concentrated, first wash the eye with a large amount of water and then continue with the bicarbonate solution.

Caustic alkali in the eye. Proceed as for acid in the eye, but wash with 1 per cent. boric acid solution in place of bicarbonate solution.

Bromine in the eye. Wash thoroughly with water and then immediately with 1 per cent. sodium bicarbonate solution.

Glass in the eye. Remove loose glass *very gently* with forceps or by washing with water in an eye bath. Call for a doctor immediately.

Soreness which may follow minor accidents to the eye may be relieved by placing 1 drop of castor oil in the corner of the eye.

FIRES

Burning clothing. Prevent the person from running and fanning the flames. Make the victim lie down on the floor, or throw him (her) down if necessary, and wrap the fireproof blanket firmly around the ignited clothes until the fire is extinguished.

Burning reagents. Turn out all gas burners and switch off all electric hot plates in the vicinity ; remove everything which may ignite. The control of the fire depends upon its size and kind.

A small fire (for example, liquid in a beaker or flask, or an oil bath) may usually be extinguished by covering the opening of the vessel with a clean damp cloth or duster : the fire usually dies out from lack of air. For larger fires, dry sand may be employed. Buckets of dry sand should be distributed round the laboratory and should be *strictly reserved* for this purpose. Most fires on the laboratory bench can be smothered by

the liberal use of sand. Sand once employed for this purpose should always be thrown away afterwards as it may contain appreciable quantities of inflammable, non-volatile substances (*e.g.*, nitrobenzene).

Although sand is usually very effective for extinguishing fires, it has the disadvantage that the compound or reaction mixture is usually lost and any glass apparatus around which the fire centres may be broken under the weight of the sand. Alternatively, *small* fires may be extinguished with carbon tetrachloride under high pressure of carbon dioxide (as contained for example, in the commercial Autelex extinguisher *) ; the mixture is directed on the fire and the " blanketing " effect of the carbon dioxide and heavy carbon tetrachloride vapour will soon put out the fire. It must be noted particularly that :—

(*a*) carbon tetrachloride should not be used if sodium or potassium is present as violent explosions may result ;

(*b*) the laboratory must be ventilated immediately the fire is extinguished in order to disperse the highly poisonous phosgene vapour which is always formed.

It is usually better to use a fire extinguisher charged with carbon dioxide under pressure * ; this produces a spray of solid carbon dioxide upon releasing the pressure intermittently and is effective for extinguishing most fires in the laboratory.

For burning oil (or organic solvents), do not use water as it will only spread the fire : a mixture of sand and sodium bicarbonate is very effective.

POISONS

Solids or liquids.

(i) **In the mouth but not swallowed.** Spit out at once and wash repeatedly with water.

(ii) **If swallowed.** Call a doctor immediately. In the meantime, give an antidote according to the nature of the poison.

(*a*) *Acids* (*including oxalic acid*). Dilute by drinking much water, followed by lime water or milk of magnesia. Milk may then be given but no emetics.

(*b*) *Caustic alkalis.* Dilute by drinking much water, followed by vinegar, lemon or orange juice, or solutions of lactic acid or citric acid. Milk may then be given but no emetics.

(*c*) *Salts of heavy metals.* Give milk or white of an egg.

(*d*) *Arsenic or mercury compounds.* Give an emetic immediately, *e.g.*, one teaspoonful of mustard, or one tablespoonful of salt or zinc sulphate, in a tumbler of warm water.

Gas.

Remove the victim to the open air, and loosen clothing at neck. To counteract chlorine or bromine fumes if inhaled in only small amounts, inhale ammonia vapour or gargle with sodium bicarbonate solution. Afterwards the patient should suck eucalyptus pastilles, or drink warm dilute peppermint or cinnamon essence, to soothe the throat and lungs.

If breathing has stopped, apply artificial respiration.

* Supplied by Read and Campbell Ltd., 75 Victoria Street, London, S.W. 1., etc.

A,7. APPLICATIONS OF INFRARED AND ULTRAVIOLET SPECTRA TO ORGANIC CHEMISTRY*

INTRODUCTION

Information about the structure of a molecule can frequently be obtained from observations of its absorption spectrum. The positions of the absorption bands due to any molecule depend upon its atomic and electronic configuration. To a first approximation, the internal energy E of a molecule can be regarded as composed of additive contributions from the electronic motions within the molecule (E_e), the vibrational motions of the constituent atoms relative to one another (E_v), and the rotational motion of the molecule as a whole (E_r) :

$$E = E_e + E_v + E_r$$

The energies of the various contributions are " quantised ", *i.e.*, in a given state the isolated molecule may possess one of a discrete set of values ; these values are often referred to as energy levels. When a molecule absorbs light, its energy is momentarily increased by an amount equal to that of the photon. The energy is related to the wave length (λ) and frequency (ν) by the equation :

$$E = h\nu = hc/\lambda$$

where h is Planck's constant and c is the velocity of light. The increase in energy can be accommodated as electronic, vibrational or rotational energy. The relative magnitudes in the changes of rotational : vibrational : electronic energies are approximately 1 : 50 : 1000 ; it is possible to excite changes in the rotational energy without affecting appreciably the vibrational or electronic energy, or vibrational-rotational energy without influencing the electronic energy to any degree. Absorption by molecules in the infrared region involves changes in their rotational and vibrational energies only ; absorption by molecules in the ultraviolet region produces changes in the electronic energies in addition. For these and other reasons, molecular absorption gives rise to bands instead of the sharp lines obtained with atoms.

The positions of lines or bands in the electromagnetic spectrum may be expressed either as wave lengths (λ) or as frequencies (ν). The units employed in the measurement of wave lengths are :

1 micron = $1\mu = 10^{-4}$ cm.
1 millimicron = $1\ m\mu = 10^{-7}$ cm.
1 Angstrom = $1\ \text{Å} = 10^{-8}$ cm.

The frequency is related to the wave length by the equation :

$$\nu = c/\lambda$$

where c is the velocity of light. When c is in cm. per sec. ($2{\cdot}99776 \times 10^{10}$ cm. per sec. in vacuo) and λ is in cm., ν is in reciprocal seconds (sec.$^{-1}$), the unit of frequency is the *fresnel*. Frequencies in the optical region of the electromagnetic spectrum are large numbers and it is more convenient to use the *wave number* ($\bar{\nu}$), which is the number of waves per cm. :

$$\bar{\nu}\ (\text{cm.}^{-1}) = 1/\lambda\ (\text{cm.}) = 10^4/(\mu) = 10^8/\lambda\ (\text{Å})$$

* Written in collaboration with R. F. Branch, B.Sc., A.R.I.C.

The conversion of wave lengths into wave numbers may be illustrated by a simple example :

$$5\mu = 5 \times 10^{-4} \text{ cm.} = 1/(5 \times 10^{-4}) \text{ wave numbers}$$
$$= 2000 \text{ wave numbers (cm.}^{-1})$$

The wave lengths of the various parts of the electromagnetic spectrum of immediate interest are :

Far ultraviolet = 1000–2000 Å = 100–200 mμ
Near ultraviolet = 2000–4000 Å = 200–400 mμ
Visible = 4000–8000 Å = 400–800 mμ
Near infrared = 0·8–2μ
Infrared = 2–25μ
Far infrared = 25–100μ

For infrared spectra, both microns and wave numbers (cm.$^{-1}$) are convenient units. For electronic spectra (ultraviolet and visible), the millimicron is largely used ; the wave numbers (cm.$^{-1}$) may range between 13,000 and 50,000 and consequently many authors employ cm.$^{-1} \times 10^{-2}$.

The *intensity of a spectral absorption band* at a given wave length is expressed in terms of absorption or extinction coefficients, defined on the basis of the Beer-Lambert law. The latter states that the fraction of incident light absorbed is proportional to the number of molecules in the light path, *i.e.*, to the concentration (c) and the path length (l). The law may be expressed mathematically as :

$$\log_{10} (I_0/I) = E = kcl$$

where I_0 and I represent the intensities (in arbitrary units) of incident and transmitted light ; E is the "extinction" or "optical density" ; and k is an absorption coefficient, the numerical value of which depends upon the units in which c and l are expressed. The two absorption coefficients now most frequently employed by chemists are :

(*a*) The *molecular extinction coefficient*, defined by

$$\varepsilon = E/cl$$

where c is in g.-mols per litre and l is in cm.

Thus ε may be regarded as the absorption of a sample 1 cm. thick and having a concentration of 1 g.-mol per litre ; this is a useful form of the equation since ε provides a comparison of intensity for equal numbers of molecules.

