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A TREATISE

ON THE

PRINCIPLES OF CHEMISTRY.

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A TREATISE

ON THE

PRINCIPLES OF CHEMISTRY

BY

M. M. PATTISON MUIR, M.A., F.R.S.E.

FELLOW, AND PRÆLECTOR IN CHEMISTRY, OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

SECOND EDITION.

"In nature everything is distinct, yet nothing defined into absolute independent singleness." WORDSWORTH.

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PREFACE.

THIS book is intended to give a fairly complete account of the present state of knowledge regarding the principles and general laws of chemistry.

It is addressed to students of this science who have already a considerable acquaintance with descriptive chemistry, but it is hoped that by such students the book will be found complete in itself; so that while it certainly deals with chemical principles and theories on the supposition that its readers have some knowledge of chemical facts, yet the book may fairly claim to rank as a systematic treatise on chemical philosophy.

While I have tried to supply full information regarding those points which appear to me of most importance, I have also sought to avoid great detail, and to present a sketch of the principles of chemistry the parts of which shall be seen as being mutually dependent.

To know what to omit has been one of the most difficult parts of my undertaking. The chemical student is subjected to a shower-bath of facts; he is made

'to sit as a passive bucket and be pumped into...can in the long-run be exhilarating to no creature.'

An attempt is made in this book to treat the principal theories of modern chemistry to some extent from an historical point of view, and to trace the connexions between the older theories and those which now prevail in the science. It is hoped that the student may thus gain a firmer grasp of those theories than he is able to do when they are put before him as entirely creations of recent times.

I have tried to deal with chemical facts and generalisations so as to shew their reality. This can best be done, I believe, by following in the very foot-prints of the great discoverers, by watching them as they make their footing sure, and as they feel their way up the heights. That the student may be able to verify the accounts I have given of the more important investigations, and more especially that he may fill in the details which I have necessarily omitted, I have given copious references to original memoirs and papers; these references will, I believe, be found correct, at least I have spared no pains to make them so. I have also endeavoured to make the index full and complete.

So far as I am aware, no sufficiently comprehensive guide to the study of the principles of chemistry exists, in an English form, although we have many excellent works dealing with descriptive chemistry, with the materials, that is to say, from which chemical science is being constructed. Prof. Lothar Meyer's *Die modernen Theorien der Chemie*, to a considerable extent meets the wants of the German student, and I have made free use of that book in preparing my own; but I venture to think I have incorporated in my general plan many important facts and principles which do not find a

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Abbreviated Titles.	Full Titles.
Annalen.	*Liebig's Annalen der Chemie und Pharmacie.* [Continued since Liebig's death under same title.]
J. für prakt. Chemie.	*Journal für praktische Chemie.* [**Series 1** and **2.**]
Ber.	*Berichte der Deutschen Chemischen Gesellschaft.* [Abstracts of papers published elsewhere are paged consecutively with the transactions until 1883; from 1884 and onwards the abstracts, **Referate,** are paged separately.]
or { *Fresenius's Zeitschr.* / *Zeitschr. anal. Chemie* }	*Zeitschrift für analytische Chemie,* herausgegeben von Dr C. R. Fresenius. [1862, onwards.]
Zeitschr. für Chemie.	*Zeitschrift für Chemie.* [Conducted by Beilstein and Fittig. **Series 1** and **2.** 1858 to 1871. Publication discontinued.]
Zeitschr. für physikal. Chemie.	*Zeitschrift für Physikalische Chemie, Stochiometrie und Verwandtschaftslehre;* herausgegeben von W. Ostwald und J. H. van't Hoff. [1887, onwards.]
Zeitschr. für Krystallog.	*Zeitschrift für Krystallographie und Mineralogie.* [1877, onwards.]
Schweigger's Journal.	*Journal für Chemie und Physik.* [Conducted by J. S. C. Schweigger. 1811–1833.]
Sitzber. der K. Akad. zu Wien.	*Sitzungsberichte der Mathematisch-naturwissenschaftliche Classe der Kaiserliche Akademie der Wissenschaften* (Wien). [Each volume contains 2 or 3 parts (*Abtheilungen*); each part is bound and paged as a separate volume; the arrangement is perplexing.]
Sitzber. der Wiss. Akad. zu Berlin.	*Sitzungsberichte der Akademie der Wissenschaften zu Berlin.* [1854, and onwards.]
Jahresberichte.	*Jahresberichte über die Fortschritte der Chemie,* &c. [Stædel edited a very useful *Jahresber. über die Fortschritte auf dem Gebiete der Reinen Chemie* 1873–1881.]
Compt. rend.	*Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.* [1835, onwards.]
Mém. de l'Acad.	*Mémoires de l'Académie Royale des Sciences de l'Institut de France.* [1816, onwards.]
Ann. Chim. Phys.	*Annales de Chimie et de Physique.* [**Series 1** to **6.**]
Bull. Soc. Chim.	*Bulletin de la Société Chimique de Paris.* [1864, onwards.]
Mém. de la Soc. d'Arcueil.	*Mémoires de Physique et de Chimie de la Société d'Arcueil.* [3 vols. 1807–1817.]
Mém. couronn. de l'Acad. Brux.	*Mémoires couronnés par l'Académie royale des Sciences et Belles-Lettres de Bruxelles.* [1827, onwards.]
Ann. Min.	*Annales des Mines.* [**Series 1** to **8.**]
Gaz.	*Gazetta chimica italiana.*

ERRATA.

The Student is advised to insert the following corrections in their proper places in the text.

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28. *Note* 1; *for* 'Chap. III.' *read* 'Chap. II. sections 4 and 5'.
33. *Dele* nos. 11 and 12 in table.
,, *Note* 2; *for* '1888' *read* '**14.** 410'.
34. *Note* 7; *for* '1888' *read* '**14.** 410'.
,, *Notes* 11 and 12; *dele*, and *substitute* 'Biltz (*Zeitschr. fur physikal. Chemie*, **2.** 920) shews that the molecular weight of sulphur gas is represented only by the formula S_2'.
38. Fourth line from top; *for* 'the weight of .....of hydrogen' *read* 'twice the specific gravity of a gas referred to hydrogen as unity'.
42. Fourth line from bottom; *for* '257·0' (in fourth column) *read* '254·84', and *for* '193' (in fifth column) *read* '191'.
43. Line 5 from bottom; *in place of* data for ferric chloride *insert* '5·15 | 148·68 | 162·01 | 55·9 iron + 106·11 chlorine'.
44. *Note* 5; *for* '1887' *read* '**14.** 410'.
,, *Note* 6; *dele* and *insert* 'Biltz and Meyer, *Zeitschr. fur physikal. Chemie*, **2.** 184'.
,, *Note* 12; *dele* and *insert* 'Grunewald and V. Meyer, *Ber.* **21.** 687'.
45. *Table*; *dele* last column.
48. *Table*; *for* '[Iron 111·8]' *read* 'Iron 55·9', and *for* '[Gallium 138]' *read* 'Gallium 69·9'.
,, *Table*; *for* 'Osmium 193 (?)' *read* 'Osmium 191'.
,, *Note* 1; *dele*.
,, *Note* 2; *for* 'elements' *read* 'element'.
53. Bottom line; *for* 'in' *read* 'on'.
60. Second line from top; *for* 'omitting the three elements which are placed in brackets in the former table, of the 43 elements' *read* 'omitting the element which is placed in brackets in the former table, of the 45 elements'.
,, Fourteenth line from top; *for* 'there are three elements.....viz. iron, copper, and gallium' *read* 'there is one element.....viz. copper'; *and make the necessary corrections in other parts of this page.*
71. Sixth line from bottom; *for* 'form' *read* 'forms'.
88. Third line from top of table, second column; *for* 'Fe_2Cl_6' *read* '$FeCl_3$'.
,, fifth column; *dele* '[see p. 60]'.

} See *Addenda*.

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91. Second line from bottom of table; *for* '193' *read* '191'; *for* '48·25' *read* '47·75'; *after* 'Osmium tetroxide' *add* 'Potassium-osmium chloride'; *dele* note in column VIII. referring to osmium; *transpose* data regarding osmium so as to come above data for iridium. See *Addenda*.

99. *Note* carried on from p. 98; *dele* last two lines of this note.

111. *Note*; *dele* this note.

126. *Note*; *dele* 'determinations of the spec. gravity..... ....this question' and *insert* 'According to Thorpe and Hambly (*C. S. Journal*, **55**. 163) there is no evidence for the separate existence of a definite gaseous molecule of hydrogen fluoride other than HF'.

128. Line 12 from bottom; *for* '37' *read* '39'
,, Line 11 from bottom; *for* 'six' *read* 'nine' } See *Addenda*.

130. Line 18 from bottom; *for* 'six' *read* 'nine', and *for* '37' *read* '39'.

131. Line 12 from bottom; *for* '37' *read* '39'.

141. Line 13 from top; *for* 'six' *read* 'five', and *dele* 'sulphur'.

,, Line 18 from top; *dele* from 'the molecule of sulphur' to '2 atoms'.

,, Line 6 from bottom; *dele* from 'of the hexatomic' to 'of sulphur'.

143. Line 13 from bottom; *dele* from 'another instance' to '$SnCl_2$'.

186. Line 2 from bottom; *for* 'carbonation' *read* 'carbon atom'.

210. Line 10 from bottom; *for* '195' *read* '195^0'.

225. *Table*, Group III; *for* 'Ga=69' *read* 'Ga=70'.
,, ,, VIII; *for* 'Os=193(?)' *read* 'Os=191', and *transpose* Os and Ir, putting Os before Ir.

229. Line 15 from top; *for* '585' *read* '585^0'.

230. Line 14 from bottom; *for* '69' *read* '70'.

231. Line 2 from top; *for* '69' *read* '69·9'.

236. *Table*, Group III; *for* 'Ga=69' *read* 'Ga=70'.
,, ,, VIII; *for* 'Os=193' *read* 'Os=191', and place Os before Ir.

292. Line 8 from bottom; *paragraphing wrong*, *for* '**41**' *read* '**141**'.

309. *Note* 3; *for* '*Journal*' *read* '*Zeitschr*'.

352. In the equation; *for* '$(p-x)=\frac{k'}{k}(p'+x)$' *read* '$(P-x)=\frac{k'}{k}(P'+x)$'.

355. Line 8 from bottom; *for* 'constant' *read* 'coefficient'.

359. Line 3 from top; *for* 'cases where more than one body undergoes' *read* 'cases where limited quantities of more than one body undergo'.

361. Line 5 from top; *for* 'if A=$FeSO_4$ and B=$KClO_3$' *read* 'if A=the quantity of potassium chlorate and B=the quantity of ferrous sulphate'.

364. Line 11 from top; *for* 'obtained' *read* 'attained'.

,, Line 14 from bottom; *dele* 'and as these masses are independent of the original values of p and p''.

365. Line 16 from bottom; *dele* 'constancy of the'.

367. Line 13 from top; *after* 'and therefore' *insert* 'by the same reasoning'.

371. Line 5 from top; *dele* 'and ξ'.

372. Lines 9 and 10 from bottom; *for* 'increase' *read* 'decrease'.

373. Line 17 from bottom; *for* 'greater' *read* 'smaller'.

,, Line 15 from bottom; *for* 'increase' *read* 'decrease'.

376. Line 15 from top; *for* 'a constant temperature' *read* 'constant temperatures'.

ADDENDA.

The Student is advised to insert the following additions in their proper places in the text.

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34. Line 3 from top; *add* 'Biltz and Meyer (*Ber.* **22.** 725) have vaporised arsenic, antimony, bismuth, phosphorus, and thallium, at about 1700°; the vapour densities point to the molecular formulae As_2, Sb_2, Bi, $?P_2$, Tl_2. These results are not regarded as final by Biltz and Meyer'.

39—43. *Insert in table;*

'[3b] Tellurium diethide	6·47	186·8	182·88	125	tellurium + 47·88 carbon + 10 hydrogen'.
'[3c] Bismuth triethide	9·1	262·2	252·91	208	bismuth + 35·91 carbon + 9 hydrogen'.
'[12a] Ferrous chloride	4·31	124·43	127·64	55·9	iron + 71·74 chlorine'.

44. *Note* 1; *add* 'See also Thorpe and Hambly *C. S. Journal*, **55.** 163'.
Insert Note; '3^b and 3^c. Marquardt, *Ber.* **21.** 2035'.
Note 11; in 10th line of note *insert* 'see also Roux and Louïse, *Compt. rend.* **106.** 73; also Quincke, *Zeit. fur physikal. Chemie*, **3.** 164. For a collection of data bearing on vapour densities of the chlorides of Al and allied metals, see Young, *Nature*, **39.** 198'.
Insert note; '12^a. Nilson and Pettersson, *C. S. Journal*, **53.** 827'.
Note 13; at end of note *add* 'See also Nilson and Pettersson, *C. S. Journal*, **53.** 822'.

76. *Note; add* 'For practical methods of applying Raoult's law see (among others) Hentschel *Zeitschr. fur physikal. Chemie*, **2.** 306; Beckmann, *ibid.* **2.** 638, Eykman, *ibid.* **2.** 964'.

83. *Note; add* 'The example given in the text is not a good one, as the existence of any definite gaseous molecules of ferric and ferrous chloride except $FeCl_3$ and $FeCl_2$ is very doubtful; see p. 44'.

88. First line of table, second column; *add* '$?CrCl_2$'.
Eighth line of table, second column; *add* '$GaCl_3$, $GaCl_2$'.

90. Sixth line of table, second column; *add* '$InCl_2$, ?InCl .

95. Reference to Os; *add* 'Seubert, *Ber.* **21.** 1839'.
Reference to Pt; *add* '(See also Seubert, *Ber.* **21.** 2179)'.

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127. To list of monovalent atoms; *add* '? **In**'.
To list of divalent atoms; *add* '**In, Ga, Fe,** ? **Cr**'.
To list of trivalent atoms; *add* '**Fe, Ga**'.
To list of data on lower part of page; *add* '?InCl, $InCl_2$, $FeCl_2$, $FeCl_3$, $GaCl_2$, $GaCl_3$, ? $CrCl_2$'.

128. Line 7 from bottom; *insert* 'the atoms of gallium, iron, and indium, and probably also the atom of chromium, are divalent and trivalent'.

229. *Note* 5; *add* to this note, 'But de Boisbaudran has calculated the atomic weights of gallium and germanium from considerations based on the relations between the atomic weights, and the wave-lengths of the chief lines in the spectra, of similar elements. (See articles **Gallium** and **Germanium** in the new edition of Watts' *Dictionary of Chemistry*, vol. II.)'.

267. *Note; add* to this note 'The following data for *solid* mercury compounds are given by Nernst (*Zeitschr. fur physikal. Chemie*, **2.** 23).
[**Hg**, Cl^2] = 53,200 [**Hg**, Br^2] = 40,5000 [**Hg**, I^2] = 24,300'.

298. *Note* 6; *add* 'See also Conrady, *Zeitschr. fur physikal. Chemie*, **3.** 210'.

299. *Note; add* 'Weegman (*Zeitschr. fur physikal. Chemie*, **2.** 218,258) has conducted a series of very careful measurements of R for chloro- and bromo-derivatives of hydrocarbons; his results on the whole confirm those of Bruhl; they also emphasise the need of further researches'.

311. *Note* 3; *add* '**1888.** 561'.

317. *Note* 2; to list of memoirs *add* 'An historical sketch, by Kopp, of the position of our knowledge of the molecular volumes of liquid compounds is to be found in *Annalen*, **250.** 1 [1889]'.

"L'action chimique est réciproque: son effet est le résultat d'une tendance mutuelle à la combinaison; on ne peut pas, à la rigeur, dire plutôt qu'un liquide agit sur un solide, qu'on ne peut dire que le solide agit sur le liquide: la commodité de l'expression fait transporter sans inconvénient toute l'action dans l'une des deux substances, quand on veut examiner l'effet de cette action plutôt que l'action elle-même." BERTHOLLET.

PREFACE TO THE SECOND EDITION.

THE aim and scope of the book have not been changed. The whole has been thoroughly revised, and Book II has been entirely rewritten. The revision will, I hope, make clearer than before the mutual dependence of the parts.

Since the first edition was published, much important work has been done on subjects treated in Book I; the results of this work have been noticed in the present edition; at the same time some chapters have been shortened, especially that dealing with valency and isomerism; the arrangement of these, and some other, chapters has been altered. The chapters on physical methods have been rewritten.

When the first edition was published, the study of chemical affinity was entering on a new phase; since 1884 progress has been very rapid, and to-day we are much nearer the goal than we were five years ago. The great importance of recent work on affinity has compelled me entirely to rewrite Book II. In doing this I have largely followed Ostwald's *Lehrbuch der allgemeinen Chemie*; without that admirable treatise, the part of my book dealing with affinity could not have been written. I am anxious to express, as strongly and warmly

as I can, my indebtedness to Prof. Ostwald. I also thank my friend Mr Douglas Carnegie, M.A. for help given in revising the proofs of Book II.

As this edition has been some time passing through the press, and as the progress of chemistry has been very rapid during that time, the lists of *errata* and *addenda* are fuller than is usual in a book of this character. The student is requested to pay attention to these lists, and to incorporate the corrections and additions in the text.

M. M. P. M.

April 1889.

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TITLES OF JOURNALS CONTAINING MEMOIRS TO WHICH REFERENCES ARE MADE.

Abbreviated Titles.	Full Titles.
Phil. Trans.	*Philosophical Transactions.*
Proc. R. S.	*Proceedings of the Royal Society.*
Proc. R. S. E.	*Proceedings of the Royal Society of Edinburgh.*
C. S. Journal.	*Journal of the Chemical Society.* [Memoirs and Proceedings, 3 vols. (1841–1847). Journal, **series 1**, 15 vols. (1848–1862). ,, **series 2**, 15 vols. (1863–1877). ,, **Transactions** and **Abstracts** paged separately, from 1878 to present time. The volumes of this Journal are sometimes referred to by numbers beginning with volume 1 of series 1, and running on consecutively to the present time.]
C. S. Proc.	*Proceedings of the Chemical Society.* [Beginning 1884.]
Phil. Mag.	*Philosophical Magazine.* [**Series 1** to **5**.]
Chem. News.	*The Chemical News.* [Beginning from 1860.]
Nature.	*Nature.* [1879, and onwards.]
Brit. Ass. Reports.	*Reports of the British Association for the Advancement of Science.* [1831, and onwards.]
Proc. R. I.	*Proceedings of the Royal Institution of Great Britain.* [1851, and onwards.]
Amer. Chem. Journal.	*American Chemical Journal.* [1879, and onwards.]
or { *Amer. Journ. of Sci. and Arts* / *Sill. Amer. Journal.* }	*American Journal of Science and Arts;* since 1880 the title is *American Journal of Science.* [Conducted by Sillimann, and subsequently by Silliman and Dana. **Series 1** to **3**.]
Proc. Amer. Acad. of Arts and Sci.	*Proceedings of the American Academy of Arts and Sciences.* [**Series 1** and **2**.]
Gilbert's Ann.	*Gilbert's Annalen der Physik und Chemie.* [1799–1824.]
Pogg. Ann.	*Poggendorff's Annalen der Physik und Chemie.* [1824–1876.]
Wied. Ann.	*Wiedemann's Annalen der Physik und Chemie.* [Continuation of *Pogg. Ann.* from 1877; frequently quoted in memoirs, &c., as *Ann. Phys. Chem.* **Series 2**.]
Pogg. Beiblatter.	*Beiblatter zu den Annalen der Physik und Chemie.* [1877, onwards.]

INTRODUCTORY.

CHEMISTRY is preeminently the science which concerns itself with the changes presented in material phenomena; it is the science which attempts to classify the mutations that matter undergoes.

In the chemical examination of any kind of matter two questions have always pressed for answers:—What can this substance do? Of what is this substance composed? While attempting to answer these questions separately, and while thus more or less adopting two schemes of classification, chemists have for the most part recognised that no complete answer could be given to either question considered wholly apart from the other; hence the two methods of chemical investigation, and the two lines of chemical advance, have generally been closely interwoven.

In older times a substance was said to be capable of doing this or that because it contained certain elements or essences; substances were classed together because of similarity of actions, but the points of resemblance on which classification was based were uncertain and undefined: the conception of element was paramount. The substances in a class shewed many or a few points of resemblance because each member of the class contained the same element, and hence was a more or less perfect means for exhibiting the properties of that element. The ideas of composition and properties, as we now use these expressions, were both implied in the older conception of element.

If it be granted that the various forms of matter are vehicles for displaying the properties of a few elements, it follows that the addition or withdrawal of this or that element will probably suffice to change one into another form of matter. Hence arose the art of alchemy and the pursuit of the philosopher's stone. This pursuit resulted in the accumulation of many facts most of which could for some time be explained by aid of the one underlying general conception of element. But as facts accumulated the foundation was found to be too narrow to bear the structure raised upon it; a need was felt for minor explanations and for partial hypotheses. Observers began to contrast sour, acid, substances, with mild, tasteless, non-corrosive, substances; hence arose the division of a large class of bodies into two minor classes, acids and alkalis. This classification when carried to completion produced the school of *iatro*-chemists, in whose hands chemical science became a branch of the art of medicine. But once again facts were observed which could not be explained by the theories of the medical chemists: the experimental method was recognised as alone leading to definite and trustworthy results in the examination of natural phenomena; but the experimental method, it was found, to be of value must be accurate, and to be accurate must be quantitative. Advance became rapid. The conception of element remained, but in modified form; the distinction between alkali and acid remained, but proved to mean at once less and more than its originators supposed. Bodies were compared as to their actions and as to their composition; the comparison led on the one hand to the recognition of force exerted by one body on another, called affinity, and on the other hand to the recognition of ultimate forms of matter, called elements, of which all bodies are composed.

From this point the two broad paths of advance become more easily distinguished; advance is made by seeking answers to questions such as these:—What is the nature of the elements? What is the composition of compounds? Can the facts regarding elementary combinations be generalised?

Advance is also made by pursuing inquiries indicated by such questions as these:—What connexion, if any, exists between the properties of elements and of compounds of these elements? What actions are these compounds capable of performing? And advance is also made by combining both methods of inquiry in seeking answers to such a question as this:—Why are the properties of these compounds such as they are observed to be?

At one time those chemists for whom the composition of compounds was all-important have been supreme; at another time the place of authority has been occupied by those who regarded function, or power of doing, as the essential subject of study. The greatest outcome of the work of the former school is the atomic hypothesis, now merged in the wider molecular and atomic theory; the most important result of the studies of the latter school is the conception of chemical affinity; both have taken part in the development of the modern views regarding molecular structure and rational formulæ.

While assigning the credit of special advances to one of the two great schools of chemistry, we cannot but recognise that these advances have been made by the help of suggestions borrowed from the other: recent developments of the atomic theory cannot be separated from the rise of the unitary system; the latest hypotheses regarding the structure of molecules are connected with the subject of chemical affinity.

Eighty years ago Berthollet attempted to arrange the facts of chemical action under a general conception which should serve to connect chemical with physical changes; but the attempt was only partially successful because of the scanty supply of purely chemical data. General views of chemical action were soon abandoned for a study of the properties of the products of this action; but of late years many chemists have resumed the investigation of the general conditions of chemical action, and have obtained results which give good grounds for hoping that this study will throw light on the masses of facts already accumulated concerning compounds, and groups of compounds, and, taken along with that method

of investigation which is based on a study of the composition of compounds, will lead to the establishment of chemistry as a branch of the science of physical dynamics.

The study of the motions of material bodies considered as accompanying mutual actions between these bodies belongs to the general science of dynamics. Phenomena presented by mutually acting bodies wherein the properties of these bodies are not permanently modified belong to the domain of physical science. Chemistry deals with those reactions between elements and compounds wherein permanent modifications in the properties of the bodies occur. Or, we may say that whereas physical science is concerned with the properties of this or that kind of matter considered for the most part apart from the action on it of other kinds of matter, chemistry is concerned with the mutual actions which occur between matter of different but definite kinds whereby persistent changes in the properties of the reacting kinds of matter occur.

Chemistry furnishes problems for the solution of which physical and dynamical methods are applicable. Chemical science is ever tending toward abstract truths, i.e. truths involved in many phenomena although actually seen in none: but before she gains abstract truths chemistry amasses many general truths, i.e. 'truths which sum up many facts.'[1]

The chemist is set to solve the problem:—Why are the properties of elements and compounds permanently modified under certain conditions? In attempting to find a solution, he must divide the phenomena which he observes into their factors, and study each of these as far as possible independently of the others.

The chemist need not regard the methods pursued by those sciences which are more concrete than his own, although he may furnish them with subject-matter for investigation; inasmuch however as the science of matter and

[1] The abstract and the general truths of chemistry are scarcely yet so differentiated as to allow of each class being considered separately. I do not purpose attempting more than a very rough separation in this book.

motion is a more abstract science than that of chemistry, he must seek help for his work in the methods of that science, always remembering that this help is given to solve chemical problems, and that with purely physical problems, he, as a chemist, is not concerned[1].

Pursuing then an almost purely analytical method the chemist finds that his subject branches off into two main divisions. The properties of bodies are modified; he studies the relations between the new substances and those by the mutual action of which the new bodies were produced: but changes in the properties of bodies involve a consideration of the relative positions of the changing body and of other bodies, in other words involve the action of force; he endeavours to elucidate the laws of action of this force.

The hypothesis that bodies consist of small parts—called molecules—in motion, is one of the lines along which dynamical science pursues its advance into the sphere of chemistry. The study of chemical phenomena is also brought within the pale of dynamical methods by the application to these phenomena of the general principles of the conservation and degradation of energy[2]. The latter (thermo-dynamic) method is more applicable to the study of the laws of chemical forces than of the properties of the substances depending on the actions of these forces, which properties have been chiefly elucidated by the help of the molecular theory.

We may indeed study relations between forces accompanying changes in the distribution of certain material magnitudes, which we may call molecules, without reference to what is generally known as the molecular theory of matter.

But it seems certain that no chemical phenomenon—and it is well for the student to bear in mind that the chemical part is always but one aspect of any natural occurrence—can be fully explained unless both methods of investigation are applied; unless the relations between the reacting bodies and the products of the reaction, and the relations between the

[1] Chemistry, being more concrete, is less exact than physics; mathematical methods can scarcely as yet be applied to purely chemical data.

[2] See Clerk Maxwell: *Science Conferences at South Kensington*, 1876.

forces exhibited in the phenomenon in question, are considered.

In the following pages an attempt is made to gather together the more important data on which the leading generalisations of chemistry are based, and in the light of this material to discuss these generalisations.

By the use of the terms *Chemical Statics* and *Chemical Kinetics* I would indicate, roughly, that the phenomena included under the first of these headings are on the whole those exhibited by chemical bodies or systems of bodies in equilibrium, while the phenomena classed together as chemical kinetics relate more to bodies or systems of bodies when chemically active.

It may seem pedantic to make use of terms having definite and precise significations when from the very nature of the facts they can be employed only in the broadest and roughest way. I only wish to indicate that the subject-matter of chemical science is considered in this book as divisible into two large parts, of which one comprises the facts and principles concerned, on the whole, with chemical composition, and the other those which, broadly speaking, relate to chemical action.

It will of course be found that chemical occurrences present, I think one may say always present, both statical and kinetical problems; the two sides of any chemical problem can scarcely be regarded apart, in the present state of knowledge at any rate, without danger; it may therefore be that phenomena ranked by one chemist as statical would by another be classed as kinetical.

I begin by considering the facts and principles roughly classed as statical, because although the study of kinetics seems naturally to precede that of statics, yet in chemistry our knowledge of composition is much in advance of our knowledge of action: I then consider the data and generalisations of so-called chemical kinetics; and lastly I endeavour to review some of those phenomena, explanations of which, generally only very partial explanations, can be gained, or hoped for, only by the help of both methods.

BOOK I.

CHEMICAL STATICS.

CHAPTER I.

ATOMS AND MOLECULES.

1 THE experimental foundations of the modern chemical atomic theory were laid in the later years of last century by the German chemist Richter[1]. The work of Bergmann[2], although of earlier date than that of Richter, cannot be regarded of equal importance as concerns the history of the atomic theory.

Richter studied the neutralisation of acids by bases, and of bases by acids, and shewed that a definite amount of acid (or base) always combines with a definite amount of base (or acid) when neutralisation is accomplished. By determining the masses of various bases neutralised by one and the same mass of each acid, and the masses of various acids neutralised by one and the same mass of each base, Richter was able to arrange many acids and bases in order of neutralisation. Fischer[3], in 1803, published the first table of chemical equivalents. Richter had given a series of numbers for each base expressing the quantities thereof which would neutralise 1000 parts by weight of sulphuric acid, or 1000 parts of hydrochloric acid, or 1000 parts of nitric acid &c.: Fischer saw that it was sufficient to attach a single number to each base and a single number to each acid; 1000 parts by weight of

[1] *Ueber die neueren Gegenstände der Chemie*, 1791—1802: and *Anfangsgründe der Stochiometrie oder Messkunst chemischer Elemente*, 1822.

[2] *Chemische Werke*, 2. 25 *et seq.*

[3] In a note to Berthollet's *Essai de Statique Chimique* (1803).

sulphuric acid being adopted as the unit of neutralisation. Fischer's numbers expressed the masses of bases, or acids, which were of equal value so far as power to neutralise a constant mass of a certain acid or base was concerned[1].

Foreshadowings of the atomic theory are to be found in a work by W. Higgins entitled *A comparative view of the Phlogistic and Antiphlogistic Theories, with Inductions* (1791) [see Henry's *Life of Dalton* p. 75 *et seq.*]; but to Dalton is undoubtedly due the signal honour of introducing a clear and self-consistent theory regarding the composition and structure of chemical substances, a theory which in its essential points has stood the test of rigorous experimental verification, and has adapted itself to the wants of each successive school of chemical thought.

2 Dalton[2], and others, found that elements were united in many compounds in fixed proportions by weight, and moreover that in certain compounds of one element with others the amount by weight of this element could be expressed by whole multiples of one fundamental number. The facts regarding the quantitative combinations of the elements are expressed in the three laws of chemical combination:—

I. The masses of the constituents of any compound stand in an unalterable proportion to each other and to the mass of the compound.

II. When two elements combine to form more than one compound the masses of one of the elements which combine with a constant mass of the other element bear a simple relation to each other.

III. The masses of different elements which severally combine with one and the same mass of another element are also the masses of those different

[1] For more details regarding the work of Richter and Fischer, see Wurtz, *The Atomic Theory*, pp. 12—22.

[2] It is important to note that Dalton's atomic theory was conceived by him in 1802 from considering the results of *physical* experiments: he distinctly states in a paper on the absorption of gases in liquids read to the Manchester Philosophical Society in that year that he had lately been prosecuting 'with remarkable success,' 'an inquiry into the relative weights of the ultimate particles of bodies.'

elements which combine with each other, or they bear a simple relation to these masses.

To account for the facts of chemical combination Dalton recalled the atomic theory of the Greek philosophers; but he transformed an interesting speculation about the possible causes of vaguely observed occurrences into a scientific theory of quantitatively established facts.

Every chemical substance, simple or compound, is made up of atoms, or small undivided parts[1]; the properties of each substance are dependent on the properties, and to some extent the arrangement, of these atoms: the old hypothesis had gone as far as this. Dalton added, the atom of every chemical substance has a definite mass, and although this mass cannot be determined, we nevertheless can determine the *relative masses* of the atoms of all bodies. It is only necessary to choose some substance as a standard, then the mass of the smallest quantity of any other substance which combines with the unit mass of the standard substance represents the mass of the atom of the combining substance in terms of the unit chosen.