(*b*) The *extinction, one per cent., one centimetre*, given by

$$E^{1\%}_{1\text{ cm.}} = E/cl$$

where c is in g. per 100 ml. and l is in cm. This is convenient when the molecular weight is unknown.

Both $E^{1\%}_{1\text{ cm.}}$ and ε are independent of concentration and cell length, provided the Beer-Lambert law is obeyed. The two quantities are related by the expression :

$$E^{1\%}_{1\text{ cm.}} = 10\varepsilon/\text{mol. wt.}$$

The absolute intensity of an absorption band may be expressed by giving the value of $\varepsilon_{max.}$, the molecular extinction coefficient at the wave

length of maximum absorption, $\lambda_{max.}$. This quantity can be determined by means of the Beer-Lambert law provided the slit widths are sufficiently narrow. This criterion can usually be fulfilled when measuring the ultra-violet spectra of solutions, but is seldom fulfilled for infrared spectra.

The term *transmittance* (T) at a given wave length is defined by

$$T = I/I_0 \quad ; \quad 100T = \text{per cent transmittance.}$$

INFRARED SPECTRA

The infrared region of the electromagnetic spectrum can, perhaps, yield the most information concerning the structure of organic molecules. The masses of the atoms, and the forces holding them together, are of such magnitude that the usual vibration of organic molecules interact with electromagnetic energy so as to absorb and radiate in the infrared region. Overtones and combinations of these vibrational frequencies may appear in the visible region and in the near-infrared (0·8–2μ), but most of the fundamental vibrations occur in the interval from 2 to 25μ. It is this region of fundamental frequencies that is generally of greatest value in the study of organic molecules. Problems of identity, purity, gross structural features, as well as many finer points of structural detail, can be solved through the use of infrared spectroscopy, often faster than by any other analytical method. For a molecule of high complexity and molecular weight and of unknown constitution, it is usually better to break it down to simpler parts just as is done when a structure is elucidated chemically by degradative methods. The infrared spectrum provides a physical constant which is more valuable than the melting point for characterising organic compounds. A mixed melting point can take as much time as is needed to obtain an infrared spectrum, yet it yields only a single fact whilst the spectrum may provide a great deal of information.

Modern automatically recording infrared spectrophotometers employ a rock-salt prism (rock salt is transparent to infrared radiation) and scan the range from 5000 cm.$^{-1}$ to 600cm.$^{-1}$ (or 2μ to 16·7μ) in a few minutes, the spectrum being obtained as a graph of frequency or wave length against percentage transmittance. Liquids are examined by placing them in cells of suitable thickness (normally about 0·05 mm.) which are equipped with rock-salt windows. Solids can either be dissolved in a solvent and placed in a rock-salt cell, or ground to a paste with pure liquid paraffin (Nujol) and examined as a fine suspension or " mull " on a rock-salt plate. The amount of sample required is 1–5 mg. If the C—H bands of the sample are to be examined, Nujol cannot be used ; it may be replaced by a completely fluorinated hydrocarbon (*e.g.*, perfluorokerosene, which is satisfactory for the region above 1450 cm.$^{-1}$) available commercially. The useful transparent regions of solvents employed in infrared work are given in Table I.

It has been observed that particular vibrational bands can be associated with specific groupings in the molecule and, furthermore, the position of a band varies only slightly in frequency throughout a large number of organic compounds. For example, all compounds containing the carbonyl (C=O) group are found to show a strong absorption band between 1800 cm.$^{-1}$ (5·56μ) and 1650 cm.$^{-1}$ (6·06μ). Also, the precise position

TABLE I. USEFUL RANGES OF SOLVENTS FOR INFRARED MEASUREMENTS

Solvent	*Range (cm.$^{-1}$)*	*Range (μ)*
Carbon tetrachloride	10000–830	1–12
Carbon disulphide	10000–2500	1–4
	2000–1670	5–6
	1330–600	7·5–16·7
Bromoform	10000–3333	1–3
	2500–1176	4–8·5
	1110–715	9–14
Chloroform	10000–3333	1–3
	2857–1250	3·5–8
	1110–830	9–12
Nujol (liquid paraffin)	10000–3333	1–3
	2500–1470	4–6·8
	1250–667	8–15
Nitromethane	909–690	11–14·5
Perfluorokerosene	10000–2000	1–5

of the carbonyl absorption band within this range is characteristic of the type of keto compound.

For purposes of discussion, it is convenient to divide the region from 5000 to 600 cm.$^{-1}$ (2 to 16·7μ) into four main divisions.

TABLE II. REGION 5000–2000 CM.$^{-1}$ (2–5μ)

Bond or Group	*Range (cm.$^{-1}$)*	*Range (μ)*
O—H (free)	3650–3590 (*v*)*	2·74–2·79 (*v*)
O—H (associated)	3570–3200 (*s*)	2·80–3·13 (*s*)
N—H	3500–3200 (*m*)	2·86–3·13 (*m*)
≡C—H (acetylenic)	3310–3200 (*s*)	3·02–3·13 (*s*)
=C—H (olefinic)	near 3030 (*m*)	near 3·3 (*m*)
C—H	2926–2850 (*s*)	3·38–3·51 (*s*)
S—H	2600–2550 (*w*)	3·85–3·92 (*w*)
C≡N	2260–2215 (*v*)	4·43–4·52 (*v*)
N≡N	2160–2120 (*s*)	4·63–4·72 (*s*)
C=C=C	near 1950 (*m*)	near 5·13 (*m*)

* (*vs*) = very strong; (*s*) = strong; (*m*) = medium; (*w*) = weak; and (*v*) = variable intensity of band.

The intensity of an absorption band assists its identification, but it is difficult to obtain accurate absolute intensity measurements with existing spectrophotometers, although a given instrument will give accurately reproducible measurements. However, a rough indication of intensity is given in the Tables by the following symbols : *vs*, very strong ; *s*, strong ; *m*, medium ; *w*, weak ; and *v*, variable.

1. **Region 5000–2000 cm.$^{-1}$ (2–5μ).** This is the region of the characteristic stretching vibrations of single and triple bonds, and it includes the strong C—H stretching absorption which occurs in the majority of organic compounds. Alcohols, phenols, amines, imines, amides, hydrocarbons, mercaptans, nitriles, azides and allenes show absorption in this region. Allenes, which contain two adjacent double bonds, behave as though they contained a triple and a single bond. The lowering of the O—H and N—H stretching frequencies by hydrogen bonding renders this region of the infrared spectrum valuable for the study of this phenomenon (see Table II).

2. **Region 2000–1500 cm.$^{-1}$ (5·00–6·67μ).** The highly characteristic stretching vibrations of double bonds are to be found here. Aldehydes, ketones, carboxylic acids and their salts, esters, acid halides, amides, lactones, nitro groups, azo compounds, ethylenes and aromatic rings absorb in this region. Conjugation of double bonds results in a shift to lower frequencies. This is illustrated for carbonyl compounds in Table IV. Full aliphatic conjugation causes a larger shift to lower frequencies than does aryl conjugation except for carboxylic acids.

TABLE III. REGION 2000–1500 CM.$^{-1}$ (5–6·67μ)

Bond or Group	*Range (cm.$^{-1}$)*	*Range (μ)*
NO_2	1560–1500 (*s*)* and 1360–1300 (*s*)	6·41–6·67 (*s*) and 7·35–7·69 (*s*)
C=C	1660–1590 (*v*)	6·02–6·29 (*v*)
C=N	1660–1590 (*v*)	6·02–6·29 (*v*)
N=N	1630–1575 (*v*)	6·14–6·35 (*v*)
Aromatic (phenyl) ring . .	near 1600 (*v*) and near 1500 (*v*)	near 6·25 (*v*) and near 6·67 (*v*)
COO^-	1610–1550 (*s*)	6·21–6·45 (*s*)

3. **Region 1500–900 cm.$^{-1}$ (6·67–11·11μ).** This is the region of deformation and skeletal vibrations ; these are less stable in frequency, and hence are less characteristic, than the stretching vibrations. The assignment of absorption bands to specific groups is less trustworthy in this region, and the spectrum is characteristic of the whole skeletal structure of the molecule. This region is known as the " fingerprint " region. Some correlations are available, but it must be remembered that many interfering bands are likely to be present (see Table IV).

* (*vs*) = very strong; (*s*) = strong; (*m*) = medium; (*w*) = weak; and (*v*) = variable intensity of band.