As this point is of supreme importance it may be well that we should have Dalton's own words before us. In the *New System of Chemical Philosophy* (1808) after discussing the constitution of mixed gases, Dalton proceeds:

"When any body exists in the elastic state its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity or otherwise are disposed to encroach upon it, at a respectful distance. When we attempt to conceive the *number* of particles in an atmosphere, it is somewhat like attempting to conceive the number of stars in the universe; we are confounded by the thought. But if we limit the subject, by taking a given volume of any gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite; just as in a given space of the universe the number of stars and planets cannot be infinite.

Chemical analysis and synthesis go no further than to the separation

[1] Dalton's application of the term *atom* to the small *chemically* indivisible parts of compounds, seems to shew that he did not regard his atoms as absolutely indivisible: see *Life* by Henry, p. 88.

of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.

In all chemical investigations it has justly been considered an important object to ascertain the relative *weights* of the simples which constitute a compound. But unfortunately the inquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results. Now it is one great object of this work, to shew the importance and advantage of ascertaining the relative weights of the ultimate particles both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.

If there are two bodies, A and B, which are disposed to combine, the following is the order in which combination may take place, beginning with the most simple: namely—

1 atom of A + 1 atom of B = 1 atom of C, binary,
1 „ „ A + 2 atoms „ B = 1 „ „ D, ternary,
2 atoms „ A + 1 atom „ B = 1 „ „ E, ternary,
1 atom „ A + 3 atoms „ B = 1 „ „ F, quaternary,
3 atoms „ A + 1 atom „ B = 1 „ „ G, quaternary."
&c., &c.

Dalton then states the following rules respecting chemical synthesis, which he employed in determining the relative weights of the smallest chemically indivisible parts of compound bodies[1].

"1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appears to the contrary.

2nd. When two combinations are observed they must be presumed to be a *binary* and a *ternary*.

3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

[1] By the 'smallest chemically indivisible part' of a substance is meant an amount such that, if divided, substances (or a substance) are produced different in properties from the original substance.

4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*." &c. &c.

"From the application of these rules," Dalton says, "to the chemical facts already well ascertained, we deduce the following conclusions: 1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7 nearly. 2nd. That ammonia is a binary compound of hydrogen and azote, and the relative weights of the two atoms are as 1 : 5 nearly.... In all these cases the weights are expressed in atoms of hydrogen each of which is denoted by unity."

As an example of Dalton's applications of these rules, let us take the two oxides of carbon. These two oxides are composed, according to Dalton, of 5·4 parts by weight of carbon combined respectively with 7 and with 14 parts by weight of oxygen: the first of these bodies, in accordance with Dalton's second rule, was considered to be a *binary*, and the second a *ternary*, compound; the formulæ given were CO and CO_2 respectively. [C = 5·4, O = 7.]

But Dalton's CO_2 might have been regarded as a compound of 2·7 parts by weight of carbon with 7 parts by weight of oxygen, in which case its formula would have been written CO [C = 2·7]; Dalton's CO would then have become C_2O [C_2 = 5·4]. The atomic weight of carbon would be determined as 2·7 or 5·4 according as carbon monoxide or carbon dioxide was decided to be a *binary* compound.

At a later time it was said by some chemists that a binary compound is always more stable than a ternary; if this rule were applied to the case of the oxides of carbon, Dalton's number for the atomic weight of carbon would be confirmed[1].

3 These examples illustrate the great shortcoming of the Daltonian theory: the atomic weights of Dalton are either multiples or submultiples of a certain number, but we cannot tell what multiple or what submultiple. Hydrogen being taken as unity, let the relative masses of two elements which form a compound B, be Q and Q_1, and let the atomic weights of these elements be A and A_1 respectively; then $Q : Q_1 :: nA : n_1A_1$, where n and n_1 are whole numbers. But inasmuch as the values of n, n_1, A, and A_1 are unknown, it is

[1] See especially Daubeny's *Atomic Theory* (2nd edition 1850), pp. 119—120.

evident that analysis alone, aided by the Daltonian theory, cannot determine the atomic weights of the elements which compose the substance *B*.

This shortcoming in the theory could not be supplied without further data: Dalton distinctly states that in order to determine the number of elementary atoms in the atom of a compound a knowledge of the composition of many compounds of the given elements is required.

4 A few months after the announcement of Dalton's law of multiple proportions and atomic theory, Gay Lussac and Humboldt[1] began their volumetric investigations which culminated three years later in the beautiful discovery of the former naturalist[2], that gaseous substances unite in fixed volumetric proportions which may be simply expressed.

There is a constant simple relation, said Gay Lussac, between the volume of a gaseous compound and the volumes of its constituent elements. Let *one volume* be defined as the volume occupied by unit mass of hydrogen; then the *combining volume* of any gaseous element is always expressed by a whole number; e.g. one volume of nitrogen combines with one volume of oxygen to form two volumes of nitric oxide, two volumes of hydrogen and one volume of oxygen combine to form two volumes of water-gas, one volume of nitrogen and three volumes of hydrogen form two volumes of ammonia, &c. &c. Condensation sometimes occurs, sometimes the volume of the compound is equal to the sum of the volumes of the combining elements.

This discovery appeared to add fresh arguments to the theory of Dalton. The ratios of the masses of these combining volumes of the elements, hydrogen being taken as unity, represent, it was said, the relative masses of the atoms of these elements; and the conclusion was drawn, 'equal volumes of gaseous substances, measured at the same temperature and pressure, contain equal numbers of atoms.'

5 Dalton however refused to accept Gay Lussac's generalisation, and regarded his experimental methods as untrustworthy. We cannot, I think, fail to be struck with

[1] *Journal de Physique*, **60**. 129. [2] *Mém. de la Soc. d'Arcueil*, **2**. 207.

the justness of Dalton's objection to the statement 'equal volumes contain equal numbers of atoms:' he argued somewhat as follows:—one volume of nitrogen and one volume of oxygen form two volumes of nitric oxide; but one atom of nitrogen and one atom of oxygen form one atom of nitric oxide; therefore, had the above statement been correct, the volume of nitric oxide would have been equal to, not twice as great as, the volume of oxygen or of nitrogen. So again, one atom of hydrogen and one atom of oxygen form one atom of water, according to Dalton's rules: but Gay Lussac shewed that two volumes of hydrogen combine with one volume of oxygen to produce two volumes of water-gas; hence the atom of hydrogen occupies twice the volume occupied by the atom of oxygen, and therefore the statement of Gay Lussac is incorrect. If Dalton's definition of atom and his rules regarding atomic synthesis are adopted, Gay Lussac's statement that 'equal volumes contain equal numbers of atoms' must be abandoned.

6 The difficulty was removed by Avogadro[1], who (in 1811) introduced the conception of two kinds of small particles:—"*molécules intégrantes*," or as we should now say *molecules*; and "*molécules élémentaires*," or as we should now say *atoms*.

The *molecules* of elements are decomposed in chemical processes, said Avogadro, and the *atoms* unite to form new compounds. "*Equal volumes of gases contain equal numbers of molecules*." The reaction between nitrogen and oxygen inexplicable by Gay Lussac's law now becomes clear; each molecule of nitrogen and each molecule of oxygen divides into two parts, and these parts unite to form the new molecules of nitric oxide; hence there are twice as many molecules of nitric oxide produced as there were molecules of nitrogen or oxygen originally present.

By thus recognising a higher order of atoms, as it were, Avogadro reconciled Dalton's theory with Gay Lussac's results.

[1] *Journal de Physique*, **73**. 58: also *Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps*, &c.

Ampère[1] in 1814 drew prominent attention to the hypothesis of Avogadro, and attempted by its help to explain the structure of crystals. But the hypothesis had come before the times were fully ripe.

7 Wollaston[2] accepted Dalton's theory but proposed to use the word *equivalent*[3] in place of atom. In his paper published in 1814 (*loc. cit.*) Wollaston drew up a table of equivalents which he thought would be serviceable to the practical chemist in determining the amount of an acid which would combine with a given weight of base, or the weight of precipitate obtainable in a given reaction, &c. He arranged his numbers on a scale with a slider attached, and adopted a mechanical contrivance for aiding the analyst in using the table. Although Wollaston employed the word equivalent in place of atom, his scale and table must be regarded as helping to extend the use of the atomic theory[4]. For the practical purpose which he had in view Wollaston did not deem it necessary to adopt any theory; at the same time he regarded the atomic weights of Dalton, especially the atomic weights of compounds, as too hypothetical, and he thought that equivalents were to be preferred for most purposes.

Wollaston referred his equivalent numbers to oxygen as 10: the amount by weight of any element which combined with 10 parts by weight of oxygen was regarded by him as the equivalent of that element. But the system of equivalents was liable to the same objection as had been urged against the system of atomic weights: it was too vague.

(1) Thus 7·5 parts by weight of carbon unite with 20 parts by weight of oxygen, said Wollaston, therefore the formula of the compound produced is CO_2.

(2) Again 7·5 parts by weight of carbon unite with 10 parts by weight of oxygen, therefore the formula of the compound produced is CO.

[1] *Ann. Chim. Phys.* **90.** 43.

[2] *Phil. Trans.* for **1814**, 1 *et seq.*

[3] Wollaston appears to have first used this term in 1808 (*Phil. Trans.*).

[4] See Cannizzaro, *C. S. Journal* [2], **10.** 945.

But he might also have said

(1) 3·75 parts by weight of carbon unite with 10 parts by weight of oxygen, and the formula of the product is CO; and

(2) 7·5 of carbon unite with 10 of oxygen, therefore the formula of the compound is C_2O.

It seemed impossible to determine the equivalent weight of carbon, just as in Dalton's system it was impossible to determine the atomic weight of carbon[1].

If the unit of equivalency is 8 parts by weight of oxygen, what is the equivalent of copper? An electric current is passed through a voltameter and also through molten cuprous chloride; for every 8 parts by weight of oxygen set free in the voltameter 63·5 parts by weight of copper appear in the second vessel: cupric chloride is substituted for cuprous chloride, and now 31·75 parts of copper are eliminated for every 8 parts of oxygen. So in the compounds of copper and oxygen, we have in one case 63·5 of copper combined with 8 of oxygen, in the other 31·75 of copper with 8 of oxygen.

So long as the term equivalent was applied to acids and bases, or to oxides, it had a definite meaning. The mass of oxide which neutralised unit mass of standard acid was the equivalent of that oxide, because it was equal, so far as neutralising power went, to some other mass of another oxide.

"When we speak of the equivalent of a body," said Gerhardt, "we should always indicate to what other body, to what functions, to what properties, that equivalent corresponds."[2]

Richter shewed that there is a constant relation between the amount of oxygen in an oxide and the amount in the acid which neutralises this oxide: e.g., in sulphuric acid, he said, the oxygen is three times, and in nitric acid five times, that in the oxide neutralised. This rule was made general. Now

[1] Thus for iron we have the equivalents 28 and 18·6: for carbon, the equivalents 3, 4, 8, and 12: for nitrogen, 4·6 and 2·3: for oxygen, 8 and 16: for silicon, 7 and 3·5, &c. &c. Williamson, *C. S. Journal*, **22**. 328.

[2] Quoted by J. J. Griffin in *The Radical Theory in Chemistry*, p. 32.

the equivalent of aluminium[1] was said to be 13·75: the formula of sodium sulphate, in accordance with Richter's rule, was written $NaO . SO_3$; hence the formula of aluminium sulphate should have been written $Al_{\frac{4}{3}}O . SO_3$ ($13{\cdot}75 \times \frac{4}{3}$ = amount of aluminium uniting with 8 parts by weight of oxygen); but the formula was almost invariably written $Al_2O_3 . 3SO_3$, which is a departure from a strictly equivalent notation.

Mohr (*Mechanische Theorie der Chemischen Affinität*), who strongly upheld an equivalent notation, admits (*loc. cit.* pp. 143—144) that no equivalency exists between the oxides RO and R_2O_3; he also despairs of determining the equivalent of phosphoric acid. Those quantities of two substances are equivalent, according to Mohr, which by interaction with other bodies produce similar compounds; but he fails to define 'similar compounds,' or rather he admits the impossibility of finding a definition.

That the masses of elements which mutually combine do not always represent equivalent quantities of these elements was gradually discovered; but the so-called equivalent notation assumed that these masses do represent equivalent quantities of the combining elements.

8 The systems of chemical notation founded respectively on the atomic weights of Dalton and on the equivalents of Wollaston continued to hold divided sway over the minds of chemists[2]. A man of preeminent powers of classification was required.

[1] The reasons for adopting the number 13·75 were somewhat as follows:—28 parts by weight of iron combine with 8 of oxygen, therefore the equivalent of iron is 28; but in ferric chloride 28×2 parts by weight of iron are combined with $35{\cdot}5 \times 3$ parts by weight of chlorine (the equivalent of chlorine is 35·5, because this is the mass of that element which combines with unit mass of hydrogen). Now aluminium chloride is very similar in properties to ferric chloride, therefore, reasoning from analogy, this compound contains two equivalents of aluminium; but aluminium chloride is composed of the elements aluminium and chlorine combined in the ratio $27{\cdot}5 : (3 \times 35{\cdot}5)$, therefore the equivalent of aluminium is $\frac{27{\cdot}5}{2} = 13{\cdot}75$.

[2] The student who wishes to pursue this subject in greater detail may consult any of the older text-books, on *the laws of combination* and *atomic weights*, e.g. Turner's *Chemistry*, pp. 212—235; he will thus become persuaded how impossible

The system of chemical classification and notation elaborated by Jacob Berzelius (1779—1848) was essentially electrical. The dualism of the Berzelian school was the logical development of the views of Lavoisier concerning salts, and of the hypothesis of Davy regarding the relations between electrical and chemical actions[1]. At present, however, this part of the work of the great Swedish chemist does not specially concern us.

Berzelius recognised the necessity of extending the generalisations already made concerning the combinations of atoms. To say that when two elements by combining together form only one compound, that compound is composed of one atom of each element, was, according to Berzelius, not fully warranted by facts.

To discover the laws of atomic combinations was the task that Berzelius proposed to himself. He argued that inasmuch as the number of compounds formed by the mutual actions of any two or three elements is evidently very limited, there must be certain laws expressing the conditions under which alone atoms combine.

Berzelius regarded Gay Lussac's law of gaseous combination—'equal volumes contain equal numbers of atoms'—as the most important of the generalisations made concerning atomic combinations, but he restricted the application of this law to elementary gases. He admitted that a compound gas might be composed of half, or even less than half, as many atoms as composed an equal volume of an elementary gas; he did not compare the atomic composition of elementary and compound gases: he thus evaded the objections urged by Dalton against the law of Gay Lussac, and at the same time he declined to accept the statement of Avogadro, 'equal volumes contain equal numbers of *molecules*.'

The ratios of the weights of the combining volumes of

it was to determine the values of atomic weights with certainty. Some interesting points especially regarding the proposal to give two equivalents, or atomic weights, to some of the elements will be found in Griffin's *Radical Theory*, pp. 30—43.

[1] For a brief notice of the system of Berzelius regarding the constitution of compounds see Chap. II. pp. 113—116.

elementary gases were regarded by Berzelius as representing the ratios of the weights of the atoms of those elements; therefore to water, nitric oxide, and ammonia he gave the formulæ, H_2O, NO, and NH_3; because two volumes of hydrogen unite with one volume of oxygen to form water, one volume of nitrogen unites with one volume of oxygen to form nitric oxide, and ammonia is produced by the union of one volume of nitrogen with three volumes of hydrogen.

But the volumetric method was of limited application to the problems of chemical synthesis. Berzelius attempted to state general rules with regard to the combinations of atoms. These rules referred chiefly to the compounds of oxygen, compounds which played so important a part in the mineral chemistry wherewith Berzelius largely concerned himself. The most important of the Berzelian rules were three.

I. If an element forms two oxides with twice as much oxygen by weight in one as in the other, that with the smaller mass of oxygen is to be represented as a compound of one atom of element united with one atom of oxygen, and that with the larger mass of oxygen as a compound of one atom of element with two atoms of oxygen.

II. If an element forms two oxides, one of which contains one and a half times as much oxygen by weight as the other, that with the less oxygen is to be represented as composed of one atom of element and one atom of oxygen, and the other compound as formed by the union of two atoms of element with three atoms of oxygen.

III. The mass of oxygen in an acid is a simple multiple of the mass of oxygen in any base with which the acid combines[1], and this multiple generally also expresses the number of atoms of oxygen in the acid: thus in the case of sulphuric acid and potash, an amount of acid containing 24 parts by weight of oxygen neutralises that amount of

[1] This had been stated by Richter many years before Berzelius: see *ante* p. 15.

potash which contains 8 parts by weight of oxygen, therefore, by the Berzelian rule, there are three atoms of oxygen in one atom of sulphuric acid. When nitric acid neutralises potash there are 40 parts by weight of oxygen in the acid for every 8 parts in the base; therefore an atom of nitric acid contains five atoms of oxygen.

By the use of these rules Berzelius determined the formulæ of many metallic oxides and salts. While he was thus engaged, Dulong and Petit[1] announced their 'law of atomic heats'; and shortly afterwards Mitscherlich[2] made known his 'law of isomorphism.'

Berzelius adopted both laws, and by their help[3], along with his own rules, he drew up a table of atomic weights which in very many cases were almost identical with those now in general use.

TABLE OF ATOMIC WEIGHTS. (*Berzelius*[4].)

Arsenic	75·33	Manganese	57·02	Silver	216·61
Calcium	41·03	Sodium	46·62	Silicon	44·47
Chlorine	35·47	Phosphorus	31·43	Nitrogen	14·18
Iron	54·36	Mercury	202·86		
Iodine	123·2	Oxygen	16·00	Hydrogen = 1.	
Carbon	12·25	Sulphur	32·24		

Berzelius himself admits that the atomic weights determined by his rules are in many cases open to doubt (*Lehrbuch*, 1st edition, vol. III. part i. pp. 87—102). Berzelius had a remarkable amount of tact; his rules were empirical, but he balanced probabilities so well that he generally got the best possible result.

9 The separation which Berzelius made between the formulæ of elementary and compound bodies, and his refusal

[1] See p. 49.

[2] See pp. 69—76.

[3] Berzelius formulated the law of isomorphism in its bearing on the problem of determining atomic weights thus; (*Lehrbuch*, 3rd ed., vol. I. p. 98) when one body is isomorphous with another the number of atoms in which is known, then the number of atoms in the other is known also, because isomorphism is a mechanical consequence of identity of atomic structure.

[4] *Jahresberichte*, 1828. 73.

to accept Avogadro's hypothesis while admitting Gay Lussac's generalisation, led him to a very curious result.

Two volumes of hydrogen, weighing 2, combine with one volume of oxygen, weighing 16, to form two volumes of water-gas. Therefore, said Berzelius, *two atoms* of hydrogen combine with *one atom* of oxygen to form *one atom* of water-gas. But water contains less oxygen, relatively to hydrogen, than any other known oxide of hydrogen, therefore it is better to regard it as a compound of one atom of oxygen with *one double atom*, or with one atom itself composed of two equivalents, of hydrogen. Again, in the formation of the lowest oxide of nitrogen two volumes of nitrogen combine with one of oxygen; but it is better to regard the nitrogen as composed of double atoms each occupying twice the volume of the atom of oxygen. Once more; hydrogen and chlorine combine in equal volumes, and the volume of the product—hydrochloric acid—is equal to the sum of the volumes of its constituents; but as the hydrogen atom was regarded by Berzelius as double, he wrote the atomic synthesis of hydrochloric acid as

$$\underset{2\text{ vols.}}{H_2} + \underset{2\text{ vols.}}{Cl_2} = \underset{4\text{ vols.}}{H_2Cl_2}.$$

These results are evidently to be traced to the failure of Berzelius clearly to distinguish atom from equivalent, and to his refusal fully to accept the distinction between atom and molecule enunciated by Avogadro[1].

To the great French chemists, Dumas, Gerhardt and Laurent, is chiefly due the introduction into general use of a system of notation and classification founded on Avogadro's distinction between atoms and molecules.

Dumas early accepted Avogadro's hypothesis; from the specific gravities of gases he deduced the relative weights of the molecules of these gases: in order to gain more information regarding molecular weights he introduced a new method for finding the specific gravities of gases. By this method he

[1] For a more detailed account of the work of Berzelius on atomic weights see Ladenburg's *Entwickelungsgeschichte der Chemie*, pp. 89—100.

determined the molecular weight of sulphur to be 96, and that of phosphorus to be 124; but from the analogy of sulphur compounds with those of oxygen, from various chemical considerations regarding phosphorus compounds, and, I think we must add, from not keeping Avogadro's statement quite distinct from that of Gay Lussac, Dumas convinced himself that these results were incorrect. The molecular weight of mercury also seemed to be abnormal. Dumas knew of exceptions to the law of Dulong and Petit. Mitscherlich's law of isomorphism remained; but Mitscherlich had himself shewn that the same compound might assume more than one crystalline form; how then could trustworthy conclusions regarding atomic structure be deduced from so vague a law? Dumas, and indeed chemists generally, began to despair of the whole theory of atoms; they tried to find relief in equivalents, so called, and in spite of the many difficulties they gradually tended towards an equivalent notation, a notation which nevertheless they could not make thoroughly self-consistent, but which seemed to involve fewer hypotheses than that founded on the theory of atoms[1].

L. Gmelin even regarded the law of fixity of composition as only true under special conditions. When the affinity between two bodies is small, they may be united, said Gmelin, in almost any proportions, when the affinity is large they tend to combine in fixed proportions. A number may be given to each element representing the relative amount of that element which combines with other elements to form stable and well-marked compounds; this 'combining weight' may be *called* 'atomic weight,' but it is only a number. Gmelin adopted 8 as the combining weight of oxygen, 6 as that of carbon &c.: the formula of water on his system again became HO.

The notation used by Gmelin was at best a compromise, and unsatisfactory, but it was very generally adopted for many years.

Inorganic chemistry had failed to introduce an accurate

[1] For a general account of Dumas' influence on chemical theories see his *Leçons sur la Philosophie Chimique*, republished in 1878.

and satisfactory theory of chemical structure; it was now the turn of organic chemistry to attempt the task.

11 Among the most ardent followers of the new chemistry introduced by Dumas, were two men whose names are ever to be associated as those of a brilliant pair of students of nature who died all too early for the work which seemed given them to do. Gerhardt and Laurent occupy a prominent place among the modern reformers of chemistry; they introduced order into chemical notation, and system, where system had been conspicuous by its absence[1].

In criticising the system of so-called equivalent weights Gerhardt adopted the only true method; he studied actually occurring chemical reactions.

In a number of reactions between compounds of carbon in which carbon dioxide, water, and ammonia were produced, Gerhardt[2] found that when so-called equivalent weights of the reacting bodies were employed, the smallest quantities of these three compounds produced were always those represented by the formulæ C_2O_4, H_2O_2, and NH_3, respectively (C = 6, N = 14, O = 8). He therefore concluded that these formulæ, rather than the commonly accepted formulæ, CO_2, HO (and NH_3), must represent equivalent weights of the compounds in question. Similarly he concluded that the equivalent formulæ of sulphur dioxide and carbon monoxide must be S_2O_4 and C_2O_2 respectively (S = 16, O = 8, C = 6): and arguing from these conclusions he thought himself justified in saying that the true equivalents of carbon, sulphur, and oxygen, are 12, 32, and 16, and not 6, 16, and 8, as generally adopted. Gerhardt likewise applied his acute reasoning powers to an examination of the arguments which determined Berzelius and others to adopt formulæ representing weights of four volumes of many carbon compounds; these arguments he proved to be fallacious.

Laurent examined the groundwork on which the systems

[1] Laurent's *Chemical Method* (Cavendish Society Publications) gives a general account of the more important work of these chemists.

[2] *J. fur prakt. Chemie*, **27**. 439; and *Ann. Chim. Phys.* [3] **7**. 129: and **8**. 238.

of equivalent and atomic notation were based. His methods of reasoning were founded on experimentally determined facts, hence their irresistible force. If formulæ are to represent equivalent masses of substances, then said Laurent, a standard must be adopted. But it had been frequently shewn that the quantities represented by so-called combining weights were not always mutually equivalent. Power of neutralising unit mass of standard substance might be adopted as the reaction on which to base the system, but this method could be applied only to a limited number of substances.

The idea of equivalency is associated with function. What is a given substance capable of doing?: this question must be answered before the equivalent of the substance can be determined. But in one action certain weights of two bodies may be equivalent, while altogether different weights of the same bodies are equivalent in another reaction.

Laurent affirmed that it was possible to found a systematic notation on equivalent weights assigned to the elements. Thus, in *ferrous* oxide 28 parts by weight of iron are combined with 8 parts by weight of oxygen; let Fe = 28, then ferrous sulphate is represented by the formula Fe_2SO_4: but in *ferric* oxide there are $2.\frac{28}{3}$ (i.e. 18·6) parts by weight of iron for every 8 parts by weight of oxygen; let fe = 18·6, then the formula for ferric sulphate is fe_2SO_4. The formulæ Fe_2SO_4 and fe_2SO_4 represent strictly equivalent quantities of the two sulphates of iron. So also if the composition of potassium-hydrogen sulphate is expressed by the formula $KHSO_4$, then, in a system of notation founded on equivalent weights, the composition of the double sulphate of potassium and aluminium is represented by the formula $K_{\frac{1}{2}}Al_{\frac{1}{3}}SO_4$ (Al = 27·3). But such a notation is inconvenient, and it frequently conceals most important facts: e.g. in a strictly equivalent notation the differences between monobasic and polybasic acids disappear; thus, the compositions of the masses of monobasic hydrochloric acid, dibasic sulphuric acid, and tribasic phosphoric acid, which severally neutralise equal masses of potash, are expressed by the formulæ HCl, $HS_{\frac{1}{2}}O_2$, and $HP_{\frac{1}{3}}O_{1\frac{1}{2}}$, respectively (Cl = 35·5, S = 32, O = 16, P = 31).

Laurent returned to the generalisation of Avogadro and made that the basis of his system; he clearly distinguished between molecules and atoms, and he applied the law of equal volumes and equal numbers to molecules only. He admitted that apparent exceptions to the Avogadrean law existed, e.g. the molecules of sulphuric acid and salammoniac vapour appeared to occupy twice the volume occupied by the molecule of hydrogen; but he said that this hypothesis generalised the facts better than any other which had been proposed.

Laurent founded his system on an atomic basis, and a fundamental point was the distinction between atom and molecule. He adopted formulæ representing two volumes: the facts of '*nascent*' action he sought to explain by the conception of atoms as distinct from molecules. A molecule he defined to be "the amount of a gaseous substance which occupies twice the volume occupied by an atom of hydrogen," or, "the smallest amount of a substance capable of taking part in a chemical reaction." An atom he defined as "the smallest amount of an element which enters into the composition of a compound." Here we have the application of the term molecule to elements and compounds alike, while atom is used of elements only.

Equivalents are the amounts of bodies which are of equal value in performing a stated action.

Gerhardt and Laurent adopted the laws of atomic heat and isomorphism as aids in determinations of atomic weights.

12 Chemical evidence in favour of the division of elementary molecules during chemical changes was accumulated by Brodie, Wurtz, Williamson and others; but the work of these chemists will be referred to in more detail when we come to speak of the chemical methods for determining molecular weights (see pp. 79—85).

Thus, at last, we have arrived at a clear separation between the meanings of the terms atom, molecule, equivalent.

The system now adopted in chemistry is essentially that of Gerhardt and Laurent; it is founded on the conception of atoms and molecules. Dalton's fundamental idea has been

amply confirmed by modern research. We have maintained the idea of equivalency, but we no longer speak, as Wollaston did, of the equivalent of an element; we compare the elementary atoms among themselves and arrange them in groups, all the members of each of which are equivalent in respect of a certain definite action they are capable of performing.

A true and fundamental conception once gained in science is never lost; it may be largely modified, it may even appear at times to be abandoned, but it develops slowly and bears much fruit at last.

The vicissitudes in the fortunes of a truly scientific idea are aptly illustrated by the history of the atomic theory. After a period of dormancy of more than 2000 years, the atomic theory was revived and rendered definite by Dalton; was firmly established on an experimental basis by Berzelius; was almost abandoned by the school founded by the same chemist; was rehabilitated and again nearly despaired of by Dumas; was largely advanced by Avogadro; was subdivided and its parts clearly distinguished by Gerhardt and Laurent, and is now the foundation-stone of a great and ever-increasing edifice.

13 Thus far I have dealt with the development of the atomic and molecular theory regarded almost entirely from the chemical point of view. So great however is the importance of clearly perceiving the position which this theory occupies in modern chemistry, and of realising the nature of the physical evidence on which, in its more recent development, the theory so largely rests, that I must endeavour very briefly to give a sketch of that evidence, remembering always that it is as chemists, not as physicists, that we are interested in this subject.

There are two general theories of the structure of material substances: one assumes that apparently homogeneous bodies are really homogeneous throughout; a theory which is incapable of explaining the observed properties of matter; and the other asserts that apparently homogeneous bodies are possessed of a grained structure.

Viewed from a distance, a brick wall, or a body of soldiers, appears to be one reddish-coloured homogeneous mass, but a nearer observer sees that the wall is made up of distinct parts, that the company is composed of individual men.

The molecular theory supposes that were our senses sufficiently acute, we should see the grains or particles of which an apparently homogeneous mass of matter is composed.

The theory begins by assuming that any material body "is made up of parts (each of which is capable of motion), and that these parts act on each other in a manner consistent with the principle of the conservation of energy."[1] These parts are called molecules.

The dynamical conception of a gaseous molecule is "*That minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.*"[2]

This conception is entirely independent of chemical facts.

All the molecules of one element are of the same mass, else differences would be observed in the properties of different parts of an elementary gas, e.g. hydrogen; such differences arising from the separation of the gas into portions each more or less unlike the others.

The relations between the motions and the space occupied by these little parts, assuming their existence and mutual independence, may be dynamically deduced by the aid of a theorem of Clausius, and, with a justifiable assumption as to the dynamical meaning of temperature, the equation thus arrived at expresses with considerable accuracy the relations actually existing between temperature and pressure, and volume, in the case of rarefied gases; the equation, that is to say, expresses the laws of Charles and Boyle. When the gas is more condensed the equation ceases to express the relations existing between temperature and pressure, and volume: hence the theory asserts the existence in such a gas of mutual attractions or repulsions between the little parts, or mole-

[1] Clerk Maxwell, Article 'Atom' in *Encycl. Britannica*. (9th Ed.)

[2] *Ibid.*

cules; it asserts that these parts are no longer mutually independent.

"The hypothesis that a gas consists of molecules in motion, which act on each other only when they come together during an encounter, but which during the intervals between their encounters—which constitute the greater part of their existence—are describing free paths, and are not acted on by any molecular forces,"[1]

having been justified by dynamical reasoning, the next step is made by investigating mathematically the properties of such a system of molecules. And one deduction thus made is "*If equal volumes of two gases are at equal temperatures and pressures, the number of molecules in each is the same, and therefore the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.*"[2]

This statement is of paramount importance to the chemist, inasmuch as on it is based his system of molecular weights. It is very necessary to bear in mind that this proposition is deduced by *dynamical reasoning* from a simple hypothesis as to the structure of matter, itself justified by many facts.

By analogous reasoning, various deductions are made from the theory, which express generalisations of experimentally determined facts concerning gaseous phenomena[3].

Passing to more complex occurrences, the molecular theory gives a simple explanation of the diffusion of matter, diffusion of motion, and diffusion of heat in gases; these phenomena being regarded by the theory as dependent on the frequency of the molecular encounters, and on the nature of the actions between the encountering molecules.

The molecular theory has also been successfully applied to explain, broadly, many of the phenomena of evaporation, condensation, electrolysis, and spectroscopy.

To explain spectroscopic phenomena it is apparently necessary to assume molecules to be elastic substances, but elasticity is just the property of matter to explain which the

[1] Clerk Maxwell, Article 'Atom' in *Encycl. Brit.*

[2] *Ibid.* Strictly speaking this statement applies only to *perfect gases*, *i.e.* gases the molecules of which are without action on each other.

[3] For some of the most important of these see Clerk Maxwell's *Theory of Heat*, pp. 307—322 (6th edition).

molecular hypothesis was first assumed. The theory of 'vortex atoms,' developed by Sir William Thomson from the original conception of Helmholtz, explains spectroscopic facts—and generally those facts which must be explained by a successful molecular theory—better than any other which has yet been suggested. A short account of this theory will be found in the article 'Atom' in the last edition of the *Encyclopædia Britannica*, where we read

"The success of this theory in explaining phenomena does not depend on the ingenuity with which its contrivers 'save appearances' by introducing first one hypothetical force and then another. When the vortex atom is once set in motion all its properties are absolutely fixed, and determined by the laws of motion of the primitive fluid which are fully expressed in the fundamental equation."[1]

Attempts have been made to determine the absolute size of molecules[2], and although the results must be regarded as but rough estimates, nevertheless they shew that to measure molecules is a legitimate object of scientific investigation. The smallest portion of matter visible by the help of a good microscope may be taken to be a cube each side of which measures $\frac{1}{4000}$th of a millimetre in length; such a cube will contain, according to the rough measurements hitherto made, from 60 to 100 millions of molecules[3].

The foundations of a truly mathematical theory of the structure of matter have been laid by Helmholtz and Thomson in their theory of vortex atoms; but, apart from this, the fact that the proposition commonly known as Avogadro's law may be deduced by dynamical reasoning from a simple hypothesis which admits, although as yet only to a limited extent, of the application of mathematical methods, and which is justified by a large number of physical facts, suffices to make that law of extreme importance.

Attempts have recently been made to apply to certain chemical phenomena a more strictly dynamical method of

[1] For a few more details regarding the application of this theory to chemical occurrences see Book II. Chap. III.

[2] See especially Sir W. Thomson, *Nature* **1.** p. 551, and also **28.** pp. 203, 250, 274.

[3] Clerk Maxwell, *loc. cit.*

reasoning than is employed in the molecular theory, the methods of which are essentially statistical; these will be referred to under the second main division of this book.

An atomic theory has been elaborated by the chemist; a molecular theory of matter has been propounded by the physicist, and has been advanced so far as to allow of wide conclusions being deduced therefrom by dynamical reasoning; no theory asserting the continuity of matter has been found capable of explaining the observed phenomena of matter; hence to accept the molecular theory, as, at present, the only feasible working hypothesis, is simply to obey the dictates of the scientific method.

14 Let us then turn to the applications of this theory to chemical facts. It is well to repeat the terms in which Clerk Maxwell has expressed the physical conception of the molecule:—"*A gaseous molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.*" One of the deductions from this conception is that *equal volumes, of so-called perfect gases, measured at the same temperature and pressure, contain equal numbers of molecules.*

This statement must now be applied to chemical interactions between gases.

Consider, for instance, the combination of hydrogen with chlorine and that of nitrogen with hydrogen.

Hydrogen combines with chlorine to form hydrochloric acid.
2 vols. combine with 2 vols. „ 4 vols. „

But since equal volumes of gases contain equal numbers of molecules, and since each molecule of hydrochloric acid is composed of both hydrogen and chlorine, it is evident that each molecule of hydrogen by combination with one molecule of chlorine produces not one but two molecules of hydrochloric acid.

So again,

Nitrogen combines with hydrogen to form ammonia.
2 vols. combine with 6 vols. „ 4 vols.

Here again each nitrogen molecule has given rise to two

molecules of ammonia. Hence it is evident that although the parts of a molecule of hydrogen, nitrogen, or chlorine "do not part company during the motion of agitation of the gas" to which the molecule belongs, these parts nevertheless do part company in those chemical reactions which are stated above. When various reactions between gaseous substances are studied this conclusion is found to hold good throughout a large range of chemical phenomena. Hence the chemist is obliged to recognise a portion of matter smaller than the molecule; this smaller portion of matter, this part of a molecule, is the atom[1].

In the above and in other reactions it is shewn that the molecules of hydrogen, nitrogen, and chlorine split into *at least* two parts when these molecules act chemically on each other or on other molecules; hence, if the symbols H, Cl, and N, are used to denote an atom of hydrogen, chlorine, and nitrogen, respectively, the molecules of these three elements may be represented by the symbols H_2, Cl_2, and N_2. These symbols represent the masses of equal volumes of the three elements; if one of these masses be taken as the unit, the others are evidently the masses of the molecules of the gases in question referred to this unit; because equal volumes contain equal numbers of molecules, and therefore 'the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.'

Hydrogen is the universally adopted standard of reference for molecular and atomic weights: the atomic weight of hydrogen is taken as unity, and therefore, according to the reasoning sketched above, the molecular weight of this element is not less than two.

But it might be urged that when molecules of hydrogen and chlorine interact, each molecule separates into more than two parts, into 3, 4, 5, &c. parts. Granting 'Avogadro's law,' the data given on p. 29 shew that the number of molecules of

[1] It is well to note that the molecular theory of matter as applied to chemical phenomena does not assert or deny the finite divisibility of matter. In *C. S. Journal* [2], **13**. 501, there is a most interesting paper by Clerk Maxwell on 'The dynamical evidence of the molecular constitution of bodies.'

hydrochloric acid produced is twice the number of molecules of hydrogen or chlorine which have interacted to produce them; therefore, if each molecule of hydrogen and each of chlorine has separated into, say, four parts, each molecule of hydrochloric acid must be composed of two of those parts of hydrogen and two of chlorine. But if this is so, it ought to be possible to remove the hydrogen, or the chlorine, from a molecule of hydrochloric acid in two separate portions; in other words, interactions ought to occur between hydrochloric acid and other bodies, not themselves compounds of hydrogen or chlorine, resulting in the evolution of hydrogen, or chlorine, and the production of a new compound, or new compounds, of chlorine, hydrogen, and the interacting body or constituents of this body. But no such interactions occur; therefore hydrogen, or chlorine, cannot be removed in parts from a molecule of hydrochloric acid; if the molecule is decomposed and hydrogen, or chlorine, is removed, the whole of the hydrogen, or chlorine, is removed. Therefore it is extremely improbable that a molecule of hydrochloric acid is built up of more than one small chemically indivisible part, or atom, of each of the elements which compose it; and therefore it is extremely improbable that when molecules of hydrogen and chlorine interact to produce molecules of hydrochloric acid, each molecule of hydrogen, or chlorine, separates into more than two parts or atoms. Therefore, as we have agreed to regard the weight of an atom of hydrogen as unity, we say that the molecular weight of hydrogen is two.

The modern molecular theory of matter is not identical with the atomic theory of Dalton; it is based on evidence of a different kind; it is essentially a physical and dynamical theory, although strengthened by chemical arguments. The atomic theory of modern chemistry may be regarded as growing out of the application of reasoning founded on chemical facts to the molecular theory of matter.

Assuming 'Avogadro's law,' and remembering that the molecule of hydrogen, which is the standard body in terms of which all other molecular weights are stated, divides into at least two, and probably into only two, parts in many chemical

changes, we arrive at the practical definition of molecular weight.

The molecular weight of a gas is the weight of that volume thereof which is equal to the volume occupied at the same temperature and pressure by two parts by weight of hydrogen[1].

In determining the specific gravity of a gas it is easier, and less liable to error, to find the weight of the vessel filled with air than with hydrogen; the result is therefore stated as specific gravity referred to air as unity. Now the specific gravity of hydrogen is ·06926 [air = 1]; the molecular weight required is equal to twice the specific gravity of the gas referred to hydrogen; hence if M = molecular weight, and d = specific gravity referred to air as unity, $M = \frac{2 \cdot d}{\cdot 06926} = 28{\cdot}87\ d$.

Hence the practical rule for determining the molecular weight of a gas :—

Find the specific gravity, i.e. the ratio between the weights of equal volumes of the gas and air under the same conditions of temperature and pressure, *and multiply this by* 28·87.

15 The following table presents the results hitherto obtained regarding the molecular weights of elementary gases.

[1] The volume occupied by two parts by weight of hydrogen, or twice the volume occupied by unit mass of hydrogen, is often called two volumes.

[The numbers in column V are not always exactly equal to the products obtained in column IV; for an explanation see par. 17.]

Molecular weights of elementary Gases.

	I Name of element	II Spec gravity (air=1)	III Temp of observation	IV Sp gr. ×28·87	V Molecular weight
1	Hydrogen	·06926	0°	2	2
2	Sodium	·87	1200°—1500°	25·5	23
3	Nitrogen	0·9713	0°	28·04	28·02
4	Oxygen	1·106	about 1400°	31·94	31·92
5	"	1·10563	0°	31·92	
6	" (ozone)	1·658	—	47·86	47·88
7	Potassium	1·3	1200°—1500°	37·7	39·04
8	Sulphur	2·23	860°	64·4	63·96
9	"	2·24	1040°	64·6	
10	"	2·17	about 1400°	62·6	
11	"	2·93	665°	84·6	?
12	"	6·62	524°	191·1	191·88
13	Zinc	2·38	about 1400°	68·7	64·9
14	Chlorine	2·45	200°	70·73	70·74
15	"	2·61	about 1000°	75·35	
16	"	2·44	about 1200°	70·72	
17	Cadmium	3·94	about 1000°	113·7	112·1
18	Phosphorus	4·35	500°	125·6	123·84
19	"	4·50	about 1000°	129·9	
20	"	3·03	1430°	87·5	[? 61·92]
21	Arsenic	10·2	860°	294·5	299·6
22	"	10·65	644°—668°	307·4	
23	"	6·53	1430°	188·5	[? 149·8]
24	Bromine	5·54	100°	159·9	159·5
25	"	5·38	100°	155·3	
26	"	4·43	about 1500°	117·9	?
27	Selenion	5·68	about 1400°	161·1	157·6
28	"	6·37	about 1000°	183·9	?
29	"	7·67	860°	221·4	236·4
30	Mercury	6·96	about 1000°	200·93	199·8
31	"	6·98	446°	201·5	
32	"	7·03	424°	203·0	
33	"	6·7	882°	193·4	
34	Iodine	8·8	250°—450°	254·0	253·07
35	"	8·72	185°	251·7	
36	"	8·70	447°	251·2	
37	"	8·72	about 1000°	251·7	
38	"	8·84	250°	255·2	
39	"	8·55	665°	246·8	
40	"	5·87	about 1100°	169·4	?
41	"	4·76	about 1500°	137·4	[? 126·53]
42	Tellurium	9·08	about 1400°	262·1	255

[1] REGNAULT, *Compt. rend.* **20.** 975. [2] SCOTT, *Proc. R. S. E.* 1888.
[3] REGNAULT, *loc. cit.* [4] V. MEYER, *Ber.* **12.** 1426. [5] REGNAULT, *loc. cit.*

Mensching and Meyer (*Annalen*, **240**. 317) have obtained values for the specific gravity of antimony gas which shew that at 1400°—1500° the molecular weight of this element is less than Sb_4.

16 So many determinations of molecular weights of compound gases have been made that an enumeration of all the results would be perplexing, and of no special value. The method is applicable to elements and compounds alike. The following numbers are given here as they illustrate a point of general importance.

Specific gravities of certain compound gases.

Phosphorus pentachloride...	Sp. gr.	5·08	4·99	4·3	3·69	3·66
	Temp.	180°	190	230	290	335
Nitrogen tetroxide	Sp. gr.	2·8	2·4	2·03	1·83	1·5
	Temp.	29°	45	66	83	151
Nitric oxide	Sp. gr.	1·039		1·039		
	Temp.	−70		16°		
Arsenious oxide	Sp. gr.	13·8		13·78		
	Temp.	570°		1400		

From these numbers, and from those of the previous table, it is apparent that the specific gravities of certain elementary and compound gases decrease as the temperature increases,

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[6] SORET, *Compt. rend.* **61**. 941; and **64**. 904. [7] SCOTT, *Proc. R. S. E.* 1888. [8 and 9] DEVILLE and TROOST, *Compt. rend.* **56**. 891. [10] V. MEYER, *Ber.* **12**. 1112. [11] TROOST, *Compt. rend.* **95**. 30. [12] DUMAS, *Ann. Chim. Phys.* (2) **50**. 170. [13] MENSCHING and MEYER, *Ber.* **19**. 3295. [14] LUDWIG, *Ber.* **1**. 232. [15] V. MEYER, *Ber.* **13**. 400. [16] *Id. do.* **15**. 2773 (mean of 5 experiments). [17] DEVILLE and TROOST, *Compt. rend.* **49**. 239. [18 and 19] *Id. do.* **56**. 891. [20] MENSCHING and MEYER, *Annalen*, **240**. 317. [21] D. and T. *loc. cit.* [22] MITSCHERLICH, *Annalen*, **12**. 159. [23] MENSCHING and MEYER, *Annalen*, **240**. 317. [24] MITSCHERLICH, *loc. cit.* [25] V. MEYER, *Ber.* **13**. 406. [26] CRAFTS, *Compt. rend.* **90**. 183. [27, 28 and 29] DEVILLE and TROOST, *loc. cit.* [30] V. MEYER, *Ber.* **13**. 1107 and 1110 (mean of 6 experiments). [31] DUMAS, *Ann. Chim. Phys.* (2) **33**. 337. [32] MITSCHERLICH, *loc. cit.* [33] BINEAU, *Compt. rend.* **49**. 799. [34] V. MEYER, and MEIER and CRAFTS, *Ber.* **13**. 868 (mean of 7 experiments). [35] DUMAS, *loc. cit.* [36 and 37] DEVILLE and TROOST, *loc. cit.* [38] V. MEYER, *Ber.* **13**. 396. [39] TROOST, *Compt. rend.* **95**. 30. [40] V. MEYER, *Ber.* **13**. 1115. [41] *Id. do.* **13**. 1010. [42] DEVILLE and TROOST, *loc. cit.*

Note to preceding table. The expression 'specific gravity of a gas' will be employed to denote the specific gravity referred to air as unity: the expression 'vapour density of a body' to denote the specific gravity of a body in the gaseous state referred to hydrogen as unity.

while in the case of other gases the density is practically independent of the temperature; a limiting value is however generally found for the specific gravity of a gas.

It would therefore appear that a chemical substance may have more than one molecular weight; but if the molecule is the smallest part of a substance which exhibits the characteristic properties of that substance, this is equivalent to saying that certain substances when heated may pass through a succession of changes, each phase being marked by the existence of a distinct kind of matter. More accurate experiment has shewn that the vapours of phosphorus pentachloride and nitrogen tetroxide, at high temperatures, are mixtures of phosphorus pentachloride and trichloride, and chlorine, and of nitrogen tetroxide and nitrogen dioxide (N_2O_4 and NO_2), respectively, so that at these temperatures we have to deal not with homogeneous vapours, but with mixtures of different gases varying in composition at different moments. The connexion existing between temperature and the densities of gaseous elements and compounds will be examined in more detail in a future chapter[1] (see Book II.).

The practical outcome of these considerations is that in determining a molecular weight the gas must be proved to be really a homogeneous substance, and not a mixture produced by the decomposing action of heat on the original substance; and, further, that the value obtained for the specific gravity must be constant throughout a considerable range of temperature.

17 In determining the specific gravity of a gas, especially if at a somewhat high temperature, many sources of error are present; the result cannot therefore be more than moderately accurate[2]. But experimental errors are more easily

[1] Avogadro's law may be deduced from the molecular theory of matter, but inasmuch as this theory is based upon more or less inexact hypotheses, and is as yet but in an early stage of development, inasmuch also as the deductions made from it concerning gaseous laws are strictly applicable only to 'perfect gases,' it follows that Avogadro's law cannot be regarded, at present, as absolutely true. The laws of Boyle and of Charles, which are also deducible from the molecular theory, do not give a complete account of the relations of gases to temperature and pressure.

[2] Dumas' method for determining vapour densities is described in *Ann. Chim.*

avoided in the determination of the mass of an element which combines with one part by weight of hydrogen, 7·98 parts by weight of oxygen, or 35·37 parts by weight of chlorine. Now, if this mass is called the *combining weight* of an element, it is evident that the molecular weight of an element must be equal to, or a multiple of, its combining weight, and the molecular weight of a compound must be equal to the sum, or to a multiple of the sum, of the combining weights of its constituent elements. Hence if the combining weight, and the specific gravity in the gaseous state, of an element are carefully determined, we have the necessary data for an *accurate* determination of the molecular weight of that element; the combining weight being an accurately determined number, and the specific gravity deciding what multiple of that number represents the molecular weight. So also the data required for an *accurate* determination of the molecular weight of a compound are; the combining weights of the constituent elements, and the specific gravity of the compound in the state of gas. Thus Regnault found for the

Phys. [2] **33.** 337; Gay Lussac's in Biot's *Traité de Phys.* **1.** 291; Hofmann's in *Ber.* **1.** 198; and Victor Meyer's in *Ber.* **11.** 1868 and 2253. For criticisms on, and modifications of, Meyer's method see *Ber.* **12.** 609 and 1112: **13.** 401, 851, 991, 1079, 1185, and 2019: **14.** 1727: and **15.** 137, 1161 and 2775: (in the last paper by V. Meyer [*Ber.* **15.** 2775] will be found an interesting and valuable criticism of the various methods for finding the Sp. Grs. of gases). See also *Ber.* **16.** 1051; **19.** 1861; also *C. S. Journal* **Trans.** for **1880.** 491. Modifications of Dumas' method are described by Bunsen, see *Gasometrische Methoden*, 2nd ed. (1877), p. 172: also by Petterson and Ekstrand, *Ber.* **13.** 1191: and especially by Pawlewski, *Ber.* **16.** 1293. Thorpe [*C. S. Journal* **Trans.** for **1880.** 147—150] has described a very complete method based on Hofmann's process. V. Meyer [*Ber.* **9.** 1260: and **10.** 2068] has described a method based on the displacement of mercury. In *Wied. Ann.* **22.** 465 and 493, von Klobukow describes two processes for determining vapour densities with great accuracy; one is adapted for bodies with low boiling points, the other for bodies which boil at high temperatures. La Coste (*Ber.* **18.** 2122) describes a modification of V. Meyer's apparatus whereby the vapour densities of easily decomposable compounds may be determined at low temperatures and under very small pressures. A modification of V. Meyer's apparatus, by which a vapour density and the exact temperature of observation can be simultaneously determined, is described by Nilson and Pettersson in *J. für prakt. Chem.* [2] **33.** 1. See also Schall, *Ber.* **20.** 1433. Malfatti and Schoop (*Zeitschr. f. physikal. Chemie*, **1.** 159) describe an apparatus for determining vapour densities under small pressures.

specific gravity of chlorine the number 2·44; this multiplied into 28·87 gives 70·44. The combining weight of chlorine as most carefully determined by Stas is 35·37: now $35{\cdot}37 \times 2 = 70{\cdot}74$, which is very nearly equal to the molecular weight calculated from Regnault's numbers; hence 70·74 is taken to be the molecular weight of chlorine. Again, Thomson found the specific gravity of marsh gas to be 0·557, which multiplied into 28·87 gives 16·1 as approximately the molecular weight of this compound: the combining weight of carbon is 2·99 (H = 1), and in marsh gas carbon and hydrogen are united in the proportion of 2·99 to 1; hence the molecular weight of this gas is 3·99 or a multiple thereof. But $3{\cdot}99 \times 4 = 15{\cdot}96$; therefore the molecular weight of marsh gas is taken to be 15·96.

The numbers in column V of the table on p. 33 represent the molecular weights of the various elements found by the method of specific gravity aided by determinations of the combining weights of the elements in question.

18 Facts have already been mentioned which on the assumption of the truth of Avogadro's law oblige us to conclude that in certain chemical reactions the molecules of the reacting elementary bodies undergo subdivision; indeed we are forced to the conclusion that the greater number of the molecules of those elements which have been gasified are not homogeneous but are built up of smaller parts[1]. These parts of molecules, or atoms, are the ultimate portions of matter with which we have at present to deal in chemistry. Now it is evident that the molecule of an element must be composed of at least two atoms, unless indeed the atom and molecule should be identical; and that the molecule of a compound must be composed of at least one atom of each of its constituent elements. Therefore if we determine the smallest mass of an element in the molecule of any compound thereof, we shall have determined the maximum atomic weight of the element in question.

Hence we arrive at the following definition.

[1] Reactions are known in which it is not necessary to assume that subdivision of elementary molecules occurs, *e.g.*

$$Hg + Cl_2 = HgCl_2,$$
Volumes 2 2 form 2.

The maximum atomic weight of an element is the smallest mass, in terms of hydrogen as unity, of that element which combines with other elements to form a gaseous molecule.

Molecular weight has been already defined as the weight of two volumes of any gas referred to the weight of two volumes of hydrogen; hence the data which must be obtained before the maximum atomic weight of an element can be determined are, (1) the specific gravities of several gaseous compounds of the element in question, and (2) careful analyses of these compounds.

Suppose it is required to determine the maximum atomic weight of oxygen, such data as are indicated in the following table are obtained.

Data for determining maximum atomic weight of oxygen.

Name of compound	Weight of 2 volumes, as gas, referred to hydrogen, i.e. *molecular weight*	Analysis of these 2 volumes
Water	17·99	15·96 oxygen + 2 hydrogen
Carbonous oxide	27·96	15·96 „ + 11·97 carbon
Carbonic dioxide	44·15	31·92 „ + 11·97 „
Nitrous oxide	43·9	15·96 „ + 28·02 nitrogen
Methylic alcohol	32·3	15·96 „ + 11·97 carbon + 4 hydrogen
Methyl nitrate	76·2	47·88 „ + 11·97 carbon + 3 hydrogen + 14·01 nitrogen
Nitric oxide	30·0	15·96 oxygen + 14·01 „
Sulphurous oxide	64·9	31·92 „ + 31·98 sulphur
Sulphuric oxide	86·9	47·88 „ + 31·98 „
Phosphorus oxychloride	155·9	15·96 „ + 30·96 phosphorus + 106·11 chlorine
Osmium tetroxide	257	63·84 „ + 198·6 osmium

If the smallest mass of hydrogen found in a molecule of any compound of that element is called one part by weight, then in no molecule of any of the compounds in this table is there less than 15·96 parts by weight of oxygen; this number is therefore adopted as the maximum atomic weight of oxygen.

19 The following table (taken for the most part from Lothar Meyer's *Die modernen Theorien der Chemie*) contains the most important data hitherto accumulated for determining the maximum atomic weights of the elements by the application of Avogadro's law.

Data for determining maximum atomic weights.*

Note. The numbers expressing specific gravities of the gaseous compounds have been determined at various temperatures; the range of temperature has been sufficient to obviate errors due to changes of specific gravity accompanying changes of temperature [see *ante*, p. 35]; in many cases the number given is the mean of several estimations.

The numbers in column IV headed 'Molecular weight' are obtained by the method of specific gravities aided by determinations of the combining weights of the various elements, as explained in par. 17.

I	II	III	IV	V	
Name of compound	Sp. gr. as gas	Sp gr ×28·87	Molecular weight	Analysis, stated in parts *per molecule*, hydrogen being taken as unity	
[1] Hydrofluoric acid	0·693	20·0	20·1	19·1 fluorine	+1 hydrogen
Hydrochloric acid	1·247	36·0	36·37	35·37 chlorine	+1 „
Hydrobromic acid	2·71	78·23	80·75	79·75 bromine	+1 „
Hydriodic acid	4·443	128·0	127·53	126·53 iodine	+1 „
Water	0·623	17·99	17·96	15·96 oxygen	+2 „
Sulphydric acid	1·191	34·4	33·98	31·98 sulphur	+2 „
Sulphurous oxide	2·247	64·9	63·90	31·98 „	+31·92 oxygen
Sulphuric oxide	3·01	86·09	79·86	31·98 „	+47·88 „
Sulphuryl chloride	4·67	134·8	134·64	31·98 „	+31·92 „ +70·74 chlorine
[2] Selenion hydride	2·795	80·54	80·8	78·8 selenion	+2 hydrogen
Selenious oxide	4·03	116·0	110·9	78·8 „	+31·92 oxygen
[3] Tellurium hydride	4·49	129·62	127·5	125 tellurium	+2 hydrogen
[3a] Tellurium tetrachloride	9·13	263·6	266·48	125 „	+141·48 chlorine
Tellurium dichloride	6·61	190·8	195·74	125 „	+70·74 „
Ammonia	0·597	17·2	17·01	14·01 nitrogen	+3 hydrogen

* It has not been considered necessary to give references to all the papers where full accounts of determinations of the specific gravities of the compounds in this table are to be found; most of the numbers have been for years considered as among the well established data of the science. Notes are appended giving references, &c. in all cases of special interest, or where explanations of the numbers appear to be called for.

I Name of compound	II Sp. gr as gas	III Sp. gr. ×28·87	IV Molecular weight	V Analysis, stated in parts *per molecule*, hydrogen being taken as unity
Nitric oxide	1·039	30·0	29·97	14·01 nitrogen +15·96 oxygen
Nitrogen dioxide	1·50	43·3	45·93	14·01 „ +31·92 „
Nitrosyl chloride	2·31	66·68	65·34	14·01 „ +15·96 oxygen+35·37 chlorine
Phosphorus trihydride	1·15	33·1	33·96	30·96 phosphorus +3 hydrogen
Phosphoric fluoride	2·19	63·23	126·46	30·96 „ +95·5 fluorine
Phosphorous chloride	4·88	140·9	137·07	30·96 „ +106·11 chlorine
Phosphorous iodide	14·46	417·1	410·55	30·96 „ +379·59 iodine
Phosphoryl chloride	5·40	155·9	153·03	30·96 „ +106·11 chlorine+15·96 oxygen
Thiophosphoryl chloride	5·88	169 7	169·05	30·96 „ +106·11 „ +31·98 sulphur
Triethyl-phosphine oxide	4·60	132·8	133·74	30·96 „ +15·96 oxygen+71·82 carbon+15 hydrogen
Arsenic trihydride	2·695	77·8	77·90	74·90 arsenic +3 hydrogen
Arsenious chloride	6·30	181·9	181·0	74·90 „ +106·11 chlorine
Arsenious oxide	13·9	401·3	395·36	299·6 arsenic +95·76 oxygen
Cacodyl chloride	4·56	131·7	140·2	74·9 „ +35·37 chlorine+23·94 carbon+6 hydrogen
Cacodyl cyanide	4 63	133·7	130·8	74·9 „ +14·01 nitrogen+35·91 carbon+6 hydrogen
Methyl arsenite	6·006	173 4	169·7	74·9 „ +47·88 oxygen+35·91 carbon+9 hydrogen
Arsenious iodide	16·1	464·8	454·5	74·9 „ +379·59 iodine
Antimonious chloride	7·8	224·7	226·1	120 antimony +106·11 chlorine
Antimonious bromide	12·2	352·2	359·25	120 „ +239·25 bromine
Antimonious ethide	7·44	214·8	206·8	120 „ +71·82 carbon+35 hydrogen
Bismuthous chloride	11·35	327·7	314·1	208 bismuth +106·11 chlorine
Boron trifluoride	2·312	66·8	68·3	10·95 boron +57·3 fluorine
Boron trichloride	3·942 4·02	113·8 116·0	117·0	10·95 „ +106·11 chlorine
Boron tribromide	8·78	253·5	250·2	10·95 „ +239·25 bromine
Boron trimethide	1·93	55·7	55·9	10·95 „ +35·91 carbon+9 hydrogen
Methane	0·555	16·0	15·97	11·97 carbon +4 hydrogen
Methyl fluoride	1·186	34·3	34·10	11·97 „ +19·1 fluorine+3 hydrogen

Methyl chloride	1·736	50·1	50·34	11·97 carbon	+35·37 chlorine+3 hydrogen
Methyl bromide	3·253	93·9	94·72	11·97 „	+79·75 bromine+3 „
Methyl iodide	4·883	141·0	141·50	11·97 „	+126·53 iodine+3 „
Chloroform	4·20	121·3	119·08	11·97 „	+106·11 chlorine+1 „
Carbon tetrachloride	5·24 5·33	151·3 153·9	135·45	11·97 „	+141·48 chlorine
Carbon monoxide	0·968	27·96	27·93	11·97 „	+15·96 oxygen
Carbon dioxide	1·529	44·15	43·89	11·97 „	+31·92 „
Carbon oxychloride	3·505	101·2	98·67	11·97 „	+15·96 „ +70·74 chlorine
Carbon oxysulphide	2·105	60·8	59·91	11·97 „	+15·96 „ +31·98 sulphur
Carbon disulphide	2·645	76·4	75·93	11·97 „	+63·96 sulphur
Hydrocyanic acid	0·948	27·4	26·98	11·97 „	+14·01 nitrogen+1 hydrogen
Cyanogen chloride	2·13	61·5	61·35	11·97 „	+14·01 „ +35·37 chlorine
Cyanic acid	1·50	43·3	42·94	11·97 „	+14·01 „ +15·96 oxygen+1 hydrogen
Methylic alcohol	1·12	32·3	31·93	11·97 „	+15·96 oxygen+4 hydrogen
Methyl nitrate	2·64	76·2	76·86	11·97 „	+14·01 nitrogen+3 hydrogen+47·88 oxygen
Silicon fluoride	3·57	103·0	104·4	28 silicon	+76·4 fluorine
Silicon tetrachloride	5·94	171·5	169·5	28 „	+141·48 chlorine
Silicon tetriodide	19·1	551·4	534·1	28 „	+506·12 iodine
Silicon tetrethide	5·13	148·1	143·8	28 „	+95·76 carbon+20 hydrogen
Silico-chloroform	4·64	133·9	135·11	28 „	+106·11 chlorine+1 hydrogen
[4] Potassium iodide	5·85	168·9	165·57	39·04 potassium	+126·53 iodine
[5] Rubidium chloride	4·83	139·4	120·57	85·2 rubidium	+35·37 chlorine
[5] Rubidium iodide	7·67	221·6	211·73	85·2 „	+126·53 iodine
[5] Cæsium chloride	6·21	179·2	168·07	132·7 cæsium	+35·37 chlorine
[5] Cæsium iodide	9·25	267	259·23	132·7 „	+126·53 iodine
[5] Silver chloride	5·57	160·8	143·03	107·66 silver	+35·37 chlorine
Titanic chloride	6·84	197·5	189·5	48 titanium	+141·48 „
Zirconium chloride	8·15	235·4	231·5	90 zirconium	+141·48 „
Stannic chloride	9·20	265·7	259·3	117·8 tin	+141·48 „
Stannic bromide	7·9	458·0	436·8	117·8 „	+319 bromine
[6] Stannous chloride	6·45	186·2	188·5	117·8 „	+70·74 chlorine
Stannic ethide	8·02	231·6	233·6	117·8 „	+99·76 carbon+20 hydrogen

I Name of compound	II Sp gr. as gas	III Sp gr ×28 87	IV Molecular weight	V Analysis, stated in parts *per molecule*, hydrogen being taken as unity
Stannic triethyl chloride	8·43	243·4	240·0	117·8 tin +35·37 chlorine +71·82 carbon +15 hydrogen
Stannic triethyl bromide	9·92	286·4	284·4	117·8 „ +79·75 bromine +71·82 „ +15 „
Stannic triethyl iodide	10·33	298·2	289·2	117·8 „ +126·53 iodine +35·91 „ +9 „
[7] Germanium chloride	7·44	215·1	213·78	72·3 germanium +141·48 chlorine
[7] Germanium iodide	20·46	590·7	578 42	72·3 „ +506·12 iodine
[7] Germanium sulphide	3·54	102·2	104·28	72·3 „ +31·98 sulphur
[8] Thorium chloride	12·4	357·9	373·35	231·87 thorium +141·48 chlorine
Thallous chloride	8·22	237·4	239·0	203·64 thallium +35·37 „
Lead tetramethide	9·6	277·2	266·3	206·4 lead +47·88 carbon +12 hydrogen
Lead dichloride	9·5	274·2	277·2	206·4 „ +70·74 chlorine
[9] Beryllium chloride	2·93	81 73	79·84	9·1 beryllium +70·74 „
[9] Beryllium bromide	6·24	180·1	168·6	9·1 „ +159·5 bromine
Zinc chloride	4·6	132·8	135·6	64·9 zinc +70·74 chlorine
Zinc methide	3·29	95·0	94·8	64·9 „ +23·94 carbon +6 hydrogen
Zinc ethide	4·62	123·0	122·8	64·9 „ +47·88 „ +10 „
Cadmium bromide	9·25	267·0	271·5	122 cadmium +159·5 bromine
[5] Manganese chloride	4·58	132·3	125·74	55 manganese +70·74 chlorine
Mercury dimethide	8·29	239·4	229 7	199·8 mercury +23·94 carbon +6 hydrogen
Mercury diethide	9·97	287·8	257·7	199·8 „ +47·88 „ +10 „
[10] Mercurous chloride	8·3	239·6	235·17	199·8 „ +35·37 chlorine
Mercuric chloride	9·8	283·0	270·5	199·8 „ +70·74 „
Mercuric bromide	12·16	351·0	359·3	199·8 „ +159·5 bromine
Mercuric iodide	16·2	468·0	452·9	199·8 „ +253·06 iodine
Osmium tetroxide	8·9	257·0	257·0	193 osmium +63·84 oxygen
[11] Aluminium chloride	4·67	135·0	133·15	27·02 aluminium +106·11 chlorine
[5] Chromium chloride	5·37	154·9	158·51	52·4 chromium +106·11 „
[11] Chromium oxychloride	5·55 5·9	159·0 170·0	155·1	52·4 chromium +31·92 oxygen +70·74 chlorine

Indium chloride	7·87	227·2	219·51	113·4 indium	+106·11 chlorine
Molybdenum pentachloride	9·46	273·0	272·7	95·8 molybdenum	+176·85 „
Tungsten pentachloride	12·7	366·0	360·5	183·6 tungsten	+176·85 „
Tungsten hexachloride	13·2	382·0	395·8	183·6 „	+212·22 „
Tungsten oxychloride	11·84	342·0	341·0	183·6 „	+15·96 oxygen+141·48 chlorine
Vanadium tetrachloride	6·69	193·0	192·7	51·2 vanadium	+141·48 chlorine
Vanadium oxychloride	6·11	176·0	173·3	51·2 „	+15·96 oxygen+106·11 chlorine
Niobium pentachloride	9·6	277·0	270·9	94·0 niobium	+176·85 chlorine
Niobium oxychloride	7·88	228·0	216·1	94·0 „	+15·96+oxygen+106·11 chlorine
Tantalum pentachloride	12·9	372·0	358·9	182·0 tantalum	+176·85 chlorine
Uranium tetrachloride	13·3	383·9	381·5	240·0 uranium	+141·46 „
Uranium tetrabromide	19·46	561·8	559·0	240·0 „	+319 bromine
[12] Ferric chloride	11·24	324·5	324·6	111·8 iron	+212·22 chlorine
Aluminium bromide	18·6	537·0	532·5	54·04 „	+478·5 bromine
Aluminium iodide	27·0	780·0	813·2	54·04 „	+759·18 iodine
Cuprous chloride	6·99	201·8	197·5	126·8 copper	+70·74 chlorine
[13] Gallic chloride	11·9	343·6	350·2	138·0 gallium	+212·22 „

Notes to the preceding Table.