TABLE IV. CARBONYL FREQUENCIES *

Compound	*Type*	*Range (cm.$^{-1}$)*	*Range (μ)*
Anhydride	normal	1860–1800 and 1800–1750	5·38–5·56 and 5·56–5·71
Aldehyde	alkyl	1740–1720	5·75–5·81
	aryl	1715–1695	5·83–5·90
	αβ-unsaturated	1705–1680	5·86–5·95
Ketone	alkyl	1725–1705	5·80–5·86
	aryl	1700–1680	5·88–5·95
	αβ-unsaturated	1685–1665	5·93–6·00
Acid	alkyl	1725–1700	5·80–5·88
	aryl	1700–1680	5·88–5·95
	αβ-unsaturated	1715–1690	5·83–5·92
Ester	alkyl	1750–1735	5·71–5·76
	aryl	1730–1717	5·78–5·83
	αβ-unsaturated	1730–1717	5·78–5·83
Acid halide	alkyl	1815–1770	5·51–5·65
	aryl	1800–1770	5·56–5·65
	αβ-unsaturated	1800–1770	5·56–5·65
Amide	alkyl	1700–1630	5·88–6·14
	aryl	1700–1630	5·88–6·14
γ-Lactone	alkyl	1780–1760	5·62–5·68
	aryl	1760–1740	5·68–5·75
	αβ-unsaturated	1760–1740	5·68–5·75

TABLE V. REGION 1500–900 CM.$^{-1}$ (6·67–11·11μ)

Bond or Group	*Range (cm.$^{-1}$)*	*Range (μ)*
C—CH_3	1470–1430 and 1380–1370 (*m*)	6·80–6·99 and 7·25–7·30 (*m*)
CH_2	1485–1445 (*m*)	6·73–6·92 (*m*)
COO^- (salt)	1420–1300 (*s*)	7·04–7·69 (*s*)
O=C—O—H (acid)	1440–1395 (*w*) and 1320–1210 (*s*)	6·94–7·17 (*w*) 7·58–8·26 (*s*)
O=C—O—C	1150–1060 (*vs*)	8·70–9·43 (*vs*)
O—H	near 1100 (*s*)	near 9·09 (*s*)
—O—O—	890–820 (*v*)	11·24–12·20 (*v*)
P=O (free)	1300–1250 (*s*)	7·69–8·00 (*s*)
P=O (bonded)	1250–1200 (*vs*)	8·00–8·33 (*vs*)
P—O—C (alkyl)	1050–1000 (*vs*)	9·52–10·00 (*vs*)
P—O—C (aryl)	1240–1190 (*vs*)	8·07–8·40 (*vs*)
C—F	1400–1000 (*vs*)	7·14–10·00 (*vs*)
S=O	1060–1040 (*s*)	9·43–9·62 (*s*)
SO_2	1160–1140 (*s*) and 1350–1300 (*s*)	8·62–8·77 (*s*) and 7·41–7·69 (*s*)

* All strong absorptions.

4. **Region 900–600 cm.$^{-1}$ (11·11–16·67μ).** This is the region of strong, aryl, out-of-plane, C–H deformation vibration absorptions, which are valuable for identifying the substitution pattern in the aromatic ring. Substitution in the ring alters the number of C–H groups which are vibrating together and causes changes in the absorption pattern. Identification is not trustworthy for heavily substituted, nitro substituted or heterocyclic ring-substituted aromatic compounds (see Table VI).

TABLE VI. AROMATIC (PHENYL) RING ABSORPTION FREQUENCIES *

Substitution	*Groups*	*Range (cm.$^{-1}$)*	*Range (μ)*
Monosubstituted	5 C—H	770–730 and 710–690	13·0–13·7 and 14·1–14·5
o-Disubstituted	4 C—H	770–735	13·0–13·6
m-Disubstituted	3 and 1 C—H	810–750 and 900–860	12·4–13·3 and 11·1–11·6
p-Disubstituted	2 C—H	860–800	11·6–12·5

* Usually all strong absorptions.

Interpretation of spectra. The infrared spectrum of *m*-hydroxybenzoic acid (solid ground in Nujol) is shown in Fig. *A*, *7*, 1. The more important bands may be interpreted as follows.

Band 1, 3·08μ (3242 cm.$^{-1}$.) Hydrogen bonded O—H absorption of the phenolic group (Table II).

Band 2, 3·48μ (2873 cm.$^{-1}$). C—H stretching absorption of Nujol. The weak =C—H stretching absorption of the aromatic (phenyl) ring is hidden by the broad Nujol band (Table II).

Band 3, 3·93μ (2548 cm.$^{-1}$). This absorption is characteristic of carboxylic acids and is due to the O—H stretching absorption in the resonance-stabilised dimer. (Carboxylic acids generally exist as dimers in the solid state and in all but very dilute solutions.)

Band 4, 5·94μ (1683 cm.$^{-1}$). Aryl carboxylic acid C=O stretching vibration (Table IV).

Band 5, 6·25μ (1601 cm.$^{-1}$). Aromatic (phenyl) ring absorption. The weak "shoulder" at 6·33μ (1580 cm.$^{-1}$) may be noted. When the aromatic ring is conjugated, as in the present example, the aromatic (phenyl) band is often split into a doublet and is usually more pronounced (Table III).

Band 6, 6·65μ (1503 cm.$^{-1}$). Aromatic ring absorption (Table III).

Band 7, 6·91μ (1447 cm.$^{-1}$). C—H deformation vibration of CH_2 groups in Nujol (Table V).

Band 8, 7·10μ (1408 cm.$^{-1}$). This is a characteristic carboxylic acid absorption band and it arises from a C—O vibration coupled with an

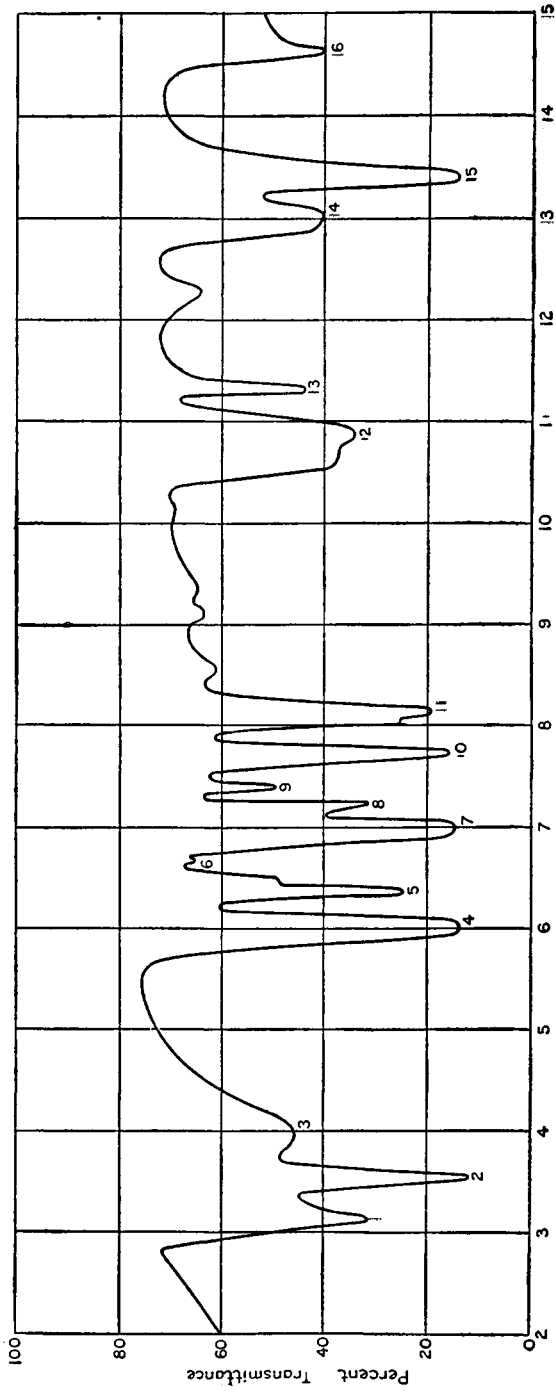


Fig. A, 7, 1.—Infrared Spectrum of *m*-Hydrobenzoic Acid.

O—H deformation vibration. It is readily observed in the spectrum as it lies between two characteristic Nujol bands in this region (Table V).

Band 9, 7·30μ (1370 cm.$^{-1}$). C—H deformation vibration absorption of C—CH_3 in Nujol (Table V).

Band 10, 7·75μ (1290 cm.$^{-1}$). This band arises from a C—O vibration coupled with an O—H deformation vibration (Table V).