[1] The density of hydrofluoric acid was determined indirectly by Gore (*Phil. Trans.* for **1869.** 173) at 100°. Mallet (*Amer. Chem. Journal* **3.** 189) by directly weighing 1 litre of the gas at 30° found the specific gravity to be 1·42, which gives a molecular weight of 41·02. The molecular weight of this gas therefore decreases as temperature increases.

[2 and 3] Indirectly determined by Bineau (*Ann. Chim. Phys.* [2] **68.** 424); two volumes of each hydride when decomposed by metal yielded 2 vols. of hydrogen, 78 parts by weight of selenion in one case, and 128 parts by weight of tellurium in the other case, being produced.

[3a] Michaelis, *Ber.* **20.** 1780, and 2488. Temp. abt. 450°.

[4] Potassium iodide was vaporised at about 1300° by means of a new apparatus described by Mensching and Meyer (*s. Zeitschr. f. physikal. Chemie*, **1.** 157).

[5] Determined at 1200°—1500° by Scott; *Proc. R. S. E.* 1887.

[6] At a temperature slightly above its boiling point the specific gravity of gaseous stannous chloride points to the molecular weight 377; but at 200° higher the specific gravity is as given in the table; this gas therefore, like hydrofluoric acid, has two molecular weights: see Meyer and Zublin (*Ber.* **13.** 811).

[7] $GeCl_4$, GeI_4, and GeS have been gasified by Nilson and Pettersson (*Zeit. f. physikal. Chemie*, **1.** 27).

[8] Kruss and Nilson, *Ber.* **20.** 1671. Temp. abt. 1200°.

[9] See Nilson and Pettersson, *Ber.* **17.** 987; also *J. für prakt. Chem.* [2] **33.** 1; and Humpidge, *Proc. R. S.* **38.** 188.

[10] There is some doubt whether the vapour of mercurous chloride does or does not contain mercury and mercuric chloride: the number in the table is from a paper by Fileti, who states that by vaporising a mixture of the two chlorides of mercury, the protochloride remains undissociated (see abstract of Fileti's paper in *C. S. Journal* **Abstracts** for **1882.** 466).

[11] Nilson and Pettersson (*Zeitschr. f. physikal. Chemie*, **1.** 459) have found that the sp. gr. of gaseous aluminium chloride at 800°—1200° agrees with the formula $AlCl_3$; at 400° or so it agrees with the formula Al_2Cl_6. Odling (*Phil. Mag.* [4] **29.** 316) gave the specific gravity of aluminium trimethide at temperatures above 200° as 2·5, and at 130° as 5·0; but it is undecided whether the gas at 200° was homogeneous or a mixture of the products of decomposition by heat of molecules existing at lower temperatures (see Wanklyn *loc. cit.* 313, and Williamson *do.* 395). If the gas at 200° was really homogeneous, we should have $2{\cdot}5 \times 28{\cdot}87 = 72{\cdot}5$ as the molecular weight of aluminium trimethide; and this quantity of the gas contains 27·02 aluminium + 35·91 carbon + 9 hydrogen (= 71·93). *Chromium hexafluoride* (CrF_6) is frequently mentioned in text-books as a gaseous compound of chromium; the evidence in favour of the existence of a definite fluoride of chromium is meagre; and no determinations of its density (if it exists) have been made: see Unverdorben (*Pogg. Ann.* **7.** 311). According to Oliveri (*Gaz.* **16,** 218) the supposed hexafluoride is really an oxyfluoride, of chromium, and has the composition CrO_2F_2.

[12] V. Meyer (*Ber.* **17.** 1335) has obtained results which seem to shew that gaseous ferrous chloride at moderate temperatures consists chiefly of molecules having the composition Fe_2Cl_4, and at higher temperatures chiefly of molecules of $FeCl_2$.

[13] At 450° the sp. gr. of the vapour of gallic chloride is 7·8, and at the same

temperature in presence of an indifferent gas acting as diluent, it is 6·6: the gas dissociates under these conditions. (See Lecoq de Boisbaudran, *Compt. rend.* **93.** 294, 329 and 815.)

The maximum atomic weights deduced from these data may in many cases be regarded with a large degree of probability as the true atomic weights of the elements. The greater the number of gaseous compounds of an element analysed, the greater is the probability that the number which represents the smallest mass of that element in two volumes, i.e. in a gaseous molecule, of any of these compounds is the true atomic weight of the element.

20 When the atomic and molecular weights of an element are known, the *atomicity of the molecule*, i.e. the number of atoms in the molecule, is known.

In the following table the molecules of the elements, so far as the relative weights of these have been determined by the method founded on Avogadro's law, are classified in accordance with their atomicity.

Atomicity of Elementary Molecules[1].

Monatomic	*Diatomic*	*Triatomic*	*Tetratomic*	*Hexatomic*
Sodium Potassium Zinc Cadmium Mercury Iodine (at about 1500°) (? Bromine at about 1800°)	Hydrogen Chlorine Bromine Iodine (200° to about 1000°) Oxygen Sulphur (at 800° and upwards) Selenion (at 1200° and upwards) Tellurium Nitrogen Phosphorus, Arsenic (at white heat)	Oxygen (ozone) Selenion (700° to 800°)	Phosphorus Arsenic (to near a white heat)	Sulphur (450° to about 550°

[1] This table shews that many elementary gases have complex structures; hence arise difficulties in forming accurate physical conceptions of actions and reactions among the parts of these structures. This will be again referred to when dealing with atomic heats (see p. 67).

The molecules of several elements in this table are diatomic, but inasmuch as the molecular *and* atomic weights of only 16 elements have been determined it is impossible to say whether a majority of all the elementary molecules are composed each of two atoms. Six, of the sixteen, elements in the table have more than one molecular weight; of the remaining ten, five are monatomic and five are diatomic.

The table contains five well-defined metals, sodium, potassium, zinc, cadmium, and mercury; the molecules of these elements are monatomic, and hence are of a simpler structure than the molecules of the distinctly nonmetallic elements.

21 Chemical formulæ for the most part profess to represent not only the elementary composition, but also the relative weights of the molecules, of the bodies formulated: but unless some method for determining molecular weights other than that founded on Avogadro's law is adopted, it is evident from the data in the table on pp. 39—43 that the majority of the formulæ employed in mineral chemistry cannot certainly be regarded as molecular formulæ. Thus analysis shews that 17·96 parts by weight of water are composed of 15·96 parts of oxygen and 2 parts of hydrogen; analysis also shews that 58·37 parts by weight of sodium chloride are composed of 23 parts of sodium and 35·37 parts of chlorine. The specific gravity of water vapour shews that the molecular weight of this compound is about 18, hence—assuming the atomic weight of oxygen to be 15·96—the molecular formula is written H_2O (17·96). But no determination of the specific gravity of sodium chloride vapour has yet been made; hence the molecular weight *may* be about 59, or it may be a multiple of this number (assuming the atomic weights of sodium and chlorine to be known), and hence the formula NaCl (58·37) is not necessarily molecular, and is therefore not strictly comparable with the formula H_2O.

Even if a formula does express the relative weight of the molecule of the body formulated it is well to remember that it is the weight of the gaseous molecule which is thus expressed; the formula does not necessarily also represent the

relative weight of the molecule of the same body when solid: indeed the definition of molecule (p. 26) is applicable to gases only.

As a general rule, the melting and boiling points of bodies with large molecular weights are high: thus in any homologous series of hydrocarbons the boiling and melting points increase with increase of molecular weight[1]; the same connexion between these constants is noticed in many series of oxides, e.g. the oxides of nitrogen[2]. It would therefore appear probable that the molecular weight of a solid, using the term *molecular weight* in a wide sense, is greater than that of the same substance when in the state of gas. So also, as a rule, the action of heat is to produce molecules of less, from those of greater, weight: thus N_2O_4 exists at low temperatures, but becomes NO_2 when heated (see numbers on p. 34); so S_6 exists at 500°, but S_2 at 1000°; at temperatures above 300° the molecule O_3 decomposes into O_2. Reactions are known in which heat appears to favour the production of particles of greater weight and complexity than those previously existing; but these more complex particles generally mark intermediate stages towards the formation of less complex and comparatively lighter particles. Thus the action of heat on sodium-hydrogen sulphate is generally formulated in two stages, (1) $2NaHSO_4 = Na_2S_2O_7 + H_2O$; (2) $Na_2S_2O_7 = Na_2SO_4 + SO_3$: so also when mercuric cyanide is decomposed by heat, molecules of cyanogen are produced having the formula nCN where $n > 2$, but at 800°—900° these are separated into the lighter molecules C_2N_2: again, lead monoxide, nPbO, when heated forms the heavier oxide $n Pb_3O_4$: &c. In many of these cases however we are not certain that the formulæ employed represent the relative weights of true molecules.

The physical phenomena presented by liquids and solids cannot be expressed by such comparatively simple generalisations as those which express the properties of gases; the

[1] Thus, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ &c.
B. P. = 1° 38° 70° 99° 124° 148° 167° &c.

[2] Thus, NO N_2O N_2O_3 N_2O_4 N_2O_5
gaseous at −110°, B. P. = −88°, about −20°, 22°. M. P. = 30°.

molecular phenomena of the former classes of bodies are evidently more complex than those of the latter class. Great caution must therefore be used in applying deductions made from the study of the molecular phenomena of gases to solid or liquid bodies[1].

22 The following table gathers together the results of observations recorded in the table on pp. 39—43, so far as regards the maximum atomic weights of elements determined by the application of Avogadro's law.

Maximum atomic weights of elements. (AVOGADRO'S law.)

Name	Maximum atomic weight	Name	Maximum atomic weight	Name	Maximum atomic weight
Hydrogen	1	Manganese	55	Antimony	120
Beryllium	9·1	Zinc	64·9	Tellurium	125
Boron	10·95	Germanium	72·3	Iodine	126·53
Carbon	11·97	Arsenic	74·9	[Copper	126·8][2]
Nitrogen	14·01	Selenion	78·8	Cæsium	132·7
Oxygen	15·96	Bromine	79·75	[Gallium	138][2]
Fluorine	19·1	Rubidium	85·2	Tantalum	182
Aluminium	27·02	Zirconium	90	Tungsten	183·6
Silicon	28	Niobium	94	Osmium	193 (?)
Phosphorus	30·96	Molybdenum	95·8	Mercury	199·8
Sulphur	31·98	Silver	107·66	Thallium	203·6
Chlorine	35·37	[Iron	111·8][2]	Lead	206·4
Potassium	39·04	Cadmium	112	Bismuth	208
Titanium	48	Indium	113·4	Thorium	231·87
Vanadium	51·2	Tin	117·8	Uranium	240
Chromium	52·4				

About two-thirds of the known elements are found in this table.

Some method other than that based on the determination of the specific gravities of gaseous compounds must if possible be discovered for finding the atomic weights of the elements.

23 In his *New System of Chemical Philosophy*[3] (pp. 70—75), Dalton discusses hypotheses regarding the quantities of

[1] The comparison of the molecular phenomena of gases with those of solids and liquids will be considered more fully in a future chapter. See Book II. Chap. IV.

[2] Especial reference will be made to the elements in brackets in a later paragraph: see p. 60.

[3] Published in 1808.

heat contained in various elastic fluids, and decides in favour of that which asserts that,

"The quantity of heat belonging to the ultimate particles of all elastic fluids must be the same under the same pressure and temperature."

From this Dalton deduced the corollary,

"The specific heats of equal weights of any two elastic fluids are inversely as the weights of their atoms or molecules."

The values of very few specific heats had been determined when Dalton wrote, and therefore he did not possess data sufficient to test the justness of his general principle. Dalton calculated the theoretical specific heats of various gases by the aid of the above corollary, employing atomic weights determined by himself. Regarding the table of numbers thus obtained he remarks,

"Upon the whole there is not any established fact in regard to the specific heat of bodies, whether elastic or fluid, that is repugnant to the above table so far as I know; and it is to be hoped that some principle analogous to the one here adopted may soon be extended to solid and liquid bodies in general."

In 1819 a paper by Petit and Dulong appeared in the *Annales de Chimie et de Physique* [**10**. 395], containing the results of determinations of the specific heats of thirteen solid elements; viz. copper, gold, iron, lead, nickel, platinum, sulphur, tin, zinc, bismuth, cobalt, silver, and tellurium. A nearly constant product was obtained by multiplying the specific heats of the nine elements from copper to zinc, in this list, by the then generally accepted atomic weights of these elements, and the specific heat of bismuth, cobalt, silver, and tellurium, by a sub-multiple of the accepted atomic weight of each of these elements. Generalising from these results the French physicists concluded that "*the atoms of all the simple bodies have exactly the same capacity for heat.*"

The introduction of more accurate methods for determining specific heats has necessitated considerable alterations in many of the numbers to be found in the original paper of Petit and Dulong, nevertheless their general conclusion remains, although it cannot now be stated in terms quite so absolute as those used by its promulgators.

24 In 1831 F. Neumann[1] published determinations of the specific heats of various solid compounds, chiefly of naturally occurring minerals, and deduced the general statement:—"*The amounts of chemically similar compounds expressed by their formulæ possess equal specific heats.*"

A few years later (1833—4) Avogadro[2] detailed measurements of the specific heat of carbon, and of various compound substances, and drew certain general conclusions therefrom; he spoke of those atomic weights which were deduced from measurements of specific heats as the weights of thermal atoms (*atomes thermiques*).

R. Hermann[3] made a number of determinations of specific heats, and from these deduced the combining weights of several elements. The weights thus obtained were in some cases different from the Berzelian weights then in general use. Hermann supposed that the specific heat of certain elements, e.g. sulphur and oxygen, varies according as the element is in the free state or in combination with other elements.

Regnault[4], in a series of classical memoirs, added much to our knowledge of specific heats, and gave a general confirmation to the laws of Dulong and Petit, and Neumann. He arranged a table of so-called thermo-atomic weights, as follows:

Regnault's Thermo-atomic weights. [See KOPP[5].]

Al = 13·7	Cr = 26·1	Mn = 27·5	Se = 39·7
Sb = 61	Co = 29·4	Hg = 100	Ag = 54
As = 37·5	Cu = 31·7	Mo = 48	Na = 11·5
Ba = 68·5	F = 9·5	Ni = 29·4	Sr = 43·8
Bi = 105	Au = 98·5	N = 7	S = 16
B = 10·9	I = 63·5	Os = 99·6	Te = 64
Br = 40	Ir = 99	Pd = 53·3	Tl = 102
Cd = 56	Fe = 28	P = 15·5	Sn = 59
Ca = 20	Li = 3·5	Pt = 98·7	Ti = 25
C = 12	Pb = 103·5	K = 19·5	W = 92
Cl = 17·75	Mg = 12	Rh = 52·2	Zn = 32·6

[1] *Pogg. Ann.* **23.** 1. Neumann measured the specific heats of 8 carbonates, 4 sulphates, 4 sulphides, 5 oxides of the type MO, and 3 of the type M_2O_3.

[2] Published in condensed form in *Ann. Chim. Phys.* [2] **55.** 80: and **57.** 113.

[3] *Nouveaux Mémoires de la Société Impériale des Naturalistes de Moscou* (1834). **3.** 137.

[4] *Ann. Chim. Phys.* [2] **63.** 5. [3] **1.** 129: **9.** 322: **26.** 261 and 268: **38.** 129: **46.** 257: **63.** 5.

[5] *Annalen*, **Supplbd. 3.** 1 and 289.

Garnier[6] (in 1852) further generalised the relations between the formulæ and the specific heats of solid compounds; and Cannizzaro[7] somewhat advanced the generalisation of Garnier.

The Garnier-Cannizzaro generalisation may be stated thus:—

$$\frac{A \cdot C}{n} = \text{constant (about } 6{\cdot}4);$$

where A = the formula-weight of a compound, C = the specific heat of the same compound, and n = the number of elementary atoms in the formula of the compound.

25 Kopp[8] has gathered together most of the trustworthy results of specific heat determinations, and added many of his own, besides discussing the whole subject in detail.

Table of Specific Heats of the Elements[9].

Name	Spec heat	Temp	Atomic weight	Sp. ht. × at wt.	Observer
Lithium	0·941		7·01	6·6	Rg.
[1] Beryllium	0·62	450° to 500°	9·1	5·6	He.
[2] Boron	?0·5	about 1000°?	10·9	5·5	Wb.
[3] Carbon	0·463	980°	11·97	5·5	Wb.
Sodium	0·293	−34° to +7°	23	6·7	Rg.
Magnesium	0·245		24	5·9	Kp.
,,	0·25		,,	6·0	Rg.
Aluminium	0·202		27·02	5·5	Kp.
,,	0·214		,,	5·8	Rg.
,,	0·225		,,	6·1	Mt.
[4] Silicon	0·203	232°	28·3	5·8	Wb.
Phosphorus (cryst.)	0·174	−78° to +10°	30·96	5·4	Rg.
,,	0·189		,,	5·9	Rg.
,,	0·202		,,	6·2	Kp.
,, (red)	0·170		,,	5·3	Rg.
Sulphur	0·188		31·98	6·0	D.P.
,, rhombic	0·163		,,	5·2	Kp.
,, ,,	0·171		,,	5·5	Bn.
,, ,,	0·178		,,	5·7	Rg.
[5] Potassium	0·166	−78° to +10°	39·04	6·5	Rg.
Calcium	0·170		39·9	6·8	Bn.
Titanium	0·1485	0° to 300°	48	7·1	N.P.

[6] *Compt. rend.* **35.** 278: **37.** 130.

[7] *Il Nuovo Cimento* **7.** 321; Abstract in *Bull. Soc. Chim.* for **1863.** 171.

[8] *Annalen*, **Supplbd. 3.** 1 and 289.

[9] When no temperature is given the determinations were made somewhere between the limits 0° and 100°: the numbers may in these cases be regarded as approximately the mean specific heats for the temperature-interval 40°—60°.

Name	Spec. heat	Temp.	Atomic weight	Sp. ht. × at. wt.	Observer
[6] Chromium	0·10		52·4	5·2	Kp.
[7] Manganese	0·122		55	6·7	Rg.
Iron	0·112		55·9	6·3	Kp.
,,	0·114		,,	6·4	Rg.
,,	0·110		,,	6·1	D.P.
Nickel	0·108		58·6	6·3	Rg.
Cobalt	0·107		59	6·3	Rg.
Copper	0·093		63·4	6·0	Kp.
,,	0·095		,,	6·1	Rg.
,,	0·095		,,	6·1	D.P.
Zinc	0·0932		64·9	6·1	Kp.
,,	0·0935		,,	6·1	Bn.
,,	0·0955		,,	6·2	Rg.
,,	0·093		,,	6·0	D.P.
[8] Gallium	0·079	12° to 23°	69	5·4	Bt.
Germanium	0·077	0° to 200°	72·3	5·64	N.P.
Arsenic—amorphous	0·076‡		74·9	5·7	B.W.
,, crystalline	0·083‡		,,	6·2	B.W.
,, ,,	0·0814		,,	7·1	Rg.
,, ,,	0·0822		,,	6·2	N.
[9] Selenion—amorphous	0·0746	−27° to +8°	78·8	5·9	Rg.
,, crystalline	0·0745	−18° to +7°	,,	5·9	Rg.
,, ,,	0·0762		,,	6·0	Rg.
,, ,,	0·0861		,,	6·8	N.
,, ,,	0·084‡		,,	6·7	B.W.
Bromine—solid	0·0843	−78° to −20°	79·75	6·7	Rg.
[10] Zirconium	0·0666		90·0	6·0	M.D.
[11] Molybdenum	0·0722		95·8	6·9	Rg.
Rhodium	0·058		104	6·0	Rg.
Ruthenium	0·0611		104·5	6·4	Bn.
Palladium	0·0593		106·2	6·3	Rg.
Silver	0·056		107·66	6·0	Kp.
,,	0·0559		,,	6·0	Bn.
,,	0·057		,,	6·1	Rg.
Cadmium	0·0542		112	6·0	Kp.
,,	0·0548		,,	6·1	Bn.
,,	0·0567		,,	6·3	Rg.
Indium	0·057		113·4	6·5	Bn.
Tin	0·0548		117·8	6·5	Kp.
,,	0·0559		,,	6·6	Bn.
,,	0·0562		,,	6·6	Rg.
,,	0·0514		,,	6·0	D.P.
Antimony	0·0523		120·0	6·2	Kp.
,,	0·0495		,,	5·9	Bn.
,,	0·0508		,,	6·0	Rg.
,,	0·0507		,,	6·0	D.P.
Tellurium	0·0475		125	5·94	Kp.
,,	0·0474		,,	5·94	Rg.
Iodine	0·0541		126·53	6·8	Rg.
Lanthanum	0·0449		138·5	6·2	Hd.
Cerium	0·0448		141	6·3	Hd.

Name	Spec. heat	Temp.	Atomic weight	Sp. ht. × at. wt.	Observer
Didymium	0·0456		144	6·5	Hd.
Tungsten	0·0334		183·6	6·0	Rg.
Osmium	0·0311		193	6·0	Rg.
Iridium	0·0326		194	6·2	Rg.
Platinum	0·0325		195	6·4	Kp.
,,	0·0324		,,	6·3	Rg.
,,	0·0314		,,	6·3	D.P.
[12] Gold	0·0324		197	6·3	Rg.
[13] Mercury—solid	0·0319	−78° to −40°	199·8	6·4	Rg.
[14] Thallium	0·0335		203·6	6·8	Rg.
Lead	0·0307		206·4	6·3	Rg.
,,	0·0315		,,	6·5	Kp.
,,	0·0314		,,	6·5	Rg.
Bismuth	0·0305		208	6·3	Kp.
,,	0·0308		,,	6·3	Rg.
Thorium	0·0276		232·4	6·4	Nn
Uranium	0·028		240	6·6	Zn.

Notes to preceding Table.

[1] The number for beryllium is that calculated by Humpidge from a series of determinations at temperatures varying from 100° to 450° made with a specimen of beryllium containing 99·2 per cent. of the metal: for fuller discussion of specific heat of beryllium see par. 28, pp. 62, 63.

[2,3,4] Spec. heats of boron, carbon, and silicon are discussed on pp. 63—65, par. 29.

[5] The higher temperature (+ 10°) is not given in Regnault's paper, but judging from the context it appears to be approximately correct.

[6] This number for chromium is probably too low; see Kopp, *Annalen*, **Supplbd. 3.** 77 (note).

[7] The specimen of manganese employed contained a little silicon.

[8] Spec. heat of molten gallium between 109° and 119° = ·0802. (Berthelot, *Bull. Soc. Chim.* **31.** 229.)

[9] Spec. heat of amorphous selenion determined at high temperatures is abnormal, because of the large quantity of heat absorbed before fusion.

[10] Spec. heat of zirconium calculated by Mixter and Dana from determinations made with a sample containing known quantities of aluminium.

[11] The specimen of molybdenum employed contained carbon.

[12] Spec. heat of gold is nearly constant from 0° to 600°; at 900° sp. ht. = ·0345; and at 1000° = ·0352. [Violle, *Compt. rend.* **89.** 702.]

[13] Spec. heat of liquid mercury at 55° = ·033 (Regnault).

[14] The specimen of thallium employed contained a little oxide.

The numbers marked with ‡ are probably too large; see Weber's papers referred to in next page.

The names of the various observers are abbreviated in the table:—

RG.	stands for REGNAULT,—his papers on spec. heat are to be found in	*Ann. Chim. Phys.* [2] **73.** 5: [3] **1.** 129: **9.** 322: **26.** 261: **38.** 129: **46.** 257: **63.** 5: and **67.** 427.
KP.	„ „ KOPP, „ „ „ „	*Annalen* **126.** 362: and **Supplbd. 3.** 1 and 289.
N.	„ „ NEUMANN, „ „ „ „	*Pogg. Ann.* **126.** 123.
BN.	„ „ BUNSEN, „ „ „ „	*Pogg. Ann.* **141.** 1.
WB.	„ „ WEBER, „ „ „ „	*Pogg. Ann.* **154.** 367 [translation in *Phil. Mag.* (4) **49.** 161 and 276.]
D. P.	„ „ DULONG and PETIT, „ „	*Ann. Chim. Phys.* **10.** 395.
BT.	„ „ BERTHELOT, „ „ „ „	*Compt. rend.* **86.** 786.
HD.	„ „ HILLEBRAND, „ „ „	*Pogg. Ann.* **163.** 71 [translation in *Phil. Mag.* (5) **3.** 109].
B. W.	„ „ BETTENDORF and WULLNER „	*Pogg. Ann.* **133.** 293.
M. D.	„ „ MIXTER and DANA, „ „	*Annalen*, **169.** 388.
NN.	„ „ NILSON, „ „ „ „	*Ber.* **15.** 2519.
HE.	„ „ HUMPIDGE „ „ „ „	*Proc. R. S.* **35.** 137: **38.** 188: **39.** 1.
MT.	„ „ MALLET, „ „ „ „	*Chem. News*, **46.** 178.
ZN.	„ „ ZIMMERMANN „ „ „	*Ber.* **15.** 849.
N. P.	„ „ NILSON and PETTERSSON „	*Zeit. f. Physikal. Chemie.* **1.** 27.

26 The preceding table contains the names of 51 elements, the specific heats of which have been directly determined.

For eleven of the remaining elements values have been obtained which are regarded by some chemists as representing the specific heats of these elements: the method employed is based on the assumption that the *molecular heat*[1] of a solid compound is equal to the sum of the atomic heats of its constituent elements. (See Kopp, *Annalen*, **Supplb. 3.** 321—339.) Thus Kopp found the mean *molecular heat*[1] of metallic sulphides of the form RS to be equal to 12: the atomic heat of sulphur is 5·7; but $12 - 5{\cdot}7 = 6{\cdot}3$; therefore 6·3 is regarded as the value of the atomic heat of any one of the metals R. The mean value of the atomic heats of these metals found by direct experiment is 6·4.

[1] By *molecular heat* is to be understood the product obtained by multiplying the specific heat of a compound into the mass expressed by the generally accepted formula of that compound; the expressions *formula-weight* and *reacting weight* will be employed to signify this mass of any compound.

Kopp has applied this indirect method to calculate the atomic heats of various elements with which direct experiments could not be made[1].

Chlorine:—

Molecular heats of metallic haloid salts :—

$$RCl = 12{\cdot}8 \quad RBr = 13{\cdot}9 \quad RI = 13{\cdot}4$$
$$RCl_2 = 18{\cdot}5 \ldots\ldots\ldots\ldots\ldots\ldots RI_2 = 19{\cdot}4.$$

Now as (1) the atomic heat of each of the metals R is about 6·4; (2) the atomic heat of solid bromine and that of iodine is about 6·6; (3) the chlorides, bromides, and iodides examined are chemically analogous; and (4) the molecular heats of the analogous salts are nearly the same; Kopp concludes that the atomic heat of solid chlorine is about 6·4.