Band 11, 8·15μ (1227 cm.$^{-1}$). The origin of this absorption (a doublet) is uncertain, but is believed to be associated with the C—O bond.

Band 12, 10·85μ (921 cm.$^{-1}$). This composite band is due partly to the O—H deformation vibration of a carboxylic acid.

Band 13, 11·45μ (873 cm.$^{-1}$). Out-of-plane C—H deformation vibration. Meta substitution (Table VI).

Band 14, 13·00μ (769 cm.$^{-1}$). Out-of-plane C—H deformation vibration. Meta substitution (Table VI).

Band 15, 13·25μ (755 cm.$^{-1}$). This may be the C—C absorption of the ring carboxyl group.

Band 16, 14·80μ (676 cm.$^{-1}$). Origin uncertain.

It must be emphasised that the above Tables must be used with caution. The presence of a specific group cannot always be established with certainty from the presence of the absorption band, particularly in the deformation vibration region ; on the other hand, the absence of the appropriate absorption band indicates that the grouping is not present. The physical state in which the substance is examined may have an appreciable influence ; the Tables apply generally to dilute solutions in organic solvents (see Table I).

Some applications of infrared spectra. A few of the applications of infrared spectroscopy may be mentioned.

1. Compound comparison. Because of the large number of absorption bands, the infrared spectrum of a molecule provides a good method of comparison. Two non-identical molecules have different infrared spectra when obtained by identical techniques ; hence identification of unknowns may be made by a direct comparison. The infrared absorption bands in the region 2–8μ are largely interpretable as due to specific functional groups. Not all bands that appear in the region of longer wave length (8–16μ) are as yet capable of interpretation but the region nevertheless is highly characteristic of the specific compound involved. This part of the infrared spectrum is called the " fingerprint " region and is very useful for the comparison of an unknown with an authentic sample ; if the two intricate spectra are exactly superposable, the compounds may be regarded as identical.

2. Testing the purity of a compound. If the spectrum of a sample of known purity is available, the presence of impurities in another sample can be detected from the additional bands in its infrared spectrum.

3. Recognition of functional groups or gross structural features.

4. Following the isolation of a desired product. The isolation of a desired substance by a purification procedure such as distillation or chromatography may be followed by a determination of the infrared spectrum. It is not essential to know what the compound is in this

connexion, since the concentration of the unknown substance can be traced by observing some characteristic absorption band.

5. Study of hydrogen bonding. Hydrogen bonding through an O—H or N—H group alters the characteristic vibrational frequency of that group: broadly, the stronger the hydrogen bonding, the greater is the lowering of the fundamental O—H or N—H vibration frequency.

6. Quantitative analysis of mixtures.

7. Following the progress of chemical operations.

ULTRAVIOLET AND VISIBLE SPECTRA

Ultraviolet and visible spectra arise from transitions between the electronic states in molecules. The terms "electronic spectra" and "ultraviolet and visible spectra" are synonymous and cover the range 200–800 mμ. The far-ultraviolet region 100–200 mμ, only partially transmitted by quartz and appreciably absorbed by air, will not be considered.

Ultraviolet and visible spectrophotometers employ a glass or quartz prism, and the necessary range is normally scanned manually; automatically recording instruments which provide a direct tracing of E against λ are available commercially. Substances are generally examined in solution in glass or quartz cells of about 1 cm. thickness. Owing to the greater energy of visible and ultraviolet radiation, the ratio of spectral slit width to band width can be made much smaller in visible and ultraviolet spectrophotometers than in infrared instruments. For this reason and also because cell thicknesses of the order of 1 cm. are easily reproducible, accurate absolute intensity measurements can be made in this region of the spectrum, and the intensity of an absorption band becomes correspondingly more important for identification purposes.

The electronic transitions which produce spectra in the visible and ultraviolet are accompanied by vibrational and rotational transitions. In the condensed state, however, rotation is hindered by solvent molecules, and stray electrical fields affect the vibrational frequencies. For these reasons, electronic bands are very broad. An electronic band is characterised by the wave length and molecular extinction coefficient at the position of maximum intensity ($\lambda_{max.}$ and $\varepsilon_{max.}$).

Electronic absorption bands can be correlated with molecular structure and therein lies the importance of visible and ultraviolet spectra to the organic chemist. For the purpose of structure analysis, infrared spectra are generally more valuable than visible and ultraviolet spectra. Infrared spectroscopy possesses the advantage that all organic compounds absorb in the region. Infrared spectra contain many sharp bands, are more sensitive to structural changes, and solid materials can be investigated. In the ultraviolet and visible portion of the electromagnetic spectrum, however, a wider range of solvents (including water) is available.

The substance is examined in a dilute solution in a solvent. A wide choice of solvents, transparent to ultraviolet radiation, is available. The paraffin hydrocarbons are all suitable, as are the aliphatic alcohols and the chlorinated hydrocarbons, such as chloroform and carbon tetrachloride. The most useful solvents are *n*-hexane, *cyclo*hexane, chloro-

form and carbon tetrachloride ; water, diethyl ether, ethanol and methanol are used only if considerations of solubility make it necessary. In general, polar solvents should be avoided. The selected solvent must be free from absorbing impurities ; " spectroscopically pure " solvents can be purchased. The possibility of interaction between the solvent and the compound under examination must always be considered. When the absorption spectrum of a pure substance is determined in each of a series of solvents, a slight difference in the location and the intensity of the absorption bands is usually observed with variation in solvent. The small solvent effects depend upon the nature of the solvent, the type of absorption band (*K*- or *R*-band *), and the nature of the solute (polar or non-polar). Marked changes in the nature of the absorption may be due to chemical interaction with the solvent, complex formation, dissociation or to equilibration of two tautomers in solution. Table VI gives the lowest wave length (mμ) at which a number of purified solvents transmit ultraviolet radiation in 1 cm. cells.

TABLE VII. LOWEST WAVE LENGTH (mμ) AT WHICH SOLVENTS TRANSMIT ULTRAVIOLET RADIATION

Solvent	*Wave Length*	*Solvent*	*Wave Length*
*cyclo*Hexane	195	Water	191
n-Hexane	200	Ethanol	204
Carbon tetrachloride	257	*iso*Propanol	205
Chloroform	237	Methanol	225
Benzene	280	Diethyl ether	225

SURVEY OF DATA

Chromophores and auxochromes. Absorption of light in the visible and ultraviolet regions is due to the excitation of relatively loosely-bound electrons, such as in multiple bonds or of lone pairs. The classical term for an arrangement of multiple bonds in adjacent positions (*i.e.*, separated by one single bond) and for the electronic interaction resulting therefrom is " conjugation ". The unsaturation electrons of multiple bonds are the π-electrons and we may adopt the term π–π conjugation for this case. In saturated organic compounds containing elements other than carbon and hydrogen, *e.g.*, nitrogen, oxygen or halogen, unshared *p*-electrons are present as well as the σ-valency electrons. The non-bonding *p*-electrons are held rather less firmly than σ-electrons. We may also have a π–*p* conjugation with certain groups, such as —NR_2 ; this is now realised to be

* Two or more chromophores (see below) in conjugation produce intense bands, which are termed *K*-bands (from the German *Konjugation*) in the neighbourhood of 230 mμ. Low intensity bands at longer wave lengths, probably due to single chromophores, are termed *R*-bands (from German *Radikal*).

as strong as π–π conjugation. The π–σ conjugation is much weaker. Each type of conjugation results in a band displacement to longer wave lengths (*bathochromic effect*). It should be noted that the term *hypsochromic* effect refers to displacement to shorter wave lengths.

In addition to π- and p-electrons, two other types of electrons contribute to ultraviolet and visible absorption; these are charge-electrons and unpaired electrons. The profound effect of introducing a permanent charge is shown, for instance, by the difference in absorption of the colourless triphenylmethane and the coloured triphenylmethyl ion. The visible band of the latter is probably due to a transition in which the distribution of the " resonating " charge between the several available positions in the phenyl rings becomes momentarily altered under the influence of the light field. Such spectra are called charge-resonance spectra; they are responsible *inter alia* for the intense long wave absorption and visible colour of triphenylmethane dyes, cyanine dyes, etc. The presence of a " resonating " unpaired electron in a conjugated system similarly produces " electron resonance " spectra, which are responsible for the visible colour, for example, of the triphenylmethyl radical.

Witt in 1876 coined the term *chromophore* for unsaturated groups such as C=C, C=O and N=N, which he thought to be essential for colour in organic compounds, and the term *auxochrome* for groups, such as $-NR_2$, thought to play an auxiliary role in producing and modifying colour. In modern usage the terms chromophore and auxochrome are employed to designate π-electron and p-electron groups respectively.

Some of the simple chromophoric groups, together with the absorption maxima of simple compounds containing these groups, are collected in

TABLE VIII. TYPICAL SINGLE CHROMOPHORIC GROUPS

Chromophore	*System*	*Example*	$\lambda_{max.}$ mμ	$\epsilon_{max.}$	*Solvent*
Ethylene	>C=C<	Oct-3-ene	185	8000	Hexane
Acetylene	—C≡C—	Acetylene	173	6000	Vapour
Carbonyl	>C=O	Acetone	188	900	Hexane
Azomethine	>C=N—	Acetoxime	279	15	—
			190	5000	Water
Nitrile	—C≡N	Acetonitrile	<160	—	—
Thiocarbonyl	>C=S	Diethyl thioncarbonate	330	5	Water
Azo	—N=N—	Ethyl diazoacetate	252	8000	Ethanol
Nitroso	—N=O	Nitrosobutane	300	100	Ether
Nitro	$-NO_2$	Nitromethane	271	19	Alcohol
Nitrite	—ON=O	Octyl nitrite	230	2200	Hexane
Nitrate	$-ONO_2$	Ethyl nitrate	270	12	Dioxan
Sulphoxide	>SO	*cyclo*Hexyl methyl sulphoxide	210	1500	Alcohol
Sulphone	$>SO_2$	Dimethyl sulphone	<180	—	—
Carboxyl	$-CO_2$	Acetic acid	204	60	Water

Table VIII. The compounds selected are as typical as possible, but it must be remembered that there are many environmental factors that produce changes in the location of the absorption bands. These displacements are usually of the order of a few mμ, but in some cases they are so great as to move the absorption band into a completely different region of the spectrum.

Typical auxochromes are hydroxyl, alkoxyl and aroxyl, amino, alkylamino and arylamino, all of which promote conjugation with lone pairs on oxygen or nitrogen atoms.

When two or more chromophores are present in the same molecule, their absorption is usually additive as long as they are separated by two or more single bonds. Two chromophores in conjugation (*i.e.*, separated by only one single bond) give rise to a new type of absorption with increased $\lambda_{max.}$ and $\varepsilon_{max.}$. Some examples are given in Table IX.

TABLE IX. TWO CONJUGATED CHROMOPHORES

System	*Example*	λ_{max} mμ	$\varepsilon_{max.}$
C=C—C=C	Butadiene	217	21000
C=C—C≡C	Vinylacetylene	219	6500
C=C—C=N	*N*-Butylcrotonaldimine	220	23000
C=C—C≡N	1-Cyano*cyclo*hexene	211	11000
C=N—N=C	Butyraldazine	205	13000
C=C—C=O	Crotonaldehyde	217	16000

The conjugation of three unsaturated centres results in a further increase in $\lambda_{max.}$ and $\varepsilon_{max.}$. Some results are given in Table X.

TABLE X. THREE CONJUGATED CHROMOPHORES

System	*Example*	$\lambda_{max.}$ mμ	$\varepsilon_{max.}$
C=C—C=C—C=C	Hexatriene	258	35000
C=C—C=C—C=O	Sorbaldehyde	263	27000
C=C—CO—C=C	Dipropenyl ketone	245	16000
O=C—C=C—C=O	Diacetylethylene	226	14500

The electronic spectra of benzenoid systems differ in a characteristic manner from their acyclic analogues. Thus benzene, unlike hexatriene,

exhibits a relatively weak band at 255 mμ, but has two strong bands at 184 mμ and 202 mμ. Fusion of two or more benzene nuclei results in changes in absorption with displacement to higher wave lengths. Some complicated selected results are collected in Table XI.

TABLE XI. AROMATIC HYDROCARBONS

	$\lambda_{max.}$	$log\ \varepsilon_{max.}$	$\lambda_{max.}$	$log\ \varepsilon_{max.}$	$\lambda_{max.}$	$log\ \varepsilon_{max.}$
Benzene . . .	184	4·67	202	3·84	255	2·35
Naphthalene . .	220	5·05	275	3·75	312	2·40
Anthracene . . .	252	5·30	375	3·90	—	—
Phenanthrene . .	252	4·70	295	4·10	330	2·90
Chrysene . . .	268	5·15	320	4·10	360	2·80
Diphenyl . . .	—	—	252	4·26	—	—

Space does not permit any further detailed discussion except for a brief account of two interesting subjects. The first is concerned with keto-enol tautomerism. The classical example is ethyl acetoacetate, which can exist in the keto form (I) and the enol form (II):

$$CH_3C(=O)-CH_2COOC_2H_5 \text{ (I)} \qquad CH_3C(OH)=CHCOOC_2H_5 \text{ (II)}$$

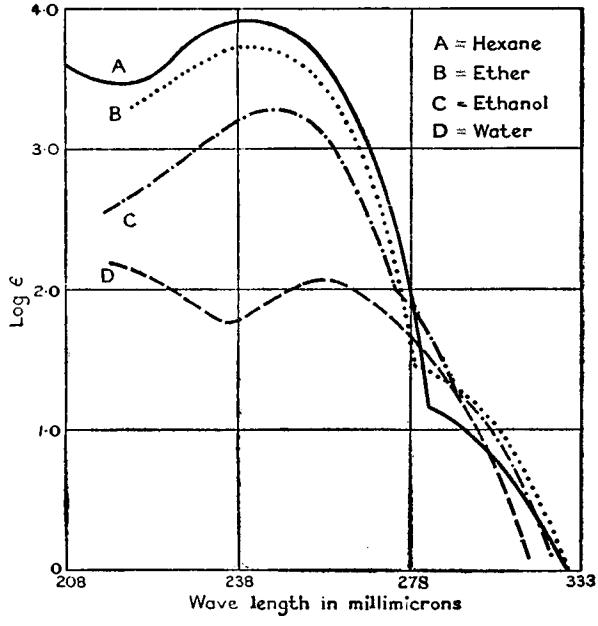


Fig. A, 7, 2.—Ultraviolet spectrum of ethyl acetoacetate in various solvents.

The former exhibits absorption typical of an isolated keto group, whereas the latter shows a high intensity *K*-band associated with the conjugated system HO—C=C—C=O. The proportions of the two forms under various conditions are readily determined from the ultraviolet spectra. The ultraviolet spectra in various solvents are shown in Fig. *A*, 7, 2. Since the absorption of the keto form is negligible, the percentage of enol present is $100(\varepsilon_m/\varepsilon_e)$, where ε_m is the observed extinction at 245 mμ and ε_e that of the pure enol. It was shown that in alcoholic solution ε_m is 1900 and the percentage of enol is 12. Thus ε_e is *ca.* 16000, and use of this value permits the approximate evaluation of the enol content in different solvents. The results are collected in Table XII.

TABLE XII. KETO-ENOL EQUILIBRIA OF ETHYL ACETOACETATE

Solvent	$\lambda_{max.}$ mμ	$\varepsilon_{max.}$	% *Enol*
Hexane . . .	243·9	8100	51
Water . . .	255·1	120	—
Ether	243·9	5100	32
Ethanol . . .	235·7	1900	12

The second subject is concerned with *cis* and *trans* isomers. The *trans* isomer has the higher $\lambda_{max.}$ value (except for azobenzene) and the larger $\varepsilon_{max.}$. This will be apparent from the data in Table XIII.

TABLE XIII. ULTRAVIOLET ABSORPTION MAXIMA OF *CIS* AND *TRANS* ISOMERS

	Cis		*Trans*	
	$\lambda_{max.}$, mμ	$\varepsilon_{max.}$	$\lambda_{max.}$, mμ	$\varepsilon_{max.}$
PhCH=CHPh . .	280	10500	295	27000
PhCH=CHCOOH .	264	9500	273	21000
PhCH=CHCOPh .	289	8900	298	24000
PhN=NPh . .	324	15000	319	20000

Some applications of electronic spectra. These include :—

1. Qualitative identification. The spectrum is of help in identifying organic compounds. If two compounds are identical, the electronic spectra must be identical : the converse is not necessarily true and in this

respect ultraviolet data are less suitable than infrared data for the "fingerprinting" of substances. The spectrum is characteristic of the chromophoric system rather than that of the complete molecule.