$RCl\ (12{\cdot}8) - R\ (6{\cdot}4) = 6{\cdot}4$: $RCl_2\ (18{\cdot}5) - R\ (6{\cdot}4) = 12{\cdot}1$, and $\frac{12{\cdot}1}{2} = 6{\cdot}05$.

A further argument in favour of this conclusion is afforded by these data:—

Molecular heat of $KClO_3 = 24{\cdot}8$
„ „ $KAsO_3 = 25{\cdot}3$;

hence the atomic heats of arsenic and chlorine are probably nearly the same; but the atomic heat of arsenic is 6·1; therefore the atomic heat of solid chlorine is probably about 6·1.

Fluorine:—

Molecular heat of $CaF_2 = 16{\cdot}4$
atomic heat of $Ca = 6{\cdot}8$,

hence atomic heat of fluorine $= \frac{16{\cdot}4 - 6{\cdot}8}{2} = 4{\cdot}8$.

Nitrogen:—

Molecular heats of various more or less analogous compounds:

$RClO_3 = 24{\cdot}8$ $RCO_3 = 20{\cdot}7$
$RAsO_3 = 25{\cdot}3$ $RSiO_3 = 20{\cdot}5$
$RPO_3 = 22{\cdot}1$ $RNO_3 = 23{\cdot}0$.

Hence, it is argued, the atomic heat of solid nitrogen is probably rather less than that of chlorine or arsenic (about 6), somewhat greater than that of carbon or silicon (about 5·2), and nearly equal to that of phosphorus (about 5·8); therefore the value of the atomic heat of solid nitrogen probably lies between 5·5 and 5·8.

[1] For detailed data see Kopp, Annalen, *Supplb.* 3. 329.

Oxygen: the molecular heats of metallic oxides are, as a rule, rather less than those of corresponding haloid salts; therefore, it is said, the atomic heat of solid oxygen is probably less than 6; thus,

$$RO = 11{\cdot}1 \ldots\ldots RCl = 12\,8 \quad RBr = 13{\cdot}9 \quad RI = 13{\cdot}4,$$
$$RO_2 = 13{\cdot}7 \ldots\ldots RCl_2 = 18{\cdot}6 \ldots\ldots\ldots\ldots RI_2 = 19{\cdot}4.$$

Further data for finding the value sought for are these:—

Molecular heats..... $R_2O_3 = 27{\cdot}2$; $KAsO_3 = 25{\cdot}3$: $KClO_4 = 26{\cdot}3$; $KMnO_4 = 28{\cdot}3$.

The values deduced for the atomic heat of solid oxygen are as follows:—

from RO ...4·6, from $KAsO_3$...4·2
„ RO_2...3·7, „ $KClO_4$...3·5 [assuming Cl=6]
„ R_2O_3...4·8, „ $KMnO_4$...3·8,

hence the mean value is 4·1.

Hydrogen: the principal data are these:—

(i) Molecular heat of ice (H_2O)=9 : molecular heat of Cu_2O = 15·6.

Hence, it is argued, the atomic heat of solid hydrogen is probably less than that of copper by the amount $\frac{15{\cdot}6 - 9}{2} = 3{\cdot}3$: but atomic heat of copper = 6·4; therefore the atomic heat of solid hydrogen = 3·1.

(ii) Molecular heat of NH_4Cl=20: $\left\{\begin{matrix}\text{but atomic heat}^1 \text{ of N is about } 5{\cdot}6\\ \text{and atomic heat}^1 \text{ of Cl } \quad \text{„ } \quad 6{\cdot}4\end{matrix}\right\}$.

Now 20 − 12 = 8, and $\frac{8}{4} = 2$; therefore the atomic heat of hydrogen is about 2.

(iii) Molecular heat of $NH_4NO_3 = 36{\cdot}4$
„ oxides $R_2O_3 = 27{\cdot}2$ }.

Hence $36{\cdot}4 - 27{\cdot}2 = 9{\cdot}2$, and $\frac{9{\cdot}2}{4} = 2{\cdot}3$.

The mean of these three results is 2·4, a number which may perhaps be provisionally accepted as the atomic heat of solid hydrogen: the method of calculation however involves many assumptions and the use of numbers themselves obtained by indirect means. From experiments with palladium

[1] Indirectly determined, see p. 55.

charged with hydrogen, Beketoff deduced the number 5·9 as representing the atomic heat of solid hydrogen[1].

The molecular heats of the oxides, chlorides, carbonates, nitrates, and sulphates, of *calcium*, *barium*, and *strontium* are nearly the same as the molecular heats of the corresponding salts of metals the atomic heats of which have been directly determined and found to be represented by the mean number 6·4; hence the atomic heats of *calcium*, *barium*, and *strontium* are probably represented by a number approximately equal to 6·4.

The agreement noticed between the values of the molecular heats of the chloride and carbonate of *rubidium*, of the oxides and chlorides of *chromium* and *titanium*, and of the oxides of *vanadium* and *zirconium*, and the molecular heats of corresponding salts of other metals which themselves exhibit the mean atomic heat 6·4, shews that the atomic heat of *rubidium*, that of *titanium*, of *zirconium*, of *chromium*, and of *vanadium*, is probably[2] about 6·4. (See notes 6 and 10 to table of specific heats of elements, p. 53.)

The following numbers representing the molecular heats of salts of some of the rarer elements are given by Nilson; (*Ber.* **13**. 1459 *et seq.*).

		Specific heat	Temperature.	Molecular heat.
Scandium salts (Sc = 44·03)	Sc_2O_3	0·153	0°—100°	20·81
	Sc_23SO_4	0·1639	„	62·42
Erbium salts (Er = 166)	Er_2O_3	0·065	„	24·7
	Er_23SO_4	0·104	„	64·5
Yttrium salts (Y = 89·5)	Y_2O_3	0·1026	„	23·3
	Y_23SO_4	0·1319	„	61·6
Ytterbium salts (Yb = 173)	Yb_2O_3	0·0646	„	25·5
	Yb_23SO_4	0·104	„	65·8
Gallium oxide	Ga_2O_3	0·1062	„	19·5
Indium oxide	In_2O_3	0·0807	„	22·2

If we assume that the atomic heat of oxygen is 4·1 (see p. 56), and regard only the oxides in the above table, then

[1] See abstract of Beketoff's paper (original is in Russian) in *Ber.* **12**. 687.

[2] For a full collection of specific heat data see F. W. Clarke's *Constants of Nature*, part II: or, Landolt and Bornstein's *Physikalisch-chemische Tabellen*. In connexion with this subject of *molecular heats* see also Kopp, *Ber.* **19**. 811.

the following values are found for the atomic heats of the metals in these oxides:—

Sc=4·2 Er=6·1 Y=5·5 Yb=6·6: Ga=3·6 In=5·0.

If a similar process is applied to the sulphates (atomic heat of S=6), then the atomic heats of the metals are all represented by negative numbers; hence either (1) the value of the atomic heat of oxygen in compounds is not constant, or (2) that of sulphur varies, or (3) that of the metals Sc, Er, Y, Yb, Ga, In, is negative in their sulphates, and, for some of these metals, is abnormal in their oxides.

The last hypothesis can scarcely be adopted. Indeed if the atomic heats of gallium and indium as determined by direct experiment are placed beside the numbers obtained by calculation from the molecular heats of the oxides (assuming O=4·1) we have this result:

	Directly determined.	Calculated from oxides.
Atomic heat of Gallium	5·4	3·6
„ Indium	6·5	5·0

We can scarcely hesitate which numbers to prefer.

It seems then that the value to be assigned to the atomic heat of oxygen in oxides[1] (and probably also the value of the atomic heat of sulphur in sulphates) is not a constant number, but varies according to the metal with which the oxygen is combined[2]: but if this is so, much doubt must necessarily be thrown on the accuracy of the conclusions regarding the atomic heats of chlorine, nitrogen, and other elements, deduced from the molecular heats of compounds of these elements. It appears then that the Garnier-Cannizzaro generalisation (see *ante*, p. 51) cannot always be applied[3].

[1] Such phrases as 'atomic heat of oxygen in oxides,' 'atomic heat of sulphur in sulphates' are perhaps rather misleading; they seem to assume that an elementary atom has different capacities for heat according to the nature (and number) of other atoms with which it is combined, and that measurements of these various capacities are obtainable; this assumption is not, I think, fully justified by facts.

[2] See Kopp, *Ber.* **19**. 813; also *post*, chapter III. par. 111.

[3] Measurements of the ratio of specific heat at constant volume to that at constant pressure for various gases composed of diatomic molecules have shewn that the value of this ratio is considerably smaller in some cases than in others;

Although a knowledge of the molecular heats (so-called) of solid compounds may give considerable help towards fixing the formulæ of these compounds, and so, indirectly, deciding what multiple of the combining number of an element is to be adopted as the atomic weight of that element, yet, it appears to me, that so far as concerns the direct determination of atomic weights, only those values for specific heats which have been obtained by experiments on the solid elements themselves are of much value.

It is certain that in some cases erroneous conclusions regarding the value of an atomic weight may be deduced from measurements of the specific heats of solid compounds. Thus it was for some time doubtful whether the value 120 or 240 should be assigned to the atomic weight of uranium. In 1878 Donath found the specific heat of uranoso-uranic oxide to be ·0798 (*Ber.* **12**. 742); assuming the specific heat of solid oxygen to be 0·25 $\left(\text{i.e. } \frac{4{\cdot}1}{16}\right)$, the specific heat of uranium was calculated to be ·0497; now ·0497 × 120 = 5·96; therefore it was concluded by Donath that the atomic weight of uranium is 120. But in 1880—1 pure uranium was prepared by Zimmermann (for details see *Ber.* **14**. 440 and 779: **15**. 849), and the specific heat of this metal was found by him to be ·028; but ·028 × 120 = 3·3: hence, to bring the atomic heat of uranium into agreement with that of the majority of the elements it is necessary to assign to the atomic weight of this metal the value 240.

27 If the table of maximum atomic weights (p. 48) is com-

hence a complete theory of specific heat, even when applied to gases, must take account not only of the number but also of the nature of the atoms in a molecule (compare Ostwald, *Lehrbuch der allgemeinen Chemie*, 1. 230). When the 'molecular heat' of a compound is smaller than the calculated value it may be that the molecule of the compound is built up of groups of atoms each of which group counts as a single atom. If the atoms forming a molecule are symmetrically arranged (i.e. if the distance between one pair of atoms is much the same as that between any other pair) then the total kinetic energy of the molecules is very probably proportional to the number of atoms; but if some of the atoms are arranged in groups or systems, the total kinetic energy will be proportional to the number of systems, and not to the number of atoms (see 'Aggregation, States of' in the new Ed. of Watts's *Dictionary of Chemistry*).

pared with that which gives the specific heats of elements (pp. 51—53), it will be found that—omitting the three elements which are placed in brackets in the former table—of the 43 elements (omitting those in brackets) whose atomic weights have been determined by the application of Avogadro's law, 34 have also had values assigned to their specific heats by direct experiments. Comparing the products obtained by multiplying the atomic weight into the specific heat in each of these 34 cases, it is found that 5 of these products fall below 5·8 (varying from 5·7 to 5·2), and that 29 vary from 6·8 to 6, giving a mean value of 6·4, round which number most of the values are grouped. The conclusion to be drawn is that the atomic heat of the 29 elements in question is represented by the number 6·4. There are three elements in brackets in the table on p. 48, viz. iron, copper, and gallium: if the maximum atomic weight of each, as deduced by Avogadro's law, is multiplied into the specific heat of the element the product is found to be about 12, but if the true atomic weights are assumed to be half as large as the numbers in the table, then the atomic heat of each of these elements is represented by the mean number 6·4. Now there are no valid reasons against adopting half the maximum values obtained by Avogadro's law as the true values of the atomic weights of the three elements in question, indeed there are strong chemical reasons in favour of this course.

Hence we have a very considerable mass of facts in favour of the generalisation:—

The atomic heat of all solid elements is nearly a constant, the mean value of which is 6·4.

If this be granted, we deduce the statement for finding an approximate value for the atomic weight of an element:—

Atomic weight is approximately equal to $\frac{6\cdot4}{\textit{spec. heat}}$;

provided always it is remembered that the specific heat is assumed to be determined with the element in the solid form, and for a considerable range of temperature throughout which the value remains nearly constant.

This method for determining the atomic weights of ele-

ments has been applied in about 14 cases, besides those cases where the method of specific gravities has also been employed; the numbers obtained are usually regarded as the true atomic weights of the elements in question.

It is evident that in determinations of the specific heats of solid elements we have a most valuable means for deciding which multiple of the combining number of an element is to be accepted as most probably expressing the value of the atomic weight of that element. When the element cannot be obtained, or cannot be obtained in sufficient quantity, in the solid form, then measurements of the specific heats of a series of its solid compounds will afford more or less valuable guidance in attempts to find the atomic weight of the element in question.

The following statements fairly sum up the results of atomic heat determinations.

I. *Solid elements, forty-five in number, whose specific heats have been directly determined, and whose atomic heats are all nearly equal to* 6·4.

Li Na Mg Al P S K Ca Ti Mn Fe Co Ni Cu Zn As
Se Br Zr Mo Rh Ru Pd Ag Cd In Sn Sb Te I La
Ce Di W Os Ir Pt Au Hg Tl Pb Bi Th U.....(C1)

II. *Solid elements, six in number, whose specific heats have been directly determined, and whose atomic heats appear to be about* 5·5.

Ga [? inaccurately determined] Be B C Si Ge.

III. *Solid elements, five in number, whose specific heats have been indirectly determined, and whose atomic heats are probably nearly equal to* 6·4.

V Rb Sr Cs Ba.

IV. *Gaseous elements; atomic heats very doubtful, apparently variable.*

H (F) N O Cl.

Of the elements whose atomic heats are decidedly less than 6·4, all, except gallium beryllium and germanium, are non-metallic and have atomic weights smaller than 33: indeed if the elements are arranged in order of increasing atomic weight, it is found that, with the exception of lithium, all having an atomic weight less than 23 have also an atomic

heat less than 6, and that these elements, except beryllium, are non-metallic.

28 The data concerning the specific heats of beryllium, boron, carbon, and silicon, must be examined in some detail.

Beryllium. R. E. Reynolds (*Phil. Mag.* (5) **3**. 38) determined the specific heat of this metal at 100° to be ·642: the metal used was however impure.

Nilson and Pettersson (*Ber.* **11**. 351) determined the specific heat of a mixture of metallic beryllium with known quantities of beryllium oxide, ferric oxide, and silica; they also determined the specific heat of pure beryllium oxide, and, the specific heats of ferric oxide and silica being known, they calculated the specific heat of the metal beryllium to be ·4079, for the temperature interval 0°—100°.

The same chemists (*Ber.* **13**. 1456: see also *Chem. News*, **42**. 297) made a second series of determinations with a sample of the metal containing only about 5 per cent. of beryllium and ferric oxides. The following table gives their more important results:—

Specific heat of Beryllium. (NILSON and PETTERSSON.)

Temperature interval.	Specific heat.	Sp ht ×13·65
0°—46°·5	0·3973	5·4
0°—100°	0·4246	5·8
0°—214°	0·475	6·4
0°—300°	0·5055	6·9.

Hence these chemists concluded that the atomic weight of beryllium ought to be taken as 13·65, and not 9·1, the value usually assigned to this constant.

The results tabulated above shew that the value of the specific heat of beryllium for the interval 0°—300° is

27 per cent. greater than the value for the interval 0°—50°; is
7 „ „ „ 0°—200°; and is
19 „ „ „ 0°—100°.

Using the data of Nilson and Pettersson, L. Meyer (*Ber.* **13**. 1780) calculated the values of the specific heat of beryllium at various temperatures, with the following results:—

True specific heat of Beryllium at various temperatures. (MEYER.)

γ = true specific heat at temperature t.

$\Delta\gamma$ = increase in value of γ per 1°C.

			Atomic heat	
t.	γ.	$\Delta\gamma$.	Be=9·1	Be=13·65
20°·2	0·3973	.....0·00101	3·62	5·43
73°·2	0·4481	.....0·00085	4·08	6·12
157°	0·5193	.....0·00063	4·73	7·10
256°·8	0·5819		5·29	8·94.

Hence, Meyer concluded that the specific heat of beryllium increases rapidly as temperature increases, but that the rate of this increase diminishes; and that the specific heat probably attains a constant value, equal to about 0·6, at 300° or so[1].

Humpidge[2], working with a specimen of beryllium containing 99·2 per cent. metal and 7 per cent. beryllium oxide, obtained the following numbers:—

Specific heat of Beryllium. (HUMPIDGE.)

Temp	Specific heat.
100°	·4702
200°	·540
400°	·6172
500°	·6206.

The value approximates to a constant (= about ·62) somewhere between 400° and 500°.

29 *Boron, Carbon, and Silicon.* Very varying values have been obtained for the specific heats of these three elements. The following table summarises the principal data previous to the publication of Weber's papers [see *Phil. Mag.* (4) **49**. 161 & 276].

Specific heats of Boron, Carbon, Silicon. (Weber's numbers not included.)

(Temperature may be taken as about 35°—55°.)

	Sp ht.	Sp. ht × at wt.	Observer.	
Boron—amorphous	0·254	2·8	Kp.	1864
„ crystalline	0·230	2·6	„	„
„ „	0·252	2·8	M.D.	1873
„ „	0·262	2·9	Rg.	1869
„ „	0·225	2·5	Rg.	1869
„ „	0·257	2·8	„	„
„ graphitic	0·235	2·6	„	„

[1] For a discussion of the value to be assigned to the atomic weight of beryllium see chapter III. par. 111.

[2] *Proc. R. S.* **35**. 137: **38**. 188; and specially **39**. 1.

	Sp. ht.	Sp ht. × at wt.	Observer	
[1]Carbon—diamond	0·143	1·7	B.W.	1868
„ „	0·147	1·8	Rg.	1841
„ gas-carbon	0·165	2·0	Kp.	1864
„ „	0·186	2·2	B.W.	1868
„ „	0·197	2·4	Rg.	1841
„ graphite	0·174	2·1	Kp.	1864
„ „	0·188	2·3	B.W.	1868
„ „	0·201	2·4	Rg.	1866
Silicon—fused	0·138	3·9	Kp.	1864
„ „	0·166	4·6	Rg.	1861
„ crystalline	0·165	4·6	Kp.	1864
„ „	0·171	4·8	M.D.	1873
„ „	0·173	4·8	Rg.	1861.

Weber (*loc. cit.*) found that the specific heats of carbon, boron, and silicon, increase rapidly as the temperature is raised, but that at high temperatures the rate of the increase becomes much smaller. The following table gives a synopsis of Weber's results:—

Specific heats of Boron, Carbon, and Silicon. (WEBER.)

	Temp.	Spec. heat	Spec ht × at. wt
Boron—crystallised	−40°	0·1915	2·11
„ „	+77°	0·2737	3·01
„ „	177°	0·3378	3·72
„ „	233°	0·3663	4·03.

These numbers shew that the specific heat of boron increases with increase of temperature, and that the value of this increase, for a given interval, is considerably less at high than at low temperatures. The variations in the rate of this increase are almost identical with the variations noticed in the case of carbon; hence at temperatures above 233° this identity will probably remain. Calculated on this assumption, the specific heat of boron at about 1000° is 0·50.

It must however be observed that Weber did not prove the purity of the specimen of crystalline boron with which he worked. The crystals were prepared by reducing boric oxide

[1] Dewar (*Phil. Mag.* [4] **44**. 461) found for the specific heat of gas-carbon between 20° and 1040° the number 0·32, for diamond the number 0·366; and, between 20° and a temperature estimated to be 2000°, for 'carbon' the number 0·42.

by aluminium; according to Hampe (*Annalen*, **183**. 75) the substance thus obtained is a definite boride of aluminium, $Al_{12}B$.

Specific heats of Boron, Carbon, and Silicon. (WEBER) continued.

	Temp.	Spec. heat.	Sp ht. × at wt
Carbon—diamond	−50°	0·0635	0·76
„ „	+10°	0·1128	1·35
„ „	85°	0·1765	2·12
„ „	250°	0·3026	3·63
„ „	606°	0·4408	5·29
„ „	985°	0·4589	5·50
„ graphite	−50°	0·1138	1·37
„ „	+10°	0·1604	1·93
„ „	61°	0·1990	2·39
„ „	201°	0·2966	3·56
„ „	250°	0·325	3·88
„ „	641°	0·4454	5·35
„ „	978°	0·467	5·60
Porous wood carbon	0°—23°	0·1653	1·95
„	0°—99°	0·1935	2·07
„	0°—223°	0·2385	2 84.

These numbers shew that the specific heat of carbon increases from −50° upwards, the value found at 600° being about seven times as great as that found at −50°; but that the rate of this increase is very small at high temperatures; from a red heat upwards the rate is about one-seventeenth of that from 0° to 100°.

The specific heats of diamond and graphite differ at temperatures below about 600°, but from this point upwards they are practically identical; the numbers given for porous wood carbon are almost the same as those for graphite for the same temperature-intervals; hence it may be said that at high temperatures (above 600°) the various modifications of carbon have probably all the same specific heat.

Table continued.

	Temp.	Spec. heat	Sp. ht × at. wt.
Silicon—crystallised	−40°	0·136	3·81
„ „	+57°	0·1833	5·13
„ „	128°	0·196	5·50
„ „	184°	0·2011	5·63
„ „	232°	0·2029	5·68

in effect was that they found that empiricism would not consort with the old logic, and without reconsidering the old logic they became sceptics. This scepticism suited Berkeley, because he wanted to attack physical science, and he did not fully realise that his destructive arguments could be turned to apply as well to our knowledge of spirit as to our knowledge of the physical world. It suited him to maintain in the face of contemporary physics that the laws of the physical world were contingent; but he did not see that he could not maintain, as he wished to, that we knew for certain that certain characteristics were essential to God's nature—one of which was that God is all-powerful and free, and therefore that the laws of physical nature are *certainly known* to be contingent. He did not see this because of his defective analysis of his own spiritualism; but as far as physical science was concerned he drew the same conclusion as Hume. However, the point that concerns us is perhaps seen most clearly in Hume. He concentrates on the causal principle, assuming that unless this principle can be established absolutely and independently *at the beginning*, all thought is invalid, since all thought depends upon it. The view that thought reconsiders, and confirms or modifies, its own basic principles as it goes along, for all the support that it finds in experience, does not really seem to him to meet the case, and he becomes a sceptic. He assumes that the causal principle must be made good once and for all at the beginning; and when he finds that this cannot be done, he turns sceptic on the ground that in thinking we always and consistently—the consistency of the practice did not, curiously enough, give him pause—make use of a principle to which we are not entitled. He regards the causal principle as a simple, general principle,

whose *meaning* is clear and definable,[1] but which is, unfortunately, just not true—and this in spite of the fact that when he comes to explain just what we *mean* by saying that *A* causes *B*, he can produce nothing better than an extremely rough and ready description, or indication, certainly not a definition. His attitude indeed involves a curious mixture of criticism and acceptance of the traditional logic, both of them to some extent explicit. There is criticism in that the logic had not shown up, as surely a sound logic should, the basic and fundamental nature of the causal principle; and there is acceptance, in that it assumes that a basic principle (on Hume's view, the causal principle) must be a simple, clearly apprehended, general principle, apprehended to be certainly true before, and independently of, its use. It was this latter acceptance which made his enquiry lead him to scepticism, in that it prevented him from canvassing any such view as that put forward by Kant.

Thus it is broadly true to say that the pre-Kantians did not recognise how complete a break was necessary with the old logic. This was left to Kant. It is true that Berkeley pointed the way, and made some small effort to make a start on a new theory. It is also true that Hume had a complete theory of thinking of his own; namely that all so-called thinking is nothing

[1]On this point Berkeley shows more insight. He does recognise that the fundamental terms of physics are not simple or definable; and he does seem to recognise that the progress which physics has made has been achieved in spite of this. But he makes only very tentative efforts to work out a theory of knowledge on this basis. While he is generally sympathetic to it, and, of course, profoundly interested in it, he never really made up his mind about physics at all, whether to call it knowledge or illusion or something between the two. Sometimes he speaks as if he was discrediting it altogether as compared with theology; sometimes as if he thought they both stood on much the same kind of ground, neither being enabled to have the last word against the other. Cf. *Alciphron*, Dialogue vii.

The specific heat of silicon attains an almost constant value at about 200°.

30 It is evident that the specific heat of an elementary body is not a constant number, but varies with the temperature, and that the relation between the variation of specific heat and that of temperature differs for each element. The following formulæ calculated from experimentally determined numbers, express the relation in question for some of the elements:—

[1]Carbon	—diamond	sp. ht.	$=0.4408+0.0000405\,t$,	where t varies from	600°—800°
„	„	„	$=0.4408+0.0000561\,t$	„	800°—1000°
„	graphite	„	$=0.4454+0.0000472\,t$	„	600°—800°
„	„	„	$=0.4454+0.0000840\,t$	„	800°—1000°
[2]Copper		„	$=0.0910+0.000023\,t$	„	0°—250°
[2]Zinc		„	$=0.0865+0.000044\,t$	„	„
[2]Lead		„	$=0.0286+0.000019\,t$	„	„
[3]Platinum		„	$=0.0317+0.000006\,t$	„	0°—1200°

The specific heat of any substance also varies with variations in the physical state of that substance, thus:—

	Sp heat		Sp heat
Bromine—solid	0.0843	Iron sulphide as pyrites ...	0.1279
„ liquid	0.1110	Chlorine—solid	0.180
Soft copper	0.0948	„ [4]gaseous ...	0.093
Hard copper	0.0934	Mercury—solid	0.032
Iron sulphide as strahlite	0.1332	„ [4]gaseous ...	0.015

The specific heats of the elementary bodies have generally been determined at temperatures situated at very varying intervals from the melting points of these elements; the physical aggregation of the specimens examined has also varied much; hence the values found for the specific heats of the elements cannot be regarded as strictly comparable.

There appears to be a certain interval of temperature within which the value of the specific heat of a solid element becomes nearly constant, and for this interval only can the element be said approximately to obey the law of Dulong

[1] Weber (*loc. cit.*).

[2] Bède, *Mém. Couronn. de l'Acad. Brux.* **27.** 3 (1855).

[3] Violle, *Compt. rend.* **85.** 543.

[4] Calculated for constant volume.

and Petit, as stated on p. 60. This temperature-interval varies for each element, especially for the nonmetallic elements with small atomic weights; for many elements it may be roughly taken as from 0° to 100°; but for several it is only attained at high temperatures.

Kopp (*loc. cit.*) has supposed that the atoms of certain elements—more especially of boron, carbon, and silicon—are built up of simpler parts, have themselves a grained structure, and that at high temperatures the atoms of these elements are composed of a smaller number of those little parts than at lower temperatures. Heat added at low temperatures is supposed, on this hypothesis, to be used in separating the atomic groups. With regard to Kopp's hypothesis it may be observed, that the facts of spectroscopy seem to point to the existence of a more complex structure in the nonmetallic than in the metallic molecules; that allotropy occurs distinctly only among the non-metals; that the molecules of the five metallic elements whose vapour-densities have been determined are monatomic; that the atomic heat of tellurium, a metal-like non-metal belonging to the oxygen group, is 6·0, of the less metal-like selenion about 5·8, of the decidedly non-metallic sulphur about 5·5, and of the typical non-metal oxygen probably not more than 4; and finally that the molecular structures of oxygen, sulphur, and selenion, vapours are more complex than that of tellurium vapour. Now as carbon, boron, and silicon are distinctly non-metallic elements, these facts lend support to the view that a part of the heat added to carbon, boron, or silicon, at low temperatures is spent in separating complex molecular groups into their constituent parts, rather than in separating the hypothetically complex atoms of these elements into smaller atoms.

31 A consideration of the data summarised in the preceding paragraphs shews, I think, that the application of Avogadro's law is of more value to the chemist as a means of determining the atomic weights of elements than the law of Dulong and Petit. From a general consideration of the molecular theory of matter it is also apparent that a deduction which does not necessitate an exact hypothesis as to the internal structure of

molecules is more trustworthy and more appropriate, in the present state of knowledge, than another which does necessitate some such hypothesis.

The molecular explanation of the gaseous laws expressing relations between volume, pressure, and temperature, and of Avogadro's law, may be considered as fairly complete; but in order to give a molecular explanation of the law of specific heats more knowledge of the internal structure of molecules than we now possess is necessary[1]. For the specific heat of a substance depends on the rate at which the whole energy of the molecule increases with increase of temperature: but this energy is made up of two parts, (1) the energy of agitation, that is, the energy the molecule would possess if it moved as a whole with the motion of its centre of mass, or in other words without rotation; and (2) the energy of rotation, that is, the energy the molecule would possess if its centre of mass were reduced to rest, in other words the energy due to the motion of the parts relatively to the centre of mass of the molecule[2]. If it is assumed that the energy due to the rotational motions of the parts of the molecule tends towards a value having a constant ratio to the energy of agitation of the molecule, then a simple expression is found for the whole energy; but this expression contains a factor which varies in different gases, and the value of which has been determined only in a few cases[3]. And moreover it is probable that when the energy due to the rotational motions of the parts of a molecule becomes greater than a certain quantity, the molecule separates into parts; hence when heat is imparted to a mass of molecules work is probably in many cases done in destroying some of the molecules as such[4]. Hence the molecular explanation of specific heat is not at present in so advanced a state as that of the relations between the volumes, pressures, and temperatures, of gases[5]. If this be true concerning gases, still

[1] Clerk Maxwell, *C. S. Journal* [2] **13**. 507.

[2] Clerk Maxwell, *loc. cit.* p. 502.

[3] See Clerk Maxwell's *Heat*, pp. 317—319 (6th ed.).

[4] See Hicks, *Phil. Mag.* (5). **4**. 80, and 174. 'On some effects of Dissociation on the Physical Properties of Gases.'

[5] See in connexion with this subject Strecker, *Wied. Ann.* **13**. 20; and Boltz-

more is it true concerning solid bodies. Our knowledge of the molecular phenomena of solids is very small; but the law of Dulong and Petit is applicable to solid elements only. Finally, when heat is added to a solid only a portion of it is used in raising the temperature; another part is spent in increasing the volume of the solid, and a third part is employed in doing work against the external pressure on the solid.

32 The so-called 'law of isomorphism' affords a basis on which is founded another method for determining the atomic weights of elementary bodies.

The views of Abbé Haüy were dominant in crystallography in the early days of this century; he admitted a close connexion between crystalline form and chemical composition, but he thought that each chemically distinct body must be characterised by a definite and peculiar form.

In 1816 Gay-Lussac noticed that the growth of crystals of potash alum was not affected by placing them in a solution of ammonia alum.

Various observations of this kind were made from time to time[1] until 1819, when E. Mitscherlich propounded the law of isomorphism, which, modified and developed, was stated by him in 1821 in the following terms: "*Equal numbers of atoms similarly combined exhibit the same crystalline form; identity of crystalline form is independent of the chemical nature of the atoms, and is conditioned only by the number and configuration of the atoms.*"

Since this date various observers have advanced the knowledge of the relations between crystalline form and chemical composition[2]. The more important generalisations are as follows.

mann, *do.* **13.** 544: and **18.** 309: also art. **Aggregation, States of,** in the new edition of *Watts's Dictionary.*

[1] For a full historical account of the development of the conception of *Isomorphism*, with copious references, see the article 'Isomorphie' in the *Neues Handwörterbuch der Chemie*, Bd. III. p. 844 *et seq.*

[2] See especially *Handwörterbuch, loc. cit.* and Kopp's *Lehrbuch der physikalischen und theoretischen Chemie* (2nd Ed.), Bd. II. pp. 136–155.

Similar chemical constitution[1] is not necessarily accompanied by identical crystalline form;

e.g. $PbCrO_4$ monoclinic, and $PbMoO_4$ quadratic;
AgCl and AgBr regular, and AgI hexagonal;
KNO_3 and $(NH_4)NO_3$ rhombic but not identical, $CsNO_3$ and $RbNO_3$ hexagonal.

Unlike chemical constitution may be accompanied by similar or identical crystalline form: thus Marignac[2] shewed that the following salts crystallise in identical forms;—

$K_2TiF_6 . H_2O$, $K_2NbOF_5 . H_2O$, $K_2WO_2F_4 . H_2O$, are isomorphous;
and $CuTiF_6 . 4H_2O$, $CuNbOF_5 . 4H_2O$, $CuWO_2F_4 . 4H_2O$, are isomorphous.

Klein[3] has shewn that the complex compounds

$9WO_3 . B_2O_3 . 24H_2O$ and $12WO_3 . SiO_2 . 33H_2O$, and
$9WO_3 . B_2O_3 . Na_2O . 23H_2O$, are isomorphous.

Klein has modified the statement of the law of isomorphism thus:

"Isomorphous bodies have either a similar chemical constitution or exhibit only slight differences in percentage composition; there is always a group of elements which is either common to all the isomorphous bodies, or exhibits identical chemical functions in these bodies, and which constitutes by far the greater part of each of the isomorphous bodies."

It would appear that all the constituents of a compound exert an influence on the form of that substance. Isomorphism may not be exhibited in comparatively simple analogous compounds of two elements, but may appear in more complex compounds of the same elements; e.g. many of the simpler compounds of cadmium are not isomorphous with the analogous compounds of the metals of the magnesium group (Mg, Mn, Fe, Co, Ni, Zn, Cu, Ca), but comparatively complex cadmium salts—such as $CdSO_4 . K_2SO_4 . 6H_2O$—are generally isomorphous with the corresponding compounds of the magnesian metals. Again, many simple salts of sodium and potassium are not isomorphous although their composition is similar, but the alums are isomorphous.

[1] This phrase must not be interpreted too strictly. Closely allied compounds the formulæ of which contain the same number of elementary atoms, or groups of atoms, may be said, for the purposes of the present argument, to exhibit a 'similar chemical constitution.'

[2] *Ann. Chim. Phys.* **60.** 257.

[3] *Compt. rend.* **95.** 781.

One may suppose that the presence of a large number of isomorphous atoms exerts a dominating influence over a smaller number of non-isomorphous atoms.

The constituents of isomorphous compounds are not themselves always isomorphous. Thus, the sulphates of nickel, magnesium, and zinc, crystallise in rhombic forms, but the oxides of the same elements are not isomorphous.

In other cases the constituents of isomorphous bodies are themselves isomorphous; e.g. the compound $3Ag_2S . Sb_2S_3$ has the same crystalline form as the compound $3Ag_2S . As_2S_3$, Sb_2S_3 and As_2S_3 are isomorphous in rhombic forms, and arsenic and antimony form almost identical rhombic crystals. Hence we must distinguish strict isomorphism as applied to bodies which, with similar composition, exhibit the same or nearly the same crystalline form; and isomorphism as more loosely applied to bodies which, although not themselves crystallising in the same form, nevertheless combine with other bodies to produce strictly isomorphous compounds into which they enter as corresponding groups[1].

A certain latitude is generally allowed in the application of the term 'isomorphous crystals.' This latitude has gradually been more and more advanced until it has become difficult to give an exact meaning to the expression. Absolute identity of the angles of two bodies occurs only when the bodies crystallise in the regular system. Chemically analogous compounds sometimes crystallise in forms closely resembling one another, yet belonging to different systems; e.g. potassium dichromate crystallises in monoclinic forms, where $a : b : c = 1{\cdot}0116 : 1 : 1{\cdot}8145$, and ammonium dichromate crystallises in triclinic form the relations of the axes of which are nearly the same as those of the monoclinic crystals, viz. $a : b : c = 1{\cdot}0271 : 1 : 1{\cdot}7665$. Salts with identical crystalline form sometimes exhibit optical differences[2]. Are all such salts to be called truly isomorphous? Kopp[3] proposes that only those salts any one of which is capable of growing in unmodified

[1] *Lehrbuch der physikalischen und theoretischen Chemie*, **2.** 139.

[2] See Baker, *C. S. Journal* **Trans.** for **1879.** 760.

[3] *Ber.* **12.** 900 *et seq.*

form when immersed in a solution of any other should be regarded as strictly isomorphous[1].

33 As we know the crystalline form of comparatively few elements[2], the statement that such or such elements form an isomorphous group, generally means only that the analogous compounds of these elements are for the most part isomorphous.

The more important groups of isomorphous elements, as thus understood, are as follows[3]:—

GROUP I. *Fluorine, Chlorine, Bromine, Iodine,* [*Cyanogen*]; in all compounds:

partially *Manganese;* in compounds of the type $RMnO_4$.

GROUP II. *Sulphur, Selenion;* in all compounds and as elements in monosymmetric forms:

partially *Tellurium;* in compounds of the type RTe:

„ *Chromium, Manganese, Tellurium;* in salts of their acids belonging to the type H_2RO_4:

„ *Arsenic, Antimony;* in compounds of the type RS_2.

GROUP III. *Arsenic, Antimony, Bismuth, Tellurium;* as elements, and the three first-named in all corresponding compounds:

partially *Phosphorus* and *Vanadium;* in salts of their acids:

„ *Nitrogen with phosphorus, arsenic,* and *antimony;* in organic bases.

GROUP IV. *Lithium, Sodium, Potassium, Rubidium, Cæsium,* [*Ammonium*]; in most compounds:

partially *Thallium;* in some compounds:

„ *Silver,* in some compounds (especially with *sodium*).

GROUP V. *Calcium, Strontium, Barium, Lead; Magnesium, Zinc, Manganese, Iron;* e.g. in carbonates:

partially *Nickel, Cobalt, Copper;* with *iron* in some compounds, e.g. sulphates:

[1] Lehmann, *Zeitschr. f. Physikal. Chemie,* **1.** 15, 49, has recorded a few cases of non-isomorphous compounds crystallising together, e.g. $CuCl_2.2H_2O$ and NH_4Cl. Many precautions must be taken in the practical application of this criterion of isomorphism (*s.* 'Isomorphie' in Ladenburg's *Handwörterbuch der Chemie,* **5.** 385).

[2] See, for the crystalline forms of elements in the free state, Watts's *Dictionary* [1st Ed.], vol. III. p. 429.

[3] From article 'Isomorphie' in *Neues Handwörterbuch, loc. cit.* For a much fuller account of the isomorphism of elements, see Ladenburg's *Handwörterbuch der Chemie,* **5.** 394.

partially *Lanthanum, Cerium, Didymium, Yttrium, Erbium;* with *calcium*, in compounds of type RO:

„ *Copper, Mercury;* with *lead*, in oxy-compounds:

„ *Beryllium, Cadmium, Indium;* with *zinc*, in some compounds:

„ *Thallium;* with *lead*, in some compounds.

GROUP VI. *Aluminium, Chromium, Manganese, Iron;* in the sesquioxides [R_2O_3] and salts derived therefrom:

partially *Cerium, Uranium;* in their sesquioxides.

GROUP VII. *Copper, Silver;* in compounds of the type R_2O:

partially *Gold;* with *silver*.

GROUP VIII. *Ruthenium, Rhodium, Palladium, Iridium, Platinum, Osmium;* in most compounds:

partially *Iron, Nickel, Gold:*

„ *Tin* [*? Tellurium*].

GROUP IX. *Carbon, Silicon, Titanium, Zirconium, Tin, Thorium;*

partially in compounds of the type RO_2, and salts derived from the type H_2RO_3: *carbon* with *silicon* in many corresponding so-called organic compounds.

„ *Iron;* with *titanium*.

GROUP X. *Niobium, Tantalum;* in all their compounds.

GROUP XI. *Molybdenum, Tungsten;* in all their compounds:

partially *Chromium;* in salts of acids of the type H_2RO_4.

The terms *dimorphous, trimorphous, polymorphous* were used by Mitscherlich. Many examples of the phenomena to which these names are applied are now known: thus calcium carbonate crystallises in hexagonal forms as calcspar, and in rhombic forms as arragonite; titanium oxide assumes two distinct quadratic forms, one being known as *rutile* the other as *anatase*, and it also crystallises as *brookite* in rhombic prisms; arsenious oxide crystallises in octahedral, antimonious oxide in rhombic, forms, but if amorphous arsenious oxide is heated in a sealed tube so that one part of the tube is at 400° and the rest below this temperature, the oxide deposited in the middle part of the tube is found to be isomorphous with rhombic antimonious oxide; the latter oxide is also known in octahedral forms, so that the *isodimorphism* of these two oxides is complete[1].

[1] *s.* Lehmann, *Zeitschr. f. physikal. Chemie*, **1.** 15.

34 If it is assumed that, as a general rule, those masses of two substances which are crystallographically equivalent have similar chemical constitutions[1]; and if we suppose that the atomic weights are known of the elements which compose one of two compounds exhibiting identical or nearly identical crystalline form, it is evident in what way determinations of crystalline form may aid in fixing atomic weights.

To take an example:—from determinations of the specific gravities of gaseous compounds and analyses of these compounds, the value 52·4 is assigned to the atomic weight of chromium; this number is verified by measurements of the specific heat of the same metal. The green oxide of chromium exhibits the same crystalline form as ferric oxide, hence these oxides should probably be represented by similar formulæ. On comparing the compositions of crystallographically equivalent quantities of the two oxides, it is found that one is composed of $52{\cdot}4 \times 2$ parts by weight of chromium and $15{\cdot}96 \times 3$ parts of oxygen, and the other of the same mass of oxygen combined with $55{\cdot}9 \times 2$ parts by weight of iron. Now the atomic weight of chromium has been determined to be 52·4, and the atomic weight of oxygen is known to be 15·96; hence the simplest formula that can be given to the green oxide of chromium is Cr_2O_3; and hence the probable formula of ferric oxide is Fe_2O_3. But if the latter formula is correct it follows that 2 atoms of chromium are replaced from one reacting weight of the oxide Cr_2O_3 by 2 atoms of iron. If this conclusion is granted, the atomic weight of iron is 55·9. As the specific heat of iron multiplied into 55·9 gives the product 6·4, 55·9 is almost certainly the true atomic weight of iron. Again, the formulæ of potassium perchlorate and permanganate were at one time written $KO.ClO_7$ and $KO.Mn_2O_7$. Berzelius proposed the formulæ $KO.ClO_7$ and $KO.MnO_7$, which on the system of notation now adopted become $KClO_4$ and $KMnO_4$ respectively; these formulæ represent crystallographically equivalent quantities of the two salts; if it is assumed that Cl (35·37) represents the weight of the atom of

[1] See note 1. p. 70.

chlorine, then Mn (55) probably represents the weight of the atom of manganese.

Observations of crystalline form have sometimes led the way to correct determinations of atomic weights, or to changes in the received values of such weights. Thus H. Rose[1] gave the name of hyponiobium to a supposed allotropic form of the metal niobium; but Marignac[2] shewed that compounds of the hypothetical metal were identical in crystalline form with certain compounds of tin and titanium, and concluded that Rose's hyponiobium was itself isomorphous with the atomic groups SnF and TiF, and was therefore probably a compound. Further experiments shewed that the hyponiobium of Rose was really composed of niobium and oxygen in the proportions expressed by the formula NbO (Nb = 94); now if it was admitted that the groups of atoms NbO, SnF, and TiF, were crystallographically equivalent, it followed, from the analyses of the various compounds, that one atom of tin or titanium (117·8 or 48 parts by weight respectively) was replaced by 94 parts by weight of niobium, and that this number therefore represented the weight of the atom of niobium[3].

Again, the isomorphism of the double compound of gallium and ammonium sulphates with ordinary ammonia-alum shewed that the former salt was a true alum; hence the formula $X_2 3SO_4 . (NH_4)_2SO_4 . 24H_2O$ was applicable to the salt in question. But in the case of common alum $X_2 = Al_2 = 2 \times 27{\cdot}02$; and in the case of gallium alum $X_2 = 138$: hence, as two atoms of aluminium were replaced by 138 parts by weight of gallium, it followed that the atomic weight of gallium was $\frac{138}{2} = 69$. This number was confirmed by the analysis of gaseous gallium chloride.

[1] *Pogg. Ann.* **108.** 273.

[2] *Ann. Chim. Phys.* **60.** 257.

[3] Marignac's conclusions were afterwards confirmed by determinations, by Deville and Troost, of the specific gravity of gaseous chloride and oxychloride of niobium: see *Compt. rend.* **69.** 1221.

Roscoe's researches on the atomic weight of vanadium afford a very instructive example of the employment of the results of crystallographic measurements in fixing atomic weights. *Phil. Trans.* for **1868,** I. *et seq.*

The facts of which an outline has been given shew that until more extended and precise knowledge of the connexions between crystalline form and chemical constitution is obtained, that method for determining the atomic weights of elements which is founded on these connexions can be applied only tentatively and in a limited number of cases. The method may however now be of considerable service in suggesting lines of research bearing on the problems connected with atomic weight determinations.

It appears probable that the crystalline form of a substance is connected at once with the internal structure of the molecules of the substance and with the configuration of the molecules themselves. No attempt has been made, nor can in the present state of knowledge hopefully be made in any but the broadest manner, to apply to the facts of crystallography the theory of the molecular structure of matter.

35 Many attempts have been made to determine molecular weights by other physical methods than the three already described. Of these attempts, that made by Raoult has led to important results[1]. This chemist has determined the amount of lowering of the freezing point of water, and various other solvents, produced by dissolving quantities of various compounds proportional to the formula-weights, or reacting weights, of these compounds; he has found that chemically similar compounds generally produce equal lowerings of the freezing points of water and some other solvents.

Let P grams of a compound be dissolved in 100 grams of water, or other solvent, and let the observed lowering of the freezing point be C; then $\frac{C}{P}$ = *coefficient of lowering of freezing point* for the compound in question. If M = molecular weight, or better, formula-weight, of a specified compound, then the product $\frac{C}{P} M$ is called by Raoult *the molecular lowering of freezing point*. $M \frac{C}{P}$ is constant for all the members of the same class of compounds; thus Raoult finds the following values, water being the solvent:—

[1] *s.* especially *Ann. Chim. Phys.* [6] 8. 317.

$M\frac{C}{P}$

19 for organic compounds, except oxalic acid and compound ammoniums;

35 for all salts of monovalent metals with monobasic acids,

e.g. NaCl, $NaC_2H_3O_2$, $NaNO_3$;

40 for all normal salts of monovalent metals with dibasic acids,

e.g. $(NH_4)_2SO_4$, K_2CO_3, K_2CrO_4;

etc. etc. etc.

When benzene was the solvent, Raoult found the values:—

$M\frac{C}{P}$

49 for all organic compounds except acids, alcohols, and phenols;

25 for the lower members of homologous series of alcohols.

Raoult found other constant values when other solvents, e.g. acetic acid, were employed.

If the value of $M\frac{C}{P}$ for a group of compounds is known, it is possible to find the formula-weight of a member of the group from observations of the coefficient of lowering of freezing point of that compound. Thus to take the case of ether.

(i) 4·47 grams of ether were dissolved in 100 grams of water, and the freezing point of the water was lowered by 1°·05; hence $\frac{C}{P}=\frac{1\cdot05}{4\cdot47}=\cdot23°$. But the value of $M\frac{C}{P}$ for organic compounds dissolved in water is 19; therefore in the present case $M=\frac{19}{\cdot23}=82$.

(ii) 2·721 grams of ether dissolved in 100 grams of benzene lowered the freezing point by 1°·826; therefore the coefficient of lowering was $\frac{1\cdot826}{2\cdot721}=\cdot671°$. Now as $M\frac{C}{P}=49$ for the class of compounds of which ether is a member, it follows that $M=\frac{49}{\cdot671}=73$.

(iii) The coefficient of lowering of freezing point of acetic acid for ether was determined to be ·529°.

Experiments had shewn that $M\frac{C}{P} = 39$ for all organic and many inorganic compounds; hence in the present case

$$M = \frac{39}{\cdot 529} = 74.$$

The mean of the three results gives the value 76·6 for the formula-weight of ether; the correct value is 74.

This method is of wide application for determining the reacting (or formula) weights of compounds, and is especially useful as it is applicable to bodies which cannot be gasified without decomposition.

36 I have endeavoured to shew that the most trustworthy method for determining molecular and atomic weights is founded on Avogadro's law, which is itself an outcome of the application of dynamical reasoning to a physical theory. Formerly it was supposed that strictly chemical evidence must be of paramount importance in determining these quantities. Although the superior importance of Avogadro's law is now admitted, this law can only be applied to a limited number of substances, hence we are frequently obliged to have recourse to purely chemical evidence in support of this or that molecular weight. The nature of such chemical evidence, and the modifications in the physical conception of molecular weight to which it leads, must now be shortly illustrated.

In 1850 Brodie[1] endeavoured to shew that there is no difference of kind between those reactions wherein elementary bodies are produced, or react, and those in which compound bodies are alone concerned. He supposed that the small particles of elementary substances set free during reactions, or taking part in reactions, are composed of smaller parts which exhibit certain mutual polar relations. Silver chloride is not decomposed by oxygen, but it readily interacts with potassium oxide with production of silver oxide and potassium chloride; hydriodic and iodic acids decompose one another with production of free iodine; silver oxide decomposes hydrogen peroxide to form silver, water, and free

[1] *Phil. Trans.* for **1850**, 759, and also *C. S. Journal*, **4**. 194.

oxygen, half of the oxygen coming from the silver oxide and half from the peroxide; iodine decomposes barium peroxide with production of barium iodide and oxygen. These reactions were thus written by Brodie (translating into the new notation):—

(1) $\overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{Ag}}\overset{+}{\mathrm{Cl}}\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{K}}\overset{+}{\mathrm{O}} = \overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{Ag}}\overset{+}{\mathrm{O}} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{K}}\overset{+}{\mathrm{Cl}}\overset{-}{\mathrm{Cl}}$

(2) $\overset{+}{\mathrm{H}}\overset{-}{\mathrm{I}}\overset{-}{\mathrm{O}}_3 + 5\overset{(+\text{and}}{\overset{+}{\mathrm{H}}}\overset{-)}{\overset{-}{\mathrm{I}}} = 3\overset{+}{\mathrm{H}}_2\overset{-}{\mathrm{O}} + 3\overset{+}{\mathrm{I}}\overset{-}{\mathrm{I}}$

(3) $\overset{+}{\mathrm{H}}_2\overset{-}{\mathrm{O}}\overset{+}{\mathrm{O}} + \overset{-}{\mathrm{Ag}}\overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{O}} = \overset{+}{\mathrm{H}}_2\overset{-}{\mathrm{O}} + \overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{Ag}} + \overset{+}{\mathrm{O}}\overset{-}{\mathrm{O}}$

(4) $\overset{+}{\mathrm{Ba}}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{O}} + \overset{+}{\mathrm{I}}\overset{-}{\mathrm{I}} = \overset{+}{\mathrm{Ba}}\overset{-}{\mathrm{I}}\overset{+}{\mathrm{I}} + \overset{-}{\mathrm{O}}\overset{+}{\mathrm{O}}.$

That part of Brodie's hypothesis which supposed a polar condition of atoms in molecules was not generally adopted by other chemists, but it was admitted that his researches established a general similarity of function and composition between elementary and compound molecules.

In the same year Williamson[1] distinguished between the atom of zinc in combination, and the free metal zinc (that is to say, he recognised that the atom of an element is not possessed of the same properties as the molecule of that element): he said it is not quite accurate to speak of 'zinc' as existing in zinc sulphate.

Recognising then that chemical reactions took place between molecules, chemists defined the molecule as the smallest part of a substance capable of taking part in a chemical change, or as the acting chemical unit. Supposing the atomic weights of the elements forming a compound to be known, the best method of determining the molecular weight of the compound appeared to be to find that formula which should express the atomic composition in the simplest manner. Thus ammonia is formed by the combination of hydrogen and nitrogen in the proportion of 3 parts by weight of the former to 14 of the latter; assuming the atomic weights of these elements to be 1 and 14 respectively, the atomic composition of ammonia may be represented by the formula NH_3. As the reactions in which this substance takes part might all be represented as involving 17, or a whole multiple of 17,

[1] *C. S. Journal*, **4**. 355.

parts by weight of this compound, and moreover as hydrogen could be removed from 17 parts by weight of ammonia in three separate and equal parts by chemical reactions, 17 was taken to be the molecular weight of ammonia.

An instructive illustration of this method of fixing a minimum molecular weight is furnished by Williamson's famous researches on ethers[1]. The formulæ generally adopted for common alcohol and ether, previous to Williamson's work, were $C_4H_6O_2$ and C_4H_5O respectively (C = 6; O = 8). Williamson allowed ethylic iodide to react on potassium alcoholate, expecting that ethylated alcohol would be produced—thus $C_4H_5KO_2 + C_4H_5I$ should give $C_4H_5(C_4H_5)O_2 + KI$—but the product was ordinary ether. If the generally accepted formula for ether were doubled the reaction would be explained, and ether would be regarded as an oxide of ethyl $(C_4H_5)_2O_2$. Again, Williamson found that when sulphuric acid acts on ethylic alcohol, and methylic alcohol is added to the mixture, a single substance having the properties of an ether, and the formula C_3H_4O or a whole multiple of this formula, distils over. If the formula of ether is C_4H_5O, then that of methylic ether is C_2H_3O, and a mixture of these ought to be obtained in the reaction just mentioned; but if ether is $(C_4H_5)_2O_2$, then the single ether obtained is probably methyl-ethyl oxide[2], i.e. $C_4H_5(C_2H_3)O_2$ $(= 2C_3H_4O)$. Thus was shewn, on purely chemical grounds, the necessity of doubling the generally accepted molecular formula for ether.

No purely chemical method capable of general application has been found for determining molecular weights; each compound must be considered as a separate problem. The more important methods may however be roughly classified.

There is the method of analogies, which is well illustrated by the example of ether already considered. The smallest amount of sulphuretted hydrogen which takes part in chemical changes is represented by the formula H_2S (assuming S = 32), the hydrogen in this compound is replaceable in two

[1] See *C. S. Journal*, **4**. 106, and 229.

[2] Translated into modern notation, these formulæ become $(C_2H_5)_2O$ and $C_2H_5(CH_3)O$ respectively.

parts—with production of KHS and KKS—hence the molecular formula is not less than H_2S. But compounds of selenion and tellurium with hydrogen, analogous in general properties to sulphuretted hydrogen, are known; from the marked similarity between these two elements and sulphur it is very probable that the molecular formulæ of the two compounds in question are H_2Se and H_2Te respectively: as these formulæ satisfy the analytical numbers, they may be adopted. The simplest formula that can be given to acetic acid—consistently with the values H = 1, C = 12, and O = 16—is CH_2O. But if this acid is neutralised by soda and the sodium salt thus produced is analysed, it is found that this salt contains one atom of sodium (the atomic weight of sodium is assumed to be known, = 23) in combination with three-fourths of the quantity of hydrogen present in the original acid, the quantities of carbon and oxygen being unchanged. Hence, it is argued, one-fourth of the total hydrogen of the acid has been replaced by sodium; but not less than one atom of hydrogen (or another element) can be removed from a molecule; hence, as one atom of hydrogen out of four atoms has been replaced by sodium, it follows that the molecule of acetic acid contains at least four atoms of hydrogen. But, in order to express this conclusion, the formula of the acid must be written $C_2H_4O_2$; and therefore the minimum molecular weight of acetic acid is 60. This conclusion is confirmed by the preparation of thiacetic acid, which is composed of 16 parts by weight of oxygen (i.e. one atom) less than enters into the composition of acetic acid, the quantities of carbon and hydrogen remaining the same, and 32 parts by weight of sulphur. Now if the atomic weight of sulphur is known to be 32, it follows that the minimum molecular weight of acetic acid is expressed by the formula $C_2H_4O_2$, and that of thiacetic acid by the formula C_2H_4OS.

The formula for water was once written HO. If potassium is thrown on to water hydrogen is evolved, and the solid product of the reaction is a white salt whose composition may be expressed by the formula HO . KO (O = 8). But this substance is undecomposed by heat, and it exhibits none of the reactions which a compound of water with a

metallic oxide might be expected to possess, nevertheless it is composed of hydrogen, oxygen, and potassium; when it is fused with potassium, hydrogen is evolved and potassium oxide remains. The oxygen of this compound cannot be removed in parts. If the molecular formula of water is written H_2O (O = 16) these facts are explained; the white solid then becomes KOH, and this formula—as the minimum molecular formula of the compound—is confirmed by the close analogies which exist between the properties of this body and those of alcohol, the molecular formula of which has been determined to be $(C_2H_5)OH$. If steam reacts with chlorine or bromine oxygen is evolved, and a compound of hydrogen and chlorine (or bromine) is produced, the simplest formula for which is HCl (or HBr); no compound of oxygen, hydrogen, and chlorine (or bromine) is formed and oxygen at the same time evolved. Hence, it is argued, the hydrogen in the molecule of water is divisible in chemical changes into two parts, but the oxygen is not divisible, and hence, the simplest molecular formula for water is H_2O; but if this is so, the atomic weight of oxygen cannot be less than 16.

The following generalisation is quoted from Horstmann[1].

"When we know that $\frac{1}{n}$ of a constituent of a molecule can be replaced by another constituent, the composition of the molecule remaining in other respects unchanged, it follows that the given molecule must contain at least n atoms of the first-named constituent, inasmuch as parts of an atom cannot be removed from a molecule.... If the atomic weight of the replacing constituent is known the minimum molecular weight of the original substance can be found, because it is easy to calculate from the empirical composition of the substance how much of the other constituents must be present in combination with n atoms of the replacing body."

Assuming the atomic weights of iron and oxygen to be (in round numbers) 56 and 16 respectively, the formula Fe_2O_3 is deduced from analyses of ferric oxide as representing the smallest quantity of this compound which neutralises one or more reacting weights of various acids, forms double compounds with other oxides &c. the reacting weights of which

[1] *Lehrbuch der physikalischen und theoretischen Chemie. Zweite Abtheilung; Theoretische Chemie (einschliesslich der Thermochemie)* von Dr A. Horstmann (1885), p. 86.

are known, interacts with chlorine to form Fe_2Cl_6, &c.; hence this formula represents the minimum molecular weight of ferric oxide. But similar reasoning leads to As_2O_3 as the minimum molecular formula of arsenious oxide; now we know that the gaseous oxide has a molecular weight expressed by the formula As_4O_6. Hence the method of analogies does not always lead to the adoption of the true molecular weight of a compound.

It should be noted here however that by 'the true molecular weight' is meant the relative weight of the gaseous molecule; but the chemical methods for finding molecular weights only profess to determine the relative weights of the chemically reacting units of bodies.

Sometimes the method of analogies becomes very indirect. Thus, ferric chloride has been gasified and the molecular formula of this compound is known to be Fe_2Cl_6: the simplest formula that can be given to ferrous chloride is $FeCl_2$; is this, or a multiple of this, to be adopted as the molecular formula of ferrous chloride? Ferric chloride is produced by the action of chlorine on ferrous chloride; now the general action of chlorine is either to add itself on to other molecules, or to decompose molecules and then substitute itself for some one or more of the atoms formerly constituting these molecules. If ferrous chloride is $FeCl_2$, the action of chlorine on this molecule is represented by the equation $2FeCl_2 + Cl_2 = Fe_2Cl_6$; but such a reaction as this does not often occur. If ferrous chloride is Fe_2Cl_4, the action of chlorine is represented by the equation $Fe_2Cl_4 + Cl_2 = Fe_2Cl_6$, and this reaction is analogous to other actions of chlorine; hence the molecular formula of ferrous chloride[1] is probably not smaller than Fe_2Cl_4.

The chemical method of determining minimum molecular weights, as applied to acids and bases, generally resolves itself into determining the basicity of the acid, or the acidity of the base. Thus, the results of analyses of sulphuric acid are satisfied by the formula $H_{2x}S_xO_{4x}$; the fact that this acid is

[1] V. Meyer has obtained results regarding the vapour density of ferrous chloride which seem to him to point to the conclusion that, like stannous chloride, this compound possesses two molecular weights expressed respectively by the formulæ $FeCl_2$ and Fe_2Cl_4; *Ber.* **14** 1455; **17.** 1335.

dibasic leads with a fair degree of certainty to the conclusion that $x = 1$, and that the molecular formula[1] of the compound is therefore H_2SO_4. The simplest formula which can be given to citric acid consistently with analytical results, and with the atomic weights C = 12, O = 16, H = 1, is $C_6H_8O_7$; that the molecular formula[1] is probably not greater than this is shewn by the tribasic character of the acid. Reasons have been already given for adopting NH_3 as the true molecular formula of ammonia; analysis shews that the alkaloid quinine cannot have a smaller molecular weight than that represented by the formula $C_{10}H_{12}NO$ (C = 12, H = 1, N = 14, O = 16); but the quantity of this alkaloid which neutralises that amount of hydrochloric acid which is neutralised by NH_3, is $2C_{10}H_{12}NO$; therefore the molecular formula[1] of quinine is probably not less than $C_{20}H_{24}N_2O_2$.

This method may also be applied to determine the formulæ of salts. Thus if sulphuric acid has the molecular formula[1] H_2SO_4, the molecule of sodium sulphate is probably represented by the formula Na_2SO_4, because the atom of sodium being very probably monovalent[2], the amount of sodium 'equivalent' to 2H is represented by 2Na. So, although orthoboric acid is non-volatile, its ethyl salt has been vaporised and found to have the formula $(C_2H_5)_3BO_3$, hence, knowing that ortho-boric acid is tribasic, we deduce for it the probable molecular formula[1] H_3BO_3.

The so-called 'law of even numbers' enunciated by Gerhardt led to the revision of many molecular formulæ: Gerhardt stated that the sum of certain elementary atoms (hydrogen, chlorine and its analogues, nitrogen and its analogues) contained in any molecule is always an even number[3]. Thus, analysis leads to the formula $C_2H_3O_3$ for tartaric acid, and as the acid is dibasic this formula is apparently molecular; but the hydrogen atoms must be expressed by an even number according to Gerhardt's law, therefore the

[1] That is, the formula expressing the smallest mass of the body capable of taking part in a chemical change.

[2] That is, capable of combining directly with not more than one atom of hydrogen, chlorine, bromine, iodine, or fluorine, to form a compound molecule. See chap. II., pars. 56, 57.

[3] See Laurent, *Chemical Method*, p. 46 *et seq.*

formula was doubled. Similar reasoning applied to the formula of nitric oxide would require this to be written N_2O_2; but we know that the molecular formula of this compound is NO; hence Gerhardt's 'law' must be applied with care[1].

37 The chemical methods for determining reacting weights and atomic weights differ in two main particulars from the physical method for determining molecular and atomic weights which is based on the molecular theory.