2. Determination of purity. The ultraviolet and visible absorption is often a fairly intensive property; thus ε values of high intensity bands may be of the order of 10^4–10^5. In infrared spectra ε values rarely exceed 10^3. It is therefore often easy to pick out a characteristic band of a substance present in small concentration in admixture with other materials. Thus small amounts of aromatic compounds can be detected in hexane or in *cyclo*hexane.

3. Determination of structural features. The ultraviolet spectrum has been of value in the determination of the structure of several vitamins. Thus the presence of an α-naphthoquinone system in vitamin K was first detected by this means. Also the 4-methylthiazole and the 2 : 5-dimethyl-6-aminopyridine system was first identified in vitamin B_1 (thiamine). α- and β-Ionones can be distinguished since the former contains two conjugated chromophores and the latter three conjugated chromophores.

4. Quantitative analysis. Spectroscopic analysis is widely used in the analysis of vitamin preparations, mixtures of hydrocarbons (*e.g.*, benzene, toluene, ethylbenzene, xylenes) and other systems exhibiting characteristic electronic spectra. The extinction coefficient at 326 mμ, after suitable treatment to remove other materials absorbing in this region, provides the best method for the estimation of the vitamin A content of fish oils.

5. Determination of the dissociation constants of acids and bases from the change of absorption spectra with *p*H. The spectrochemical method is particularly valuable for very weak bases, such as aromatic hydrocarbons and carbonyl compounds which require high concentrations of strong mineral acid in order to be converted into the conjugate acid to a measurable extent.

6. Detecting steric hindrance. Hindered rotation about single bonds may be studied. Diphenyls containing bulky *ortho* substituents can exist as two optical enantiomorphs. For a hindered diphenyl to be resolved, the energy barrier must be of the order of 20 k. cal./mol, but electronic spectra are a much more sensitive test of non-planarity. Thus in *ortho*-ditolyl the *K* band near 250 mμ (present in diphenyl) has completely disappeared and the planes of the two rings must be at an angle of over 45°. The method is therefore of advantage when optical resolution cannot be used as a criterion.

7. Study of reaction rates.

The above account of infrared and ultraviolet spectra should provide an introduction to the subject. Further information can be obtained by reference to the books listed below.

SELECTED BIBLIOGRAPHY

Bellamy, *The Infra-Red Spectra of Complex Molecules*, 1954 (Methuen).

Randall, Fowler, Fuson and Dangl, *Infrared Determination of Organic Structures*, 1942 (Van Nostrand).

Gilman, *Organic Chemistry*, Volume III, 1953 (J. Wiley : Chapman and Hall).

Braude and Nachod, *Determination of Organic Structures by Physical Methods*, 1955 (Academic Press).

Strouts, Gilfillan and Wilson, *Analytical Chemistry. The Working Tools*, Volume II, 1955 (Oxford University Press).

Gillam and Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 1954 (Arnold).

Braude, *Ultra-Violet Light Absorption and the Structure of Organic Compounds* {Annual Reports, **42**, 105 (1945)}.

TABLE A,8,1. AQUEOUS ETHYL ALCOHOL

Per Cent. C_2H_5OH by Weight	Density $d_{4°}^{20°}$	Density $d_{4°}^{25°}$	Per Cent. C_2H_5OH by Volume (20°)	Per Cent. C_2H_5OH by Weight	Density $d_{4°}^{20°}$	Density $d_{4°}^{25°}$	Per Cent. C_2H_5OH by Volume (20°)
5	0·98938	0·98817	6·2	75	0·85564	0·85134	81·3
10	0·98187	0·98043	12·4	80	0·84344	0·83911	85·5
15	0·97514	0·97334	18·5	85	0·83095	0·82660	89·5
20	0·96864	0·96639	24·5	90	0·81797	0·81362	93·3
25	0·96168	0·95895	30·4	91	0·81529	0·81094	94·0
30	0·95382	0·95067	36·2	92	0·81257	0·80823	94·7
35	0·94494	0·94146	41·8	93	0·80983	0·80549	95·4
40	0·93518	0·93148	47·3	94	0·80705	0·80272	96·1
45	0·92472	0·92085	52·7	95	0·80424	0·79991	96·8
50	0·91384	0·90985	57·8	96	0·80138	0·79706	97·5
55	0·90258	0·89850	62·8	97	0·79846	0·79415	98·1
60	0·89113	0·88699	67·7	98	0·79547	0·79117	98·8
65	0·87948	0·87527	72·4	99	0·79243	0·78814	99·4
70	0·86766	0·85340	76·9	100	0·78934	0·78506	100·0

TABLE A,8,2. **AQUEOUS METHYL ALCOHOL**

Per Cent. CH_3OH by Weight	Density $d_{4^\circ}^{15^\circ}$	Per Cent. CH_3OH by Volume	Per Cent. CH_3OH by Weight	Density $d_{4^\circ}^{15^\circ}$	Per Cent. CH_3OH by Volume
5	0·99029	6·22	75	0·86300	81·34
10	0·98241	12·35	80	0·85048	85·50
15	0·97518	18·38	85	0·83742	89·45
20	0·96814	24·33	90	0·82396	93·19
25	0·96108	30·19	91	0·82124	93·91
30	0·95366	35·95	92	0·81849	94·63
35	0·94570	41·59	93	0·81568	95·33
40	0·93720	47·11	94	0·81285	96·02
45	0·92815	52·49	95	0·80999	96·70
50	0·91852	57·71	96	0·80713	97·37
55	0·90839	62·78	97	0·80428	98·04
60	0·89781	67·69	98	0·80143	98·70
65	0·88662	72·42	99	0·79859	99·35
70	0·87507	76·98	100	0·79577	100·00

TABLE A,8,3. **AQUEOUS HYDROCHLORIC ACID**

Per Cent. HCl by Weight	Density $d_{4°}^{20°}$	Grams HCl per 100 Ml.	Per Cent. HCl by Weight	Density $d_{4°}^{20°}$	Grams HCl per 100 Ml.	Per Cent. HCl by Weight	Density $d_{4°}^{20°}$	Grams HCl per 100 Ml.
1	1·0032	1·003	14	1·0675	14·95	28	1·1392	31·90
2	1·0082	2·006	16	1·0776	17·24	30	1·1492	34·48
4	1·0181	4·007	18	1·0878	19·58	32	1·1593	37·10
6	1·0279	6·167	20	1·0980	21·96	34	1·1691	39·75
8	1·0376	8·301	22	1·1083	24·38	36	1·1789	42·44
10	1·0474	10·47	24	1·1187	26·85	38	1·1885	45·16
12	1·0574	12·69	26	1·1290	29·35	40	1·1980	47·92

TABLE A,8,4. **AQUEOUS SULPHURIC ACID**

Per Cent. H_2SO_4 by Weight	Density $d_{4°}^{20°}$	Grams H_2SO_4 per 100 Ml.	Per Cent. H_2SO_4 by Weight	Density $d_{4°}^{20°}$	Grams H_2SO_4 per 100 Ml.	Per Cent. H_2SO_4 by Weight	Density $d_{4°}^{20°}$	Grams H_2SO_4 per 100 Ml.
1	1·0051	1·005	40	1·3028	52·11	91	1·8195	165·6
2	1·0118	2·024	45	1·3476	60·64	92	1·8240	167·8
3	1·0184	3·055	50	1·3951	69·76	93	1·8279	170·0
4	1·0250	4·100	55	1·4453	79·49	94	1·8312	172·1
5	1·0317	5·159	60	1·4983	89·90	95	1·8337	174·2
10	1·0661	10·66	65	1·5533	101·0	96	1·8355	176·2
15	1·1020	16·53	70	1·6105	112·7	97	1·8364	178·1
20	1·1394	22·79	75	1·6692	125·2	98	1·8361	179·9
25	1·1783	29·46	80	1·7272	138·2	99	1·8342	181·6
30	1·2185	36·56	85	1·7786	151·2	100	1·8305	183·1
35	1·2579	44·10	90	1·8144	163·3			

TABLE A,8,5. **AQUEOUS NITRIC ACID**

Per Cent. HNO_3 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HNO_3 per 100 Ml.	Per Cent. HNO_3 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HNO_3 per 100 Ml.	Per Cent. HNO_3 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HNO_3 per 100 Ml.
1	1·0036	1·004	40	1·2463	49·85	91	1·4850	135·1
2	1·0091	2·018	45	1·2783	57·52	92	1·4873	136·8
3	1·0146	3·044	50	1·3100	65·50	93	1·4892	138·5
4	1·0201	4·080	55	1·3393	73·66	94	1·4912	140·2
5	1·0256	5·128	60	1·3667	82·00	95	1·4932	141·9
10	1·0543	10·54	65	1·3913	90·43	96	1·4952	143·5
15	1·0842	16·26	70	1·4134	98·94	97	1·4974	145·2
20	1·1150	22·30	75	1·4337	107·5	98	1·5008	147·1
25	1·1469	28·67	80	1·4521	116·2	99	1·5056	149·1
30	1·1800	35·40	85	1·4686	124·8	100	1·5129	151·3
35	1·2140	42·49	90	1·4826	133·4			