The chemical methods as a class do not attempt to distinguish between solids, liquids, and gases; so far as the application of these methods is concerned the reacting weight of a solid, liquid, or gaseous, substance is the smallest mass of that substance which takes part in a chemical reaction: the physical method for finding molecular weights is strictly applicable only to gases; but the terms in which the physical definition of molecule is stated are much more precise than those which describe the chemical conception of reacting weight.

The chemical methods sometimes attempt to determine the atomic weights of the elements which form a specified compound, and from these and other data to deduce the reacting weight of the compound; sometimes the reacting weight of the compound is first determined, and then deductions are drawn regarding the atomic weights of the constituent elements. The physical method, on the other hand, begins by defining molecule, and then, applying this definition to chemical reactions, arrives at a definition of atom, both definitions being so stated as to indicate the data which are required before the relative weights of either atoms or molecules can be determined.

38 In the following table I have sought to summarise many facts concerning the atomic weights of the elements: it is well that the student should have placed before him a synopsis of the evidence on which these all-important numbers are based.

[1] For further examples of the application of chemical methods to determinations of molecular and atomic weights see Watts's *Dict.* (1st Ed.) vol. 1. pp. 457—8 and 460—1; also Williamson 'On the Atomic Theory,' *C. S. Journal*, **22**. 328. See also Chapter III. of this Book, *The Periodic Law*.

Atomic Weights of the Elements.

I *Element*	II *Principal compounds, vapour densities of which have been determined*	III *Specific heat: how determined*	IV *Isomorphism: compounds compared* [See note *A*, p 92
HYDROGEN	HF, HCl, HBr, HI, H_2S, H_2Se, H_2Te, H_3N, H_3P, H_4C, &c	indirectly [from sp heat of H_2O, NH_4Cl, NH_4NO_3] [atomic heat abnormal[9]]	—
LITHIUM	none	directly	Li compounds with analogous compounds of alkali metals
BERYLLIUM	$BeBr_2$, $BeCl_2$	directly: sp. heat varies much with temperature	a few Be compounds with analogous compounds of Cd and Zn
BORON	BF_3, BCl_3, BBr_3, $B(CH_3)_3$	directly. sp heat varies much with temperature	—
CARBON	CH_4, CH_3F, CH_3Cl, CH_3Br, CH_3I, $CHCl_3$, CO, CO_2, $COCl_2$, COS, CS_2, CHN, C_2H_6O, $C_4H_{10}O$, &c	directly sp heat varies much with temperature	CN compounds with those of F, Cl, Br and I
NITROGEN	NH_3, NO, NO_2, NOCl, N_2O, N_2O_4, &c.	indirectly. very undecided [from sp. ht of various compounds]	NH_4 compounds with those of alkali metals
OXYGEN	OH_2, ON_2, OC, OCl_2P, O_2C, O_2S, O_3S, O_4Os, &c	indirectly: very undecided [from sp ht. of various compounds]	—
FLUORINE	FH, $F(CH_3)$, F_3B, F_4Si, F_5P, &c	indirectly: very undecided [from sp ht. of CaF_2, &c]	metallic fluorides with analogous compounds of Cl, Br and I
SODIUM	none	directly	Na compounds with those of other alkali metals
MAGNESIUM	none	directly	Mg compounds generally with those of Zn, Mn, and Fe (in ferrous salts)
ALUMINIUM	$AlCl_3$, Al_2Br_6, Al_2I_6	directly	with Cr, Mn, and Fe in R_2O_3 and derivatives
SILICON	SiF_4, $SiCl_4$, SiI_4, $Si(CH_3)_4$, SiH_3Cl, Si_2OCl_6, $Si_2O(C_2H_5)_6$	directly. sp ht varies much with temperature	with C, Zr, Sn, and Ti in compounds of type RO_2
PHOSPHORUS	PH_3, PCl_3, PI_3, PF_5, $POCl_3$ $PSCl_3$, P_2I_4, P_2H_4, $P_3N_3Cl_6$, &c	directly	phosphates with vanadates and arsenates, organic compounds of P with those of N, As, and Sb
SULPHUR	SH_2, SO_2, SO_3, $SOCl_2$, S_2C, S_2Cl_2, &c	directly	with Se compounds, with Te compounds of type RTe Salts of H_2SO_4 with those of H_2SeO_4 and H_2TeO_4
CHLORINE	ClH, $Cl(CH_3)$, ClI, Cl_2Zn, Cl_2Hg, Cl_3HC, Cl_3Bi, Cl_3Sb, Cl_4C, Cl_4Si, Cl_4Ti, Cl_5Ta, Cl_6Mo, Cl_6W, &c	indirectly. doubtful [from comparison of specific heats of various haloid compounds]	Chlorides, with analogous compounds of Br and I
POTASSIUM	KI	directly	K compounds with those of other alkali metals
CALCIUM	none	directly	Ca compounds with those of Sr, Ba, and in some cases Pb
SCANDIUM	none	sp. heats of some compounds determined	[? Sc compounds with those of other earth metals]
TITANIUM	$TiCl_4$	directly	TiO_2 and some derivatives with analogous compounds of C, Si, Zr, Sn, and Th
VANADIUM	VCl_4, $VOCl_3$	sp heats of one or two compounds determined	Vanadates with phosphates and arsenates

Atomic Weights of the Elements.

V *Atomic weight* (1) *by vapour density method*	V *Atomic weight* (2) *by sp. heat method*	VI *Compounds analysed, &c. in order to find combining weight of the element* [See note *B*, p 92]	VII *Combining weight*	VIII *Remarks* [See note *C*, p 92
[for more details concerning these numbers see Tables, pp 39—44 and pp 51—53.]				
1				
—	7 01	[1] Lithium chloride	7'01	
9'08	9'08	[2] Beryllium sulphate	4'54	
10'95	10'95	[3] Borax, boron chloride	3'65	
11'97	11'97	[4] Diamond burnt to CO_2	2'99	
14'01	— —	[5] Ammonium chloride, silver nitrate	4 67	
15'96	—	[6] Synthesis of water	7'98	
19'1	—	[7] Sodium fluoride, potassium fluoride, calcium fluoride	19'1	
—	23	[8] Sodium chloride	23	
—	24	[9] Magnesium sulphate, do chloride, synthesis of magnesium sulphate	12	
27'02	27 02	[10] Ammonia alum, aluminium bromide, solution of aluminium in soda	9 007	
28'3	28'3	[11] Silicon chloride; decomposition of silicon bromide by water	7'08	
30'96	30'96	[12] Phosphorus chloride, synthesis of phosphorus pentoxide	10'32	
31'98	31 98	[13] Synthesis of silver sulphide, reduction of silver sulphate by hydrogen	10'66	
35'37	— —	[14] Potassium chlorate, synthesis of silver chloride	35'37	
39 04	39'04	[15] Potassium chloride, do. bromide	39'04	
—	39'9	[16] Calcium chloride, calcium carbonate	19'95	
—	—	[17] Synthesis of scandium sulphate	14'68	*Sc* The atomic weight of this metal is most probably $14'68 \times 3 = 44'04$: if this is so, the oxide is Sc_2O_3, and is analogous with the oxides of the earth metals
48	48	[18] Titanium chloride, bromide and oxide	12	
51 2	—	[19] Vanadium pentoxide, do oxychloride	12'8	

Atomic Weights of the Elements.

I *Element*	II *Principal compounds, vapour densities of which have been determined*	III *Specific heat: how determined*	IV *Isomorphism: compounds compared* [See note *A*, p. 92.]
CHROMIUM	CrO_2Cl_2, $CrCl_3$	directly [? too low]	Salts of H_2CrO_4 with those of H_2MnO_4 and H_2TeO_4, Cr_2O_3 with Al_2O_3 Mn_2O_3 and Fe_2O_3
MANGANESE	$MnCl_2$	directly [? too high]	Mn_2O_3 with Al_2O_3 Cr_2O_3 and Fe_2O_3, R_2MnO_4 with R_2CrO_4 and R_2TeO_4, $RMnO_4$ with $RClO_4$
IRON	Fe_2Cl_6	directly	Fe_2O_3 and derivatives with Al_2O_3 Cr_2O_3 Mn_2O_3 and derivatives, some Fe salts with those of Ni Co and Cu
NICKEL	none	directly	Ni with Co compounds, some Ni compounds with those of Fe (ferrous salts)
COBALT	none	directly	Co with Ni compounds, some Co compounds with those of Fe (ferrous salts)
COPPER	Cu_2Cl_2	directly	most Cu compounds with those of Ni and Co, some with Fe (ferrous) compounds, Cu with Ag compounds of type R_2O
ZINC	$ZnCl_2$, $Zn(CH_3)_2$, $Zn(C_2H_5)_2$	directly	Zn compounds with those of Mg and Mn
GALLIUM	Ga_2Cl_6	directly [? too low]	Ga alum with other alums
GERMANIUM	$GeCl_4$, GeI_4, GeS	directly: sp heat becomes constant only at high temperature	
ARSENIC	AsH_3, $AsCl_3$, AsI_3, $As(CH_3)_2Cl$, As_4O_6, &c	directly	As compounds with those of Sb and Bi, organic compounds of As with those of N P and Sb, arsenates with phosphates and vanadates
SELENION	SeH_2, SeO_2	directly	Se with S compounds
BROMINE	BrH, $Br(CH_3)$, Br_2Cd, Br_3B, Br_4Sn, Br_4U, &c	directly	Bromides with analogous compounds of Cl and I
RUBIDIUM	RbCl, RbI	indirectly: doubtful [from comparison of specific heats of some compounds with those of other alkali metals]	Rb compounds with those of other alkali metals
STRONTIUM	none	indirectly: doubtful [comparison of specific heats of compounds of Sr, Ca, and Ba]	Sr compounds with those of Ca and Ba, and with some Pb salts
YTTRIUM	none	sp. heats of a few compounds determined	Yt compounds with those of other earth metals
ZIRCONIUM	$ZrCl_4$	directly [? too low]	ZrO_2 with TiO_2 ThO_2 SnO_2 and SiO_2
NIOBIUM	$NbCl_5$, $NbOCl_3$	——	Nb with Ta compounds, Nb fluorides and oxyfluorides with Mo do do
MOLYBDENUM	$MoCl_5$	directly [? too high]	Mo with W compounds, some salts of H_2MoO_4 with those of H_2CrO_4, Mo with Nb fluorides and oxyfluorides

Atomic Weights of the Elements.

V *Atomic weight* (1) *by vapour density method*	V *Atomic weight* (2) *by sp. heat method*	VI *Compounds analysed, &c. in order to find combining weight of the element* [See note *B*, p 92.]	VII *Combining weight*	VIII *Remarks* [See note *C*, p 92.]
for more details concerning these numbers see Tables, pp 39—44 and pp 51—53.]				
52·4	52·4	[20] Chromium chloride, silver chromate, potassium dichromate	26 2	
55	55	[21] Manganese chloride, manganous-manganic oxide, manganous oxalate, silver permanganate, &c	27·5	
55 9 [see p. 60]	55 9	[22] Synthesis of ferric oxide, reduction of ferric oxide, analysis of ferrous and ferric chlorides	27 95	
——	58 6	[23] Nickel chloride, nickelous oxide, strychnine-nickel cyanide brucine-nickel cyanide, &c	29·3	
——	59	[24] Ammonium-cobalt cyanide, phenyl-ammonium cobalt cyanide, strychnine and brucine-cobalt cyanides	29 5	
63 4 [see p 60]	63·4	[25] Reduction of copper oxide, electrolysis of copper sulphate, &c	31·7	
65 48	65·48	[26] Synthesis of zinc oxide, analysis of potassium-zinc chloride, solution of zinc in acid	32·74	
69 [see p 60]	69	[27] Oxidation of the metal, analysis of gallium-ammonia alum	23	
72·3	72 3	[27a] Germanium chloride	18·08	
74 9	74 9	[28] Arsenic bromide, do chloride, do oxide	24 97	
78·8	78 8	[29] Reduction of selenion dioxide, reduction of silver selenite	39 4	
79·75	70·75	[30] Synthesis of silver bromide, analysis of potassium bromide	79 75	
85 2	— ·	[31] Rubidium chloride	85 2	
——	——	[32] Strontium chloride	43 65	*Sr* The atomic weight of strontium must be taken as 43 65×2=87 3 if the formulæ of its salts are to become analogous to those of the Ba and Ca salts
——	——	[33] Synthesis of yttrium sulphate	29 87	*Yt* Atomic weight probably =29 87 ×3=89 6 because of analogy of Yt salts with those of the earth metals
90	90	[34] Zirconium chloride, potassium zirconium fluoride	45	
94	——	[35] Niobium chloride, potassium niobium oxyfluoride	31 32	
95 8	95 8	[36] Molybdenum dichloride, tetra chloride, and pentachloride	19·16	

Atomic Weights of the Elements.

I	II	III	IV
Element	*Principal compounds, vapour densities of which have been determined*	*Specific heat: how determined*	*Isomorphism: compounds compared* [See note A, p 92]
RHODIUM	none	directly	most Rh compounds with those of Ru, Pd, Ir, Pt, and Os
RUTHENIUM	none	directly	most Ru compounds with those of Rh, Pd, Ir, Pt, and Os
PALLADIUM	none	directly	most Pd compounds with those of Ru, Rh, Ir, Pt, and Os
SILVER	AgCl	directly	some Ag compounds with those of Na and other alkali metals, Ag with Cu compounds of type R_2O, a few Ag and Au compounds
CADMIUM	$CdBr_2$	directly	some Cd compounds with those of Be and Zn
INDIUM	$InCl_3$	directly	some In compounds with those of Cd and Be
TIN	$SnCl_2$, $SnCl_4$, Sn_2Cl_4	directly	SnO_2 with TiO_2 ZrO_2 and ThO_2
ANTIMONY	$SbCl_3$, SbI_3, $SbBr_3$, $Sb(CH_3)_3$, Sb_4O_6	directly	Sb compounds with those of As and Bi
TELLURIUM	TeH_2, $TeCl_4$, $TeCl_2$	directly	most Te compounds with those of S and Se
IODINE	IH, ICl, $I(CH_3)_3$, I_2P_4, I_2Hg, I_3P, I_3As, I_3Sb, I_6Al_2, &c.	directly	Iodides with analogous compounds of Cl and Br
CÆSIUM	CsCl, CsI	indirectly doubtful [comparison of specific heats of compounds with those of other alkali metals]	Cs compounds with those of other metals of alkalis
BARIUM	none	indirectly doubtful [comparison of specific heats of compounds of Ca, Sr, and Ba]	Ba compounds with those of Ca and Sr
LANTHANUM	none	directly	most La compounds with those of Ce, Di, Er and Yt, some compounds of these metals with Ca compounds
CERIUM	none	directly	
DIDYMIUM	none	directly	
ERBIUM	none	sp heats of a few compounds determined	
YTTERBIUM	none	sp heats of a few compounds determined	[? a few Yb compounds with those of other earth metals]
TANTALUM	$TaCl_5$	——	Ta with Nb compounds
TUNGSTEN	$WOCl_4$, WCl_5, WCl_6	directly	W with Mo compounds, some salts of H_2WO_4 with those of H_2CrO_4 and H_2TeO_4
IRIDIUM	none	directly	Os, Ir, and Pt, compounds with those of Ru, Rh, and Pd
OSMIUM	OsO_4	directly	
PLATINUM	none	directly	

Atomic Weights of the Elements.

V *Atomic weight* (1) *by vapour density method* [for more details concerning these numbers see Tables, pp. 39—44 and pp 51—53]	V *Atomic weight* (2) *by sp. heat method*	VI *Compounds analysed, &c. in order to find combining weight of the element* [See note *B*, p. 92]	VII *Combining weight*	VIII *Remarks* [See note *C*, p 92]
——	104	[37] Potassium-rhodium chloride	26	
	(103)	([37a] Purpureo-rhodium chloro-and bromo-compounds)	(25 75)	
——	104·5	[38] Potassium-ruthenium chloride	26·1	
——	106·2	[39] Palladium chloride	26·55	
107 66	107·66	[40] Silver chlorate, bromate, iodate, synthesis of silver bromide and iodide	107·66	
112	112	[41] Cadmium bromide	56	
113 4	113·4	[42] Synthesis of indium oxide	37 8	
117 8	117 8	[43] Synthesis of stannic oxide	58·9	
120	120	[44] Antimony bromide, reduction of antimony oxide, also analysis of antimony sulphide	40	
125	125	[45] Oxidation of tellurium, analysis of potassium-tellurium bromide, synthesis of basic tellurium sulphate and of copper telluride	62·5	
126 53	126 53	[46] Silver iodate, silver iodide, synthesis of do	126 53	
132 7	——	[47] Cæsium chloride	132 7	
——	——	[48] Barium chloride	68 43	*Ba* Atomic weight probably 68 43 ×2−136 86 because of analogies between salts of Ba, Sr, and Ca.
——	138 5	[49] Lanthanum sulphate, do oxide, do oxalate	46 17	
——	139 9	[50] Cerium oxalate, do chloride, do sulphate	46 66	
——	144	[51] Didymium oxide and sulphate	48	
——	(142)	([51a] " " ")	(47 6)	
——	——	[52] Erbium sulphate	55 33	*Er* This metal belongs to the earth group, hence the atomic weight is taken as 55 33×3−166
——	——	[53] Ytterbium sulphate	57 69	*Yb* For similar reasons to those which apply in cases of Sc, Yt, and Er, the atomic weight of Ytterbium is regarded as 3 times its combining weight (−173)
182	——	[54] Potassium-tantalum fluoride ammonium-tantalum fluoride	60 67	
183 6	183 6	[55] Reduction of tungstic oxide, analysis of tungsten hexachloride	30 6	
——	192 5	[56] Potassium-iridium chloride	48·13	
193	193	[57] Osmium tetroxide	48 25	*Os.* The number given is calculated from 2 determinations of vapour density of OsO_4 by Deville and Debray, other experimenters have found numbers for the atomic weight of this metal varying from 195 to 199.
——	194 3	[58] Potassium-platinum chloride, platinum tetrachloride and bromide, &c.	48 57	

Atomic Weights of the Elements.

I	II	III	IV
Element	*Principal compounds, vapour densities of which have been determined*	*Specific heat: how determined*	*Isomorphism: compounds compared* [See note *A*, p. 92]
GOLD	none	directly	some Au compounds with those of Ag, a few Au compounds with those of Ni and Fe
MERCURY	[HgCl] $HgCl_2$, HgI_2, $Hg(CH_3)_2$, &c.	directly	Hg and Cu compounds of type RO
THALLIUM	TlCl	directly	Tl compounds with those of Pb of type RCl_2, Tl compounds of type TlCl with those of alkali metals
LEAD	$PbCl_2$, $Pb(CH_3)_4$	directly	some Pb with Tl compounds, many Pb with Cu and Hg compounds
BISMUTH	$BiCl_3$	directly	Bi compounds with those of As and Sb
THORIUM	$ThCl_4$	directly	ThO_2 with SiO_2 TiO_2 SnO_2 and ZrO_2
URANIUM	UCl_4, UBr_4	directly	some compounds of type U_2O_3 with those of Al, Cr, Mn, and Fe

Notes to Table of Atomic Weights.

A. As the method based on isomorphism of compounds is chiefly used as a means of verifying values assigned to atomic weights by other methods, no numbers are given in column IV., but merely an indication of the various compounds which have been compared crystallographically, and on which arguments for or against a given value for the atomic weights in column V. have been, or may be, based.

B. This column (VI.) is not to be regarded as containing anything like a complete summary of the processes employed for determining the combining numbers of the elements; only the more important processes are indicated;—references are given to the original papers. References to the papers on the spec. heats of the elements will be found on pp. 53—54.

A complete account of all researches on this subject will be found in *A Recalculation of the Atomic Weights*, by F. W. Clarke [Part V. of the *Constants of Nature* published by the Smithsonian Institution], and also in *Die Atomgewichte der Elemente*, by L. Meyer and K. Seubert [Leipzig, 1883].

C. When the atomic weight given in column V. section (2) is a multiple of the combining number in column VII., no number being given in section (1) of column V., it is to be inferred that, besides the argument drawn from the value of the specific heat of the element in question, there are other chemical reasons for adopting the special multiple which appears in V. (2). These reasons may be broadly described as based on analogies between salts of the given element and salts of other elements the atomic weights of which have been established by the two leading physical methods.

Atomic Weights of the Elements.

V *Atomic weight* (1) *by vapour density method* [for more details concerning these numbers see Tables, pp. 39—44 and pp. 51—53]	V *Atomic weight* (2) *by sp. heat method*	VI *Compounds analysed, &c. in order to find combining weight of the element* [See note *B*, p. 92.]	VII *Combining weight*	VIII *Remarks* [See note *C*, p. 92.]
——	197	[59] Gold chloride, potassium-gold chloride, potassium-gold bromide	65·66	
199·8	199 8	[60] Mercuric chloride, do. oxide	99·9	
203 64	203 64	[61] Synthesis of thallium nitrate	203 64	
206 4	206 4	[62] Synthesis of lead nitrate, do do sulphate	103 2	
208	208	[63] Synthesis of bismuthous oxide, &c., analysis of bismuthous chloride	69·33	
231 87	231 87	[64] Thorium sulphate	57 97	
240	240	[65] Uranium acetate, do oxalate	60	

References to Table of Atomic Weights.

[1] *Li.* J. W. MALLET, *Sill. Amer. Journal* (2) **22.** 349. STAS, *Nouvelles Recherches*, pp. 268 and 274.

[2] *Be.* NILSON and PETTERSSON, *Ber.* **13.** 1451.

[3] *B.* BERZELIUS, *Pogg. Ann.* **2.** 129. DEVILLE, *Ann. Chim. Phys.* (3) **55.** 180.

[4] *C.* DUMAS and STAS, *Ann. Chim. Phys.* (3) **1.** 5. ERDMANN and MARCHAND, *J. fur prakt. Chemie.* **23.** 159. ROSCOE, *Compt. rend.* **94.** 1180.

[5] *N.* STAS, *Rapports*, pp. 50, 87, 92; and *Nouvelles Recherches*, pp. 57, 281.

[6] *O.* ERDMANN and MARCHAND, *J. fur prakt. Chemie*, **26.** 468. DUMAS, *Ann. Chim. Phys.* (3) **8.** 189. KEISER, *Ber.* **20.** 2323. COOKE and RICHARDS, *Proc. Amer. Acad. of Arts and Sci.* **23.** 149.

[7] *F.* LOUYET, *Ann. Chim. Phys.* (3) **25.** 291. DUMAS, do. (3) **55.** 170. DE LUCA, *Compt. rend.* **51.** 299.

[8] *Na.* PELOUZE, *Compt. rend.* **20.** 1050. DUMAS, *Ann. Chim. Phys.* (3) **55.** 182. STAS, *Rapports*, p. 78; and *Nouvelles Recherches*, p. 248.

[9] *Mg.* JACQUELAIN, *Ann. Chim. Phys.* (3) **32.** 202. BAHR, *J. fur prakt. Chemie*, **56.** 310. DUMAS, *Ann. Chim. Phys.* (3) **55.** 187. MARIGNAC, *Archiv. Scien. Phys. nat.* (3) **10.** 5, 193.

[10] *Al.* J. W. MALLET, *Phil. Trans. for* **1880.** 1003 *et seq.*

[11] *Si.* PELOUZE, *Compt. rend.* **20.** 1052. DUMAS. *Ann. Chim. Phys.* (3) **55.** 183. J. SCHIEL, *Annalen*, **120.** 94. THORPE and YOUNG, *C. S. Journal*, **51.** 576.

[12] *P.* PELOUZE, *Compt. rend.* **20.** 1053. SCHROTTER, *Ann. Chim. Phys.* (3) **38.** 131. DUMAS, *Ann. Chim. Phys.* (3) **55.** 172.

[13] *S.* STAS, *Rapports*, p. 53.

[14] *Cl.* STAS, *Rapports*, pp. 38, 42, 44, 118; and *Nouvelles Recherches*, p. 208.

[15] *K.* STAS, *Rapports*, pp. 69, 91, 118; and *Nouvelles Recherches*, p. 244.

[16] *Ca.* BERZELIUS, *Pogg. Ann.* **8.** 189. DUMAS, *Ann. Chim. Phys.* (3) **55.** 190. ERDMANN and MARCHAND, *Annalen*, **44.** 216: **52.** 210: **76.** 219. SALVÉTAL, *Compt. rend.* **17.** 318.

[17] *Sc.* NILSON, *Ber.* **13.** 1439.

[18] *Ti.* H. ROSE, *Pogg. Ann.* **15.** 145. J. PIERRE, *Ann. Chim. Phys.* (3) **20.** 257. THORPE, *Ber.* **16.** 3014; and (in full) *C. S. Journal*, **Trans.** for **1885.** 108.

[19] *V.* ROSCOE, *Phil. Trans. for* **1868.** 8, 23.

[20] *Cr.* E. PELIGOT, *Ann. Chim. Phys.* (3) **12.** 528. BERLIN, *Annalen*, **56.** 207: **60.** 108 *et seq.* F. KESSLER, *Pogg. Ann.* **95.** 211. SIEWERT, *Zeitschrift fur die gesammten Naturwissenschaften*, **17.** 530.

[21] *Mn.* DUMAS, *Ann. Chim. Phys.* (3) **55.** 150. SCHNEIDER, *Pogg. Ann.* **107.** 605: Id. *Annalen*, **113.** 78. DEWAR and SCOTT, *Proc. R. S.* **35.** 44. MARIGNAC, *Archiv. Scien. Phys. nat.* (3) **10.** 5, 193.

[22] *Fe.* BERZELIUS, *Annalen*, **50.** 432. ERDMANN and MARCHAND, *Annalen*, **52.** 212. L. E. RIVOT, *Annalen*, **78.** 214. DUMAS, *Ann. Chim. Phys* (3) **55.** 157.

[23] *Ni.* DUMAS, *Ann. Chim. Phys.* (3) **55.** 149. RUSSELL, *C. S. Journal* (2) **1.** 51: **7.** 294. SOMARUGA, *Fresenius's Zeitschr.* **6.** 347. R. H. LEE, *Ber.* **4.** 789. BAUBIGNY, *Compt. rend.* **97.** 951.

[24] *Co.* WESELSKY, *Ber.* **2.** 592. R. H. LEE, *Ber.* **4.** 789. RUSSELL, *loc. cit.*

[25] *Cu.* BERZELIUS, *Pogg. Ann.* **8.** 182. ERDMANN and MARCHAND, *J. fur prakt. Chemie*, **31.** 391. W. HAMPE, *Fresenius's Zeitschr.* **13.** 352. BAUBIGNY, *Compt. rend.* **97.** 906. RICHARDS, *Proc. Amer. Acad.* **23.** 177.

[26] *Zn.* GAY-LUSSAC and THENARD, *Gilbert's Annalen*, **37.** 460. BERZELIUS, *Pogg. Ann.* **8.** 184. ERDMANN, Berzelius's *Lehrbuch*, (5th ed.) **3.** 1219. P. A. FAVRE, *Ann. Chim. Phys.* (3) **10.** 163. MARIGNAC, *Archiv. Scien. Phys. nat.* (3) **10.** 5, 193. REYNOLDS and RAMSAY, *C. S. Journal*, **Trans.** for **1887.** 854.

[27] *Ga.* LECOQ DE BOISBAUDRAN, *Compt. rend.* **86.** 941.

[27a] *Ge.* WINKLER, *J. fur prakt. Chemie*, (2) **34.** 177.

[28] *As.* W. WALLACE, *Phil. Mag.* (4) **18.** 279. DUMAS, *Ann. Chim. Phys.* (3) **55.** 174. F. KESSLER, *Pogg. Ann.* **95.** 204.

[29] *Se.* PETTERSSON and EKMAN, *Ber.* **9.** 1210.

[30] *Br.* STAS, *Nouvelles Recherches*, pp. 158, 170 and 199.

[31] *Rb.* BUNSEN, *Pogg. Ann.* **113.** 339. PICCARD, *J. fur prakt. Chemie*, **86.** 453. GODEFFROY, *Annalen*, **181.** 189.

[32] *Sr.* MARIGNAC, *Annalen*, **106.** 168. DUMAS, *Ann. Chim. Phys.* (3) **55.** 191.

[33] *Yt.* CLEVE, *Ber.* **6.** 1467. RAMMELSBERG, *Ber.* **9.** 1580.

[34] *Zr.* HERMANN, *J. fur prakt. Chemie*, **31.** 77. MARIGNAC, *Ann. Chim. Phys.* (3) **60.** 257.

[35] *Nb.* MARIGNAC, *Fresenius's Zeitschr.* **5.** 480.

[36] *Mo.* P. LIECHTI and B. KEMPE, *Annalen*, **169.** 344.

[37] *Rh.* BERZELIUS, *Pogg. Ann.* **13.** 437.

[37a] *Rh.* JORGENSEN, *J. fur prakt. Chemie* (2) **27.** 433.

[38] *Ru.* CLAUS, *Pogg. Ann.* **65.** 218.

[39] *Pd.* BERZELIUS, *Pogg. Ann.* **13.** 442.

[40] *Ag.* STAS, *Rapports*, pp. 38, 42, 44; and *Nouvelles Recherches*, pp. 109, 158, 171, 189, 193, 208.

[41] *Cd.* O. W. HUNTINGTON, *Proc. Amer. Acad. of Arts and Sci.* **17.** 28 [*Chem. News*, **44.** 268].

[42] *In.* C. WINKLER, *J. für prakt. Chemie*, **94.** 8: **102.** 282. BUNSEN, *Pogg. Ann* **141.** 28.

[43] *Sn.* DUMAS, *Ann. Chim. Phys.* (3) **55.** 154.

[44] *Sb.* R. SCHNEIDER, *Über das Atomgewicht des Antimons* (Berlin), 1880. J. P. COOKE, *Proc. Amer. Acad. of Arts and Sci.* **13.** 1: **17.** 13. J. BONGARTZ, *Ber.* **16.** 1942.

[45] *Te.* W. L. WILLS, *C. S. Journal*, **Trans.** for **1879.** 704. BRAUNER, *Ber.* **16.** 3055.

[46] *I.* STAS, *Nouvelles Recherches*, pp. 135, 152, 189, 193.

[47] *Cs.* BUNSEN, *Pogg. Ann.* **119.** 1. JOHNSON and ALLEN, *Sill. Amer. Journal*, (2) **35.** 94. R. GODEFFROY, *Annalen*, **181.** 185.

[48] *Ba.* MARIGNAC, *Annalen*, **68.** 215. DUMAS, *Ann. Chim. Phys.* (3) **55.** 137.

[49] *La.* MARIGNAC, *Ann. Chim. Phys.* (4) **30.** 67. CLEVE, *Bull. Soc. Chim.* **50.** 212· (2) **39.** 151, 289. BRAUNER, *C. S. Journal*, **Trans.** for **1882.** 75.

[50] *Ce.* MARIGNAC, *Annalen*, **68.** 212. H. BUHRIG, *J. für prakt. Chemie* (2) **12.** 222. ROBINSON, *Proc. R. S.* **37.** 150. BRAUNER, *C. S. Journal*, **Trans.** for **1885.** 879.

[51] *Di.* B. BRAUNER, *C. S. Journal*, **Trans.** for **1882** 68.

[51a] *Di.* P. T. CLEVE, *Bull. Soc. Chim.* (2) **39.** 289.

[52] *Er.* P. T. CLEVE, *Compt. rend.* **91.** 381. NILSON, *Ber.* **13.** 1459.

[53] *Yb.* NILSON, *Ber.* **12.** 550: **13.** 1430.