TABLE A,8,6. **AQUEOUS ACETIC ACID**

Per Cent. CH_3COOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams CH_3COOH per 100 Ml.	Per Cent. CH_3COOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams CH_3COOH per 100 Ml.	Per Cent. CH_3COOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams CH_3COOH per 100 Ml.
1	0·9996	0·9996	40	1·0488	41·95	91	1·0652	96·93
2	1·0012	2·002	45	1·0534	47·40	92	1·0643	97·92
3	1·0025	3·008	50	1·0575	52·88	93	1·0632	98·88
4	1·0040	4·016	55	1·0611	58·36	94	1·0619	99·82
5	1·0055	5·028	60	1·0642	63·85	95	1·0605	100·7
10	1·0125	10·13	65	1·0666	69·33	96	1·0588	101·6
15	1·0195	15·29	70	1·0685	74·80	97	1·0570	102·5
20	1·0263	20·53	75	1·0696	80·22	98	1·0549	103·4
25	1·0326	25·82	80	1·0700	85·60	99	1·0524	104·2
30	1·0384	31·15	85	1·0689	90·86	100	1·0498	105·0
35	1·0438	36·53	90	1·0661	95·95			

TABLE A,8,7. **AQUEOUS FORMIC ACID**

Per Cent. HCOOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HCOOH per 100 Ml.	Per Cent. HCOOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HCOOH per 100 Ml.	Per Cent. HCOOH by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams HCOOH per 100 Ml.
1	1·0019	1·002	40	1·0963	43·85	91	1·2059	109·7
2	1·0044	2·009	45	1·1085	49·88	92	1·2078	111·1
3	1·0070	3·021	50	1·1207	56·04	93	1·2099	112·5
4	1·0093	4·037	55	1·1320	62·26	94	1·2117	113·9
5	1·0115	5·058	60	1·1424	68·54	95	1·2140	115·3
10	1·0246	10·25	65	1·1543	75·03	96	1·2158	116·7
15	1·0370	15·66	70	1·1655	81·59	97	1·2170	118·0
20	1·0488	20·98	75	1·1769	88·27	98	1·2183	119·4
25	1·0609	26·52	80	1·1860	94·88	99	1·2202	120·8
30	1·0729	32·19	85	1·1953	101·6	100	1·2212	122·1
35	1·0847	37·96	90	1·2044	108·4			

TABLE A,8,8. **AQUEOUS PHOSPHORIC ACID**

Per Cent. H_3PO_4 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams H_3PO_4 per 100 Ml.	Per Cent. H_3PO_4 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams H_3PO_4 per 100 Ml.	Per Cent. H_3PO_4 by Weight	Density $d_{4^\circ}^{20^\circ}$	Grams H_3PO_4 per 100 Ml.
2	1·0092	2·018	40	1·254	50·16	80	1·633	130·6
4	1·0200	4·080	45	1·293	58·19	85	1·689	143·6
6	1·0309	6·185	50	1·335	66·75	90	1·746	157·1
8	1·0420	8·336	55	1·379	75·85	92	1·770	162·8
10	1·0532	10·53	60	1·426	85·56	94	1·794	168·6
20	1·1134	22·27	65	1·475	95·88	96	1·819	174·6
30	1·1805	35·42	70	1·526	106·8	98	1·844	180·7
35	1·216	42·56	75	1·579	118·4	100	1·870	187·0

TABLE A,8,9. **AQUEOUS HYDROBROMIC ACID**

Per Cent. HBr by Weight	Density $d_{4°}^{20°}$	Grams HBr per 100 Ml.	Per Cent. HBr by Weight	Density $d_{4°}^{20°}$	Grams HBr per 100 Ml.	Per Cent. HBr by Weight	Density $d_{4°}^{20°}$	Grams HBr per 100 Ml.
10	1·0723	10·7	40	1·3772	56·1	60	1·6787	100·7
20	1·1579	23·2	45	1·4446	65·0	65	1·7675	114·9
30	1·2580	37·7	50	1·5173	75·8			
35	1·3150	46·0	55	1·5953	87·7			

TABLE A,8,10. **AQUEOUS HYDRIODIC ACID**

Per Cent. HI by Weight	Density $d_{4°}^{15°}$	Grams HI per 100 Ml.	Per Cent. HI by Weight	Density $d_{4°}^{15°}$	Grams HI per 100 Ml.
20·77	1·1758	24·4	56·78	1·6998	96·6
31·77	1·2962	41·2	61·97	1·8218	112·8
42·7	1·4489	61·9			

TABLE A,8,*11*. **FUMING SULPHURIC ACID (OLEUM)**

Per Cent. free SO_3 by Weight	Density $d^{20°}_{20°}$	Grams free SO_3 per 100 Ml.	Per Cent. free SO_3 by Weight	Density $d^{20°}_{20°}$	Grams free SO_3 per 100 Ml.	Per Cent. free SO_3 by Weight	Density $d^{20°}_{20°}$	Grams free SO_3 per 100 Ml.
1·54	1·860	2·8	8·16	1·890	15·4	15·95	1·920	30·6
2·66	1·865	5·0	9·43	1·895	17·7	18·67	1·925	35·9
4·28	1·870	8·0	10·07	1·900	19·1	21·34	1·930	41·2
5·44	1·875	10·2	10·56	1·905	20·1	25·65	1·935	49·6
6·42	1·880	12·1	11·43	1·910	21·8			
7·29	1·885	13·7	13·33	1·915	25·5			

Per Cent. free SO_3 by Weight	Density $d^{15°}_{15°}$	Per Cent. total SO_3 by Weight	Per Cent. free SO_3 by Weight	Density $d^{15°}_{15°}$	Per Cent. total SO_3 by Weight	Per Cent. free SO_3 by Weight	Density $d^{15°}_{15°}$	Per Cent. total SO_3 by Weight
10	1·888	83·46	50	2·009	90·81	90	1·990	98·16
20	1·920	85·30	60	2·020	92·65	100	1·984	100·00
30	1·957	87·14	70	2·018	94·48			

Note. Oleum with 0–30 per cent. free SO_3 is liquid at 15°.
30–56 per cent. free SO_3 is solid at 15°.
56–73 per cent. free SO_3 is liquid at 15°.
73–100 per cent. free SO_3 is solid at 15°.

TABLE A,8,*12*. **AQUEOUS AMMONIA SOLUTIONS**

Per Cent. NH_3 by Weight	Density $d_{4°}^{20°}$	Grams NH_3 per 1000 Ml.	Per Cent. NH_3 by Weight	Density $d_{4°}^{20°}$	Grams NH_3 per 1000 Ml.	Per Cent. NH_3 by Weight	Density $d_{4°}^{20°}$	Grams NH_3 per 1000 Ml.
1	0·9939	9·94	10	0·9575	95·75	20	0·9229	184·6
2	0·9895	19·79	12	0·9501	114·0	22	0·9164	201·6
4	0·9811	39·24	14	0·9430	132·0	24	0·9101	218·4
6	0·9730	58·38	16	0·9362	149·8	26	0·9040	235·0
8	0·9651	77·21	18	0·9295	167·3	28	0·8980	251·4
						30	0·8920	267·6

TABLE A,8,*13*. **AQUEOUS SODIUM HYDROXIDE**

Per Cent. NaOH by Weight	Density $d_{4°}^{20°}$	Grams NaOH per 100 Ml.	Per Cent. NaOH by Weight	Density $d_{4°}^{20°}$	Grams NaOH per 100 Ml.	Per Cent. NaOH by Weight	Density $d_{4°}^{20°}$	Grams NaOH per 100 Ml.
1	1·0095	1·010	18	1·1972	21·55	36	1·3900	50·04
2	1·0207	2·041	20	1·2191	24·38	38	1·4101	53·58
4	1·0428	4·171	22	1·2411	27·30	40	1·4300	57·20
6	1·0648	6·389	24	1·2629	30·31	42	1·4494	60·87
8	1·0869	8·695	26	1·2848	33·40	44	1·4685	64·61
10	1·1089	11·09	28	1·3064	36·58	46	1·4873	68·42
12	1·1309	13·57	30	1·3279	39·84	48	1·5065	72·31
14	1·1530	16·14	32	1·3490	43·17	50	1·5253	76·27
16	1·1751	18·80	34	1·3696	46·57			

TABLE A,8,*14*. AQUEOUS POTASSIUM HYDROXIDE

Per Cent. KOH by Weight	Density $d_{4°}^{15°}$	Grams KOH per 100 Ml.	Per Cent. KOH by Weight	Density $d_{4°}^{15°}$	Grams KOH per 100 Ml.	Per Cent. KOH by Weight	Density $d_{4°}^{15°}$	Grams KOH per 100 Ml.
1	1·0083	1·008	18	1·1688	21·04	36	1·3549	48·78
2	1·0175	2·035	20	1·1884	23·77	38	1·3769	52·32
4	1·0359	4·144	22	1·2083	26·58	40	1·3991	55·96
6	1·0544	6·326	24	1·2285	29·48	42	1·4215	59·70
8	1·0730	8·584	26	1·2489	32·47	44	1·4443	63·55
10	1·0918	10·92	28	1·2695	35·55	46	1·4673	67·50
12	1·1108	13·33	30	1·2905	38·72	48	1·4907	71·55
14	1·1299	15·82	32	1·3117	41·97	50	1·5143	75·72
16	1·1493	19·70	34	1·3331	45·33	52	1·5382	79·99

TABLE A,8,*15*. AQUEOUS SODIUM CARBONATE

Per Cent. Na_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams Na_2CO_3 per 100 Ml.	Per Cent. Na_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams Na_2CO_3 per 100 Ml.	Per Cent. Na_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams Na_2CO_3 per 100 Ml.
1	1·0086	1·009	8	1·0816	8·653	16	1·1682	18·50
2	1·0190	2·038	10	1·1029	11·03	18	1·1905	21·33
4	1·0398	4·159	12	1·1244	13·49	20	1·2132	24·26
6	1·0606	6·364	14	1·1463	16·05			

TABLE A,8,*16*. **AQUEOUS POTASSIUM CARBONATE**

Per Cent. K_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams K_2CO_3 per 100 Ml.	Per Cent. K_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams K_2CO_3 per 100 Ml.	Per Cent. K_2CO_3 by Weight	Density $d_{4°}^{20°}$	Grams K_2CO_3 per 100 Ml.
1	1·0072	1·007	14	1·1291	15·81	28	1·2756	35·72
2	1·0163	2·033	16	1·1490	18·38	30	1·2979	38·94
4	1·0345	4·138	18	1·1692	21·05	35	1·3548	47·42
6	1·0529	6·317	20	1·1898	23·80	40	1·4141	56·56
8	1·0715	8·572	22	1·2107	26·64	45	1·4759	66·42
10	1·0904	10·90	24	1·2320	29·57	50	1·5404	77·02
12	1·1096	13·32	26	1·2536	32·59			

TABLE A,8,*17*. **AQUEOUS SODIUM CHLORIDE**

Per Cent. NaCl by Weight	Density $d_{4°}^{20°}$	Grams NaCl per 100 Ml.	Per Cent. NaCl by Weight	Density $d_{4°}^{20°}$	Grams NaCl per 100 Ml.	Per Cent. NaCl by Weight	Density $d_{4°}^{20°}$	Grams NaCl per 100 Ml.
1	1·0053	1·005	10	1·0707	10·71	20	1·1478	22·96
2	1·0125	2·025	12	1·0857	13·03	22	1·1640	25·61
4	1·0268	4·107	14	1·1009	15·41	24	1·1840	28·33
6	1·0413	6·248	16	1·1162	17·86	26	1·1972	31·13
8	1·0559	8·447	18	1·1319	20·37			

TABLE A,8,*18*. **AQUEOUS POTASSIUM CHLORIDE**

Per Cent. KCl by Weight	Density $d_{4°}^{20°}$	Grams KCl per 100 Ml.	Per Cent. KCl by Weight	Density $d_{4°}^{20°}$	Grams KCl per 100 Ml.	Per Cent. KCl by Weight	Density $d_{4°}^{20°}$	Grams KCl per 100 Ml.
1	1·0046	1·005	8	1·0500	8·400	16	1·1043	17·67
2	1·0110	2·022	10	1·0633	10·63	18	1·1185	20·13
4	1·0239	4·096	12	1·0768	12·92	20	1·1328	22·66
6	1·0369	6·221	14	1·0905	15·27	22	1·1474	25·24
						24	1·1623	27·90

TABLE A,8,*19*. **AQUEOUS SODIUM NITRITE**

Per Cent. $NaNO_2$ by Weight	Density $d_{4°}^{15°}$	Grams $NaNO_2$ per 100 Ml.	Per Cent. $NaNO_2$ by Weight	Density $d_{4°}^{15°}$	Grams $NaNO_2$ per 100 Ml.	Per Cent. $NaNO_2$ by Weight	Density $d_{4°}^{15°}$	Grams $NaNO_2$ per 100 Ml.
1	1·0058	1·006	8	1·0535	8·428	16	1·1103	17·76
2	1·0125	2·025	10	1·0675	10·68	18	1·1248	20·25
4	1·0260	4·104	12	1·0816	12·98	20	1·1394	22·79
6	1·0397	6·238	14	1·0959	15·34			

A,9. **DENSITY AND VAPOUR PRESSURE OF WATER: 0° TO 35° C.**

$t°$ C	Density $d^{t°}_{4°}$	Vapour Pressure (Mm. of Mercury)	$t°$ C	Density $d^{t°}_{4°}$	Vapour Pressure (Mm. of Mercury)	$t°$ C	Density $d^{t°}_{4°}$	Vapour Pressure (Mm. of Mercury)
0°	0·99987	4·58	12°	0·99952	10·48	24°	0·99733	22·18
1°	0·99993	4·92	13°	0·99940	11·19	25°	0·99708	23·54
2°	0·99997	5·29	14°	0·99927	11·94	26°	0·99682	24·99
3°	0·99999	5·68	15°	0·99913	12·73	27°	0·99655	26·50
4°	1·00000	6·09	16°	0·99897	13·56	28°	0·99627	28·10
5°	0·99999	6·53	17°	0·99880	14·45	29°	0·99597	29·78
6°	0·99997	7·00	18°	0·99862	15·38	30°	0·99568	31·55
7°	0·99993	7·49	19°	0·99843	16·37	31°	0·99537	33·42
8°	0·99988	8·02	20°	0·99823	17·41	32°	0·99505	35·37
9°	0·99981	8·58	21°	0·99802	18·50	33°	0·99473	37·43
10°	0·99973	9·18	22°	0·99780	19·66	34°	0·99440	39·59
11°	0·99963	9·81	23°	0·99757	20·88	35°	0·99406	41·85

A,10. **ATOMIC WEIGHTS**

Aluminium	Al	26·98	Manganese	Mn	54·94
Antimony	Sb	121·76	Mercury	Hg	200·61
Arsenic	As	74·91	Molybdenum	Mo	95·95
Barium	Ba	137·36	Nickel	Ni	58·69
Beryllium	Be	9·03	Nitrogen	N	14·008
Bismuth	Bi	209·00	Oxygen	O	16·000
Boron	B	10·82	Palladium	Pd	106·7
Bromine	Br	79·92	Phosphorus	P	30·98
Cadmium	Cd	112·41	Platinum	Pt	195·23
Calcium	Ca	40·08	Potassium	K	39·10
Carbon	C	12·011	Selenium	Se	78·96
Cerium	Ce	140·13	Silicon	Si	28·09
Chlorine	Cl	35·46	Silver	Ag	107·88
Chromium	Cr	52·01	Sodium	Na	22·99
Cobalt	Co	58·94	Strontium	Sr	87·63
Copper	Cu	63·54	Sulphur	S	32·066
Fluorine	F	19·00	Tellurium	Te	127·61
Germanium	Ge	72·60	Thorium	Th	232·05
Gold	Au	197·0	Tin	Sn	118·70
Hydrogen	H	1·008	Titanium	Ti	47·90
Iodine	I	126·91	Tungsten	W	183·92
Iron	Fe	55·85	Uranium	U	238·07
Lead	Pb	207·21	Vanadium	V	50·95
Lithium	Li	6·940	Zinc	Zn	65·38
Magnesium	Mg	24·32	Zirconium	Zr	91·22