[54] *Ta.* MARIGNAC, *Annalen*, **Supplbd. 4.** 351.

[55] *W.* ROSCOE, *Chem. News*, **25.** 61, 73.

[56] *Ir.* K. SEUBERT, *Ber.* **11.** 1767.

[57] *Os.* DEVILLE and DEBRAY, *Ann. Chim. Phys.* (3) **56.** 403.

[58] *Pt.* K. SEUBERT, *Ber.* **14.** 865. [*Annalen*, **207.** 29.] W. HALBERSTADT, *Ber.* **17.** 2962.

[59] *Au.* BERZELIUS, *Lehrbuch*, (5th ed.) **3.** 1212. JAVAL, *Ann. Chim. Phys.* **17.** 337. LEVOL, *Ann. Chim. Phys.* (3) **30.** 355. THORPE and LAURIE, *C. S. Journal*, **51.** 565.

[60] *Hg.* ERDMANN and MARCHAND, *J. für prakt. Chemie*, **31.** 392. SVANBERG, *J. für prakt. Chemie*, **45.** 468. MILLON, *Ann. Chim. Phys.* (3) **18.** 345.

[61] *Tl.* W. CROOKES, *Phil. Trans.* for **1873.** 277.

[62] *Pb.* STAS, *Rapports*, pp. 101 and 106.

[63] *Bi.* SCHNEIDER, *Pogg. Ann.* **82.** 303. DUMAS, *Ann. Chim. Phys.* (3) **55.** 176. MARIGNAC, *Archiv. Scien. Phys. nat.* (3) **10.** 5, 193. Id. *Ann. Chim. Phys.* (6). 1, 289. LOWE, *Zeitschr. anal. Chemie*, **22.** 498. SCHNEIDER, *J. für prakt. Chemie*, (2) **30.** 237.

[64] *Th.* NILSON, *Ber.* **15.** 2527. KRUSS and NILSON, *Ber.* **20.** 1665.

[65] *U.* PELIGOT, *Ann. Chim. Phys.* (3) **20.** 329.

Note. The full titles of Stas's treatises which are referred to in this table are: (1) *Recherches sur les rapports réciproques des poids atomiques, par J. S. Stas*, Bruxelles, 1860. (2) *Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels, par J. S. Stas*, Bruxelles, 1865. A translation into German of both treatises was published in 1867 under the title *Untersuchungen uber die Gesetze der chemischen Proportionen, uber die Atomgewichte und ihre gegenseitigen Verhaltnisse.*

CHAPTER II.

ATOMIC AND MOLECULAR SYSTEMS.

SECTION I. *Nascent Actions.*

39 WE have now gained the conception of chemical change as consisting in the interaction of molecules, or atomic aggregates. The molecules are sometimes shattered into parts which rearrange themselves to form new molecules, or aggregates of atoms; sometimes new and more complex molecules are formed by the coalescence or combination of less complex molecules.

We have then to examine the properties which the atoms of elements, and the molecules, or the atomic aggregates, of elements and compounds, exhibit in their mutual actions and reactions.

Can a distinction be based on chemical facts between the atoms and the molecules of elements?

What are the chemical properties of the atoms, as distinguished from the molecules, of elements?

When answers have been found to these questions, it will then be necessary to examine the relations between the properties of molecules and the properties of the atoms which compose them.

Brodie applied his hypothesis regarding the structure of elementary molecules (see *ante*, p. 78, par. 36) to explain a number of phenomena generally grouped together under the

name *nascent actions*. That explanation, somewhat simplified and also developed by subsequent research, is usually regarded as the most satisfactory that can be given in the present state of knowledge, when regard is paid to the configurations of the systems exhibiting the phenomena in question.

When hydrogen is passed into water containing silver chloride in suspension no chemical change occurs; when hydrogen is generated in the vessel which contains the silver chloride decomposition of this salt proceeds rapidly with production of silver and hydrochloric acid. Nitrobenzene is converted into aniline by the action of hydrogen produced in contact with it, but not by hydrogen produced in another vessel and conducted into that containing the nitrobenzene. Carbon, hydrogen, and nitrogen do not combine directly; but if electric sparks are passed through a mixture of benzene vapour and nitrogen, hydrocyanic acid is produced. Sulphur dioxide and water when heated with oxygen are only very partially changed into sulphuric acid; but if the oxygen is produced in contact with the moist dioxide (e.g. by decomposition of nitrogen trioxide) the change into sulphuric acid is rapidly completed. Sulphur is not oxidised to sulphuric acid by bromine in presence of water; but if the sulphur is produced from a compound in presence of bromine water, it is then oxidised, e.g. sulphuretted hydrogen passed into bromine water gives hydrobromic acid and sulphur, and also sulphuric acid. Metallic chlorides (e.g. aluminium chloride) produced by the action of metals with chlorine only at very high temperatures, and in small quantities for a given time of action, are sometimes much more easily prepared by the action of chlorine on a mixture of the metallic oxide and carbon. The general reaction of metals with dilute cold sulphuric acid is to produce a sulphate and evolve hydrogen, but with nitric acid to produce a nitrate and evolve oxides of nitrogen, nitrogen, or ammonia; many metals when heated with concentrated sulphuric acid evolve sulphur dioxide, either alone, or in some cases mixed with hydrogen and sulphuretted hydrogen.

40 These phenomena, and many others of the same class,

find a partial explanation in terms of the molecular theory, that explanation being based on the distinction, already insisted on, between molecules and atoms. Any mass of a gaseous element under ordinary conditions is built up of molecules, but if we assume that when a compound molecule undergoes decomposition a short but appreciable time elapses before the greater number of the elementary atoms which composed it have rearranged themselves to form new molecules, we have the materials for a fairly satisfactory explanation, from one point of view, of the phenomena of nascent actions. This explanation does not necessitate, as some of its opponents say it does, the assumption of strange and inexplicable properties as belonging to the elementary atoms. Indeed the occurrence of the phenomena of 'nascent action' seems to follow as a necessary deduction from the molecular theory applied to chemical phenomena. When a chemical reaction occurs between two molecules, the first step in that process must in very many cases consist in a breaking up of the molecular structures, and the second, in a rearrangement of the parts of the molecules, i.e. of the atoms, to form a configuration stable under the conditions of the experiment: and although these changes occur almost simultaneously, nevertheless, if, by the presentation of molecules of a third chemical substance, there is rendered possible the adoption by the various atoms of another configuration, more stable than that just supposed to be assumed, this, the most stable configuration, will be adopted. But if the earlier stable configuration has been assumed by the atoms, it does not follow that the introduction of the third class of molecules will *now* cause this configuration to become unstable[1].

[1] It may be urged that the energy or part of the energy which is set free during the mutual actions of the molecules of the reacting bodies, instead of being run down to the form of heat and so lost to the system, becomes available for performing chemical work; and that the only difference between e.g. ordinary and 'nascent' hydrogen is to be found in the greater chemical energy of the latter. The importance of this point of view is of course admitted by the upholders of the atomic explanation of nascent actions, but they would supplement this by the statement that the configuration with which the greater quantity of energy is associated is atomic, and they contrast this with a molecular and comparatively inactive configuration.

41 Following out this line of argument, it would appear probable that compounds should present phenomena somewhat analogous to those exhibited by elements when in the nascent, i.e. on the hypothesis now adopted the atomic, state Let it be supposed that no chemical change occurred when the compound molecules *a* and *b* were brought into contact, nevertheless if the atoms constituting these molecules were allowed to react a chemical change might occur. In a reaction wherein any given compound is produced there must be a moment of time when this compound can only be said to exist potentially, when the atoms which constitute its molecules have not settled down into stable configurations; at this moment the compound may be said to exist in the nascent state If the atomic vibrations and interactions are allowed to run what may be called their normal course, the compound molecules are certainly produced, but if these interactions are interfered with, a new set of molecules may be formed, which molecules bear a more or less simple genetic relation to those produced in the normal process of the chemical change[1].

The following among other cases of chemical change find a partial explanation in terms of this hypothesis. Nitrous acid has no action on the primary mononitroparaffins ($C_nH_{2n+1}.NO_2$), but these compounds are converted into nitrolic acids ($C_nH_{2n}.N_2O_3$) by the action of potassium nitrite and sulphuric acid, i.e. by the action of reagents which by their mutual decomposition produce nitrous acid. Nitric

The experiments of Victor Meyer on iodine give direct evidence of the separation of elementary molecules into atoms by the addition of energy in the form of heat. (See *ante*, p. 33 par. 15.)

In Book II. chapter II. par. 189, will be found some facts regarding dissociation which bear on the subject of nascent actions.

[1] In all such considerations we can deal with molecular phenomena only by a statistical method, we can reason only as to the average condition of the mass of molecules constituting a substance at any moment of time.

It seems not improbable that there may sometimes be nearly as great differences between the properties of a number of elementary atoms all of one kind and the elementary molecules which are produced by the union of these atoms, as between the properties of a number of atoms of different kinds and the compound molecules produced by the union of these atoms.

acid does not act on napthol to produce dinitronapthol, but if napthol be produced in contact with nitric acid—e.g. by boiling diazonapthalene hydrochloride in presence of nitric acid—dinitronapthol is formed. Carbon monoxide and ethylene do not react to form acroleïn even under the influence of electric sparks, but if ethylene is exploded with a quantity of oxygen less than sufficient for complete oxidation, carbon monoxide is produced and simultaneously acroleïn is formed, i.e. the chemical change proceeds partly in its normal way and at the same time the 'nascent' carbon oxide interacts with the ethylene with production of acroleïn. When paraiodophenol is fused with potash at 163° hydroquinone is produced, but at higher temperatures only resorcin is formed: now as fusing potash does not act on hydroquinone it seems necessary to conclude, that in the fusion of paraiodophenol at high temperatures hydroquinone is produced, but is immediately changed into resorcin.

42 Whether the course of a chemical action is or is not to be regarded as an example of the particular application of the molecular theory now under consideration, must be decided by the nature of the change in question. Some of the changes which occur when metals and acids interact probably belong to this class of chemical actions.

The products of the mutual actions of metals and sulphuric and nitric acid, respectively, have already been broadly stated. That no hydrogen is evolved in the case of nitric acid is generally said to be due to the oxidation, by the nitric acid, of the atoms of hydrogen, assumed to be produced by the interaction of the metal and acid, with a corresponding reduction of the acid to oxides of nitrogen, nitrogen, and sometimes ammonia.

Direct proof in favour of this hypothesis, in the case of the interaction of nitric acid and magnesium, has been given by Gladstone and Tribe[1], who have shewn that when a small piece of magnesium is placed in a large excess of nitric acid (strengths 1 : 1 and 1 : 2—acid to water—were employed) the gas at first evolved consists of nearly pure hydrogen, but

[1] *C. S. Journal* **Trans.** for **1879.** 178.

that oxides of nitrogen are very quickly produced. The same chemists[1] have established a close relation between the reaction with sulphuric and nitric acids of the hydrogen produced by electrolysis of these acids, and the hydrogen occluded by platinum or palladium; they have also shewn that hydrogen evolved by the action of the copper zinc couple is very analogous in general reducing actions to hydrogen occluded by platinum or palladium.

When concentrated nitric acid is subjected to electrolysis no hydrogen is evolved, but the acid is reduced; when more dilute acid is used hydrogen is evolved, reduction of the acid also occurs, and the more rapid the electrolysis the greater is the quantity of hydrogen evolved. Concentrated nitric acid rapidly acts on hydrogen occluded by platinum or palladium, with oxidation of the hydrogen and reduction of the acid. In the electrolysis of concentrated sulphuric acid sulphur is produced, and also sulphur dioxide with traces of sulphuretted hydrogen, a portion of the hydrogen formed is oxidised and a portion escapes, and the stronger the battery power the greater is the quantity of hydrogen evolved. When the electrolysis is *extremely slow*, no hydrogen is evolved, and sulphur dioxide is produced in small quantity unmixed with free sulphur. Hydrogen occluded by palladium or platinum also reduces sulphuric acid, with production of sulphur dioxide and escape of a portion of the hydrogen.

Gladstone and Tribe regard the metal (platinum or palladium) present in their experiments as instrumental in the chemical change. They think that the hydrogen produced is occluded by the metal and again given off to the acid, and that if the gas is produced more quickly than it can be occluded the excess escapes oxidation by the acid: it is probable that occluded hydrogen forms a compound with the occluding metal, and that therefore hydrogen coming from this source is for the most part in the nascent, i.e. on the present hypothesis the atomic, state. Their experiments certainly establish the fact that maximum reduction of either acid is obtained when hydrogen is evolved therein near an

[1] *C. S. Journal* **Trans.** for **1878.** 139 and 306.

electro-negative metal; but a comparison of the results with occluded and electrolytically evolved hydrogen shews that the reducing action of the latter on sulphuric acid is more complete than that of the former.

There are two hypotheses regarding the mechanism of the changes which occur when metals and aqueous solutions of nitric acid interact. One hypothesis asserts that these changes generally proceed in two stages, taking place simultaneously; in the first stage the metal and acid react to produce a nitrate and hydrogen; in the second stage the hydrogen, or a portion of it, interacts with another portion of the acid to produce oxides of nitrogen, ammonia, or nitrogen, and water. The other hypothesis regards the various gaseous products as direct results of the deoxidation of the acid by the reaction with the metal, and denies that hydrogen is produced at any stage of the process. The facts, taken as a whole, seem to me to be more in keeping with the first than with the second of these hypotheses. Indeed to formulate the reaction of zinc and nitric acid on the latter hypothesis requires that nitric acid should be regarded as a variable compound of nitrogen pentoxide and water, and necessitates considerable skill in the manipulation of formulæ[1].

The interaction of copper and concentrated sulphuric acid has been studied by Pickering[2]. The ease with which this acid undergoes deoxidation is shewn by the slow production of cuprous sulphide even at 20°; the equation

$$5Cu+4H_2SO_4=Cu_2S+3CuSO_4+4H_2O,$$

which represents the change as consisting in deoxidation of part of the acid, and does not involve, nor according to Pickering's experiments allow, an intermediate stage wherein hydrogen reacts with the acid, is nearly realized at this temperature. At higher temperatures sulphur dioxide is evolved, until at about 270° the action consists entirely of a change which may be formulated as

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O,$$

[1] Deville, *Compt. rend.* **70**, 20 and 550; or in abstract, Watt's *Dict.* **Suppl. 2**, 304. See also Acworth and Armstrong, *C. S. Journal*, vol. **2**. for 1877, 54 *et seq.*

[2] *C. S. Journal* **Trans.** for **1878.** 112.

and which is most readily explained as consisting of two parts proceeding simultaneously

$$\left.\begin{array}{ll}(1) & Cu+H_2SO_4=CuSO_4+H_2\\(2) & H_2+H_2SO_4=2H_2O+SO_2\end{array}\right\}.$$

Tin and lead are dissolved by hot concentrated sulphuric acid, with production of sulphates and evolution of hydrogen *and* sulphur dioxide, sometimes accompanied by sulphuretted hydrogen, and with separation of sulphur. With more dilute acid tin evolves hydrogen, and as temperature is increased, sulphuretted hydrogen also. The reaction of zinc with sulphuric acid is broadly analogous to that of tin: with pure zinc and very concentrated hot acid, the products are hydrogen and sulphur dioxide; with less pure zinc, sulphuretted hydrogen and sulphur are also formed, the sulphur compounds (SO_2 and SH_2) appearing even when the acid is very dilute and is kept cold; with moderately dilute pure acid and pure zinc hydrogen is the only gaseous product (*s.* Pattison Muir and Adie, *C. S. Journal*, **Trans. 1888,** 47).

Quantitative analyses of the products of reduction of nitric acid by magnesium, zinc, and cadmium, respectively shew that reduction is carried furthest by magnesium, and further by zinc than by cadmium. Now the 'heats of formation' (see Chap. IV.) of the oxides of these metals are, for Mg 147,132, for Zn 88,244, and for Cd 30,364 thermal gram-units; hence in these cases that reaction in which the greatest amount of heat is produced is accompanied by the greatest reduction of the acid.

The following numbers representing quantities of heat produced in the chemical changes formulated were obtained by Thomsen[1]:—

$[H^2, S, O^4, Aq]$ = 210,760 gram-units +.
$[H, N, O^3, Aq]$ = 34,270 „ +.
$[Zn, H^2SO^4Aq]$ = 106,090 „ +.
$[Zn, 2HNO^3Aq]$ = 136,340 „ +.

[1] These equations tell that e.g. when 2 grams of hydrogen, 32 grams of sulphur, and 64 grams of oxygen interact in presence of a large quantity of water to form a dilute aqueous solution of 98 grams of sulphuric acid, 210,760 gram-units of heat are produced. (For fuller explanations *s.* Chap. IV.)

Berthelot gives the thermal value 21,500 gram-units to the chemical change

$$HNO_3Aq \text{ (dilute)} + 8H = NH_3Aq \text{ (dilute)} + 3H_2O.$$

From these numbers we should expect sulphuric acid to be more stable, towards heat, than nitric acid, and we should expect the reaction of zinc with these acids to result in a more complete deoxidation of nitric than of sulphuric acid.

In the interaction of a metal with nitric acid in aqueous solution at ordinary temperatures, we have then, an unstable acid, a considerable quantity of heat produced, and the formation of hydrogen in contact with the acid; we have conditions eminently favourable to deoxidation. In the interaction of a metal with dilute sulphuric acid, on the other hand, we have a more stable acid and a smaller quantity of heat produced; the hydrogen escapes unchanged; but when the acid is so concentrated that addition of heat from without is required to start the reaction, and when the acid is therefore in a condition more comparable with that of nitric acid at ordinary temperatures, a portion of the hydrogen then evolved undergoes oxidation at the expense of the oxygen of the acid. If however hydrogen is evolved, as in the experiments of Gladstone and Tribe, in contact with the concentrated acid at ordinary temperatures, a part of this hydrogen is always oxidised[1]; this shews that all the reacting substances, and also the conditions of the reaction, must be considered, and that attention must not be confined to the hydrogen only.

The facts, that hot sulphuric acid is deoxidised by carbon, and apparently by phosphorus also[2], and that it is possible by heat alone to decompose this acid into sulphur dioxide, oxygen, and water, have caused some chemists to regard the reactions of metals with this acid as simply cases of direct deoxidation: but it seems to me that the facts enumerated—both chemical and physical, with regard to the interactions of

[1] When however vapour of sulphuric acid *mixed with hydrogen* is passed through a hot tube, sulphuretted hydrogen is produced.

[2] Cross, *C. S. Journal* **Trans.** for **1879.** 253.

metals with this acid and with nitric acid—are more in keeping with that hypothesis according to which hydrogen plays an essential part in the series of changes, than with any other hitherto advanced. There may be, indeed there undoubtedly is, more than one process of chemical change resulting in the deoxidation of sulphuric acid; in some cases direct deoxidation preponderates, in others hydrogen plays the more important part.

Experiments conducted by Thorpe[1] on the reducing action of zinc, magnesium, and tin, on acidulated solutions of ferric sulphate, shewed that whatever condition tends to give greater chances of contact between the hydrogen produced in the liquid and the ferric sulphate in solution, increases the rate of reduction; that increase of the rate at which hydrogen is evolved, other conditions remaining constant, is accompanied by decrease of the amount of reduction in unit of time; and that the presence of certain salts, e.g. zinc sulphate, causes a decrease in the rate of reduction. Thorpe's results also established a distinct connexion between the nature of the metal used and the influence on the rate of reduction of the varying conditions under which the experiments were conducted.

These experiments, and indeed all experiments on the interactions of metals and acids, emphasise the necessity that exists for considering all the reacting substances which take part in a process of reduction by hydrogen, and not confining attention to the hydrogen alone. The results of experiments by Tommasi[2] also shew this need: Tommasi found that potassium chlorate was not deoxidised by hydrogen evolved by the action of sodium-amalgam, but was reduced by hydrogen evolved by the action of zinc on diluted sulphuric acid, but that the latter agents failed to remove oxygen from potassium perchlorate. Experiments conducted in my laboratory have shewn that an aqueous solution of potassium chlorate is reduced by the action of magnesium or sodium, and by that of the copper-zinc couple; and that an aqueous

[1] *C. S. Journal* **Trans.** for **1882.** 289.

[2] See especially *Pogg. Beiblatter*, **2.** 205.

solution of potassium perchlorate is very slightly reduced (to chloride) by the action of sodium, and by the prolonged action of magnesium, but is not reduced by the action of the copper-zinc couple, by that of zinc dust and potash, or by electrolysis.

43 The conception which underlies such expressions as *nascent actions*, *action of nascent hydrogen*, &c., is that implied in the distinction drawn between atom and molecule. That this distinction is not one merely of terminology but is based on actual reactions, is rendered apparent by the results of experiments by Traube[1] on the electrolysis of water, using electrodes of different materials. For instance, he found that when palladium is charged with hydrogen and made the positive pole of the battery no hydrogen peroxide is produced, but the oxygen which is being evolved is absorbed by the palladium and is combined with the occluded hydrogen to form water. When however the hydrogenised palladium is made the negative pole a little hydrogen peroxide is produced; and the quantity of this compound may be considerably increased by causing bubbles of air to rise through the liquid near the negative pole. If however no air is passed through the water, and at the same time the transference of oxygen from the positive pole (where it is being liberated) through the liquid to the negative pole is mechanically prevented, no hydrogen peroxide, or only a trace of this compound, is produced. Further, if hydrogenised palladium is made the positive pole, and bubbles of air are at the same time caused to rise through the liquid around the pole, a little, but only a little, hydrogen peroxide is produced.

Finally if the electrodes are made of palladium uncharged with hydrogen the maximum yield of hydrogen peroxide is obtained (entirely at the negative pole) by arranging the rate of electrolysis so that the whole of the hydrogen produced is occluded by the palladium; the more rapid the evolution of hydrogen from the liquid the smaller is the quantity of hydrogen peroxide produced[2]. Now it is generally supposed

[1] *Ber.* 15. 659, 2421, 2434: 16. 1201.

[2] These results are confirmatory of those obtained by Gladstone and Tribe in their electrolytic experiments on the reduction of acids. See *ante*, p. 100.

that the greater part of the oxygen or hydrogen liberated during the electrolysis of water is at the moment of its production in the state of atoms, and that the greater part of the oxygen in ordinary air is composed of molecules; if this be granted, it follows that Traube's experiments establish a marked difference between the reactions of oxygen atoms and oxygen molecules: by their reaction with hydrogen occluded by palladium, the former produce water, the latter produce hydrogen peroxide; if a few atoms and many molecules of oxygen are present much peroxide and little water are the products, while if many atoms and few molecules of oxygen are brought into contact with the hydrogen, much water and little peroxide is the result.

44 But the experiments of Traube also shew that the direction and final goal of the chemical change depends not only on the structure of the particles of oxygen, but also on the source and conditions of supply of the hydrogen. If the hydrogen is produced by rapid electrolysis little peroxide is formed; indeed if the hydrogen is produced, rapidly or slowly, by electrolysis with carbon poles no peroxide is obtained. The chemical nature and the mass of each of the members of the changing system influence the final configuration. The importance of considering the conditions under which hydrogen is produced when we are attempting to explain any of the phenomena classed together as nascent, is emphasised by the fact that the metals which decompose water in *absence* of oxygen do not give rise to the production of hydrogen peroxide by their action on water in *presence* of oxygen; for instance, hydrogen peroxide is never produced by the action of sodium on water. It is not enough then that oxygen molecules should be present in contact with atoms of hydrogen as these are liberated from water. The peroxide results from the mutual interactions of the three substances, metal, water, and oxygen; if the water is decomposed by the metal alone, hydrogen is evolved rapidly and escapes the pursuit of the oxygen molecules; the peroxide appears to be a product of the joint action of the metal and oxygen on the molecules of water.

The conception of a joint action of metal and oxygen with water may be used to explain some of the phenomena exhibited when metals and acids interact. Traube seeks to explain many of these reactions in this way.

Copper does not remove oxygen from an aqueous solution of potassium nitrate as zinc does: but if copper is brought into contact with dilute sulphuric acid in presence of oxygen, hydrogen peroxide is produced. The joint action of copper and potassium nitrate is not sufficient to decompose water-molecules; but copper and oxygen aided by a little sulphuric acid suffice to complete this change. The reaction in question is represented thus by Traube:—

(*a*) $Cu+\left\{\begin{matrix}OH & H\\ OH & H\end{matrix}\right\}+\left\{\begin{matrix}O\\ |\\ O\end{matrix}\right.=Cu(OH)_2+\begin{matrix}H-O\\ |\\ H-O\end{matrix}$

(*b*) (when a certain amount of H_2O_2 is produced)

$$Cu+H_2O_2=Cu(OH)_2$$

(*c*) $Cu(OH)_2+H_2SO_4=CuSO_4+2H_2O.$

If some compound which is readily acted on by hydrogen is substituted for oxygen in this series of changes, then copper and dilute sulphuric acid form a reducing agent; ferric sulphate e.g. is reduced under these conditions to ferrous sulphate:—

$$Cu+\left\{\begin{matrix}OH & H\\ OH & H\end{matrix}\right\}+Fe_2.3SO_4+xH_2SO_4=Cu(OH)_2+2FeSO_4+(x+1)H_2SO_4$$
$$[=CuSO_4+2FeSO_4+2H_2O+xH_2SO_4].$$

Similarly the interaction of copper with dilute nitric acid would be represented thus:—

$$3Cu+3\left\{\begin{matrix}OH & H\\ OH & H\end{matrix}\right\}+3(O\ NO_2H)=3Cu(OH)_2+3H_2O+NO_2H$$

[but $3NO_2H$ rapidly decomposes to give $HNO_3+2NO+H_2O$].

As thus regarded, these reactions of metals with acids are complex changes; at one stage or other of the complete change hydrogen plays an important part, and it does this in virtue of being itself a product of another part of the whole

reaction. Hydrogen imported from without the system fails to accomplish actions which are brought about by hydrogen generated within the system, provided this hydrogen be produced at the proper rate and under conditions generally favourable to the action it is to perform.

The investigation of Divers[1] 'On the production of hydroxylamine from nitric acid' is an interesting and instructive example of the need of considering all the members of a changing system in attempting to find an explanation of the change. Hydroxylamine is produced in very small quantities during the reaction of tin, zinc, and some other metals, with nitric acid; but if hydrochloric or sulphuric acid is added to the zinc and nitric acid a marked increase in the yield of hydroxylamine is noticed. When a mixture of nitric and sulphuric acids reacts with zinc it is probable, from the experiments made by Divers, that the ammonia which is produced in considerable quantities is a product of the direct mutual action of the zinc and nitric acid, and that the hydroxylamine is a product of the reduction of the nitric acid by the combined interaction with that acid of zinc and sulphuric acid. Zinc and sulphuric acid in presence of nitric acid, according to Divers, form an hydrogenising mixture; the chief products of this action are hydrogen and hydroxylamine, besides sulphate and nitrate of zinc. Zinc and aqueous nitric acid alone also form an hydrogenising mixture; but the chief product of this action, other than zinc nitrate, is ammonia. Hydroxylamine is not therefore an invariable product of the reaction of hydrogen with nitric acid even when that hydrogen is evolved in contact with the acid; it is rather to be regarded as a product of the combined interaction of nitric acid and sulphuric acid with zinc, this reaction being such that the nitric acid is supplied with hydrogen whereby it is reduced to hydroxylamine.

45 The expression 'nascent action' has probably been at once helpful and harmful to the progress of chemistry. By classing under a common name many phenomena that might otherwise have been lost in the vast mass of facts with which the

[1] *C. S. Journal*, **Trans.** for **1883.** 443: also Divers and Shimidzu, *C. S. Journal*, **Trans.** for **1885.** 597.

science has to deal, the expression has, I think, done good service; but in so far as its use has tended to prevent investigation—for it is always easier to say of any unusual reactions, 'these are cases of nascent action,' than to examine carefully into their course and conditions—and also in so far as it has favoured the impression that 'nascent' hydrogen or 'nascent' oxygen, &c. is ordinary hydrogen or oxygen, &c. with certain indefinite properties which always belong to the hydrogen, or other element, when in this peculiar condition the use of the expression has, I think, been unfavourable to the best interests of chemical science.

A study of the reactions in which nascent substances play important parts appears to me to keep before the student that all-important distinction between the atom and the molecule which is so vital in chemical considerations, and also to draw attention in a marked way to the complexity of all chemical changes. We find, or think we find, that when atoms of hydrogen are presented to another substance in a given chemical reaction, certain definite products result; and we are apt to conclude that the interaction of hydrogen atoms with this substance will always give this result; but investigation discovers that not only the course of the reaction, but also the final configuration of the changing system, is dependent on the whole previous history of the reacting bodies. Hydrogen as it is produced by the action of sodium-amalgam appears to possess properties different from those which characterise hydrogen produced by the reaction of zinc with dilute sulphuric acid. Attempts to explain these apparent differences lead to fresh researches; the results of these researches shew the danger of using such an expression as *the properties of hydrogen produced by the action of sodium-amalgam*, and contrasting these with *the properties of hydrogen produced by the reaction of zinc with dilute sulphuric acid;* they teach that every chemical change is composed of parts, and that the occurrence of one part is dependent on the occurrence of the other parts, that we cannot, except occasionally, alter one part of the complete change and expect the other parts to proceed as before. The change of hydrogen and potassium chlorate

in aqueous solution to potassium chloride and water, for instance, is dependent not only on the interaction of the chlorate and hydrogen but also on the interaction whereby the hydrogen is itself produced. It is not that hydrogen produced in one way has certain properties and hydrogen produced in another way has other properties, but rather that the members of the system composed of potassium chlorate, water, and sodium-amalgam, interact to produce potassium chlorate, soda, water, mercury, and hydrogen, whereas the members of the system composed of potassium chlorate, water, zinc, and sulphuric acid, interact to produce potassium chloride, water, zinc sulphate, and hydrogen. We thus become impressed with the conviction that chemistry is not the study of this element or that, regarded as a kind of matter with certain fixed physical properties, but that processes of change are the subject-matter of the science, and that to explain any one of these we must take into account each and all of the reacting bodies, and each and all of the conditions under which the total change is proceeding.

If the expression 'nascent action' does in any way help to emphasise such considerations as these, I think it ought to be retained in chemical nomenclature[1].

SECTION II. *The Dualistic and Unitary Hypotheses.*

We must now examine the relations between the chemical properties of atoms and of the molecules, or atomic aggregates, which are formed by the union of these atoms. We must inquire whether the properties of the molecule are the sum of the properties of its constituent atoms; or whether the latter properties are modified by the mutual interactions of the atoms. We must endeavour to learn something regarding the structure of molecules.

46 Partly from his definition of element, partly from his study of the products of combustion in oxygen, of phosphorus, carbon, sulphur, &c., Lavoisier was led to regard every salt

[1] See also Book II. chapter II.

as formed by the union of an acid with a radicle, the latter being itself either simple or compound.

Davy began his electro-chemical researches in the early years of the present century. In the *Philosophical Transactions* for 1807[1], and in his *Elements of Chemical Philosophy*[2], he regards chemical combination as accompanied by an exchange of quantities of electricity of opposite sign between the combining bodies. He found that when sulphur and copper are rubbed together the sulphur is negatively, the copper positively, electrified; and that when the sulphur is heated the electrical activities become more apparent, until the sulphur melts, when chemical combination occurs, and the product, copper sulphide, exhibits neither positive nor negative electricity. If the quantity of electricity lost in the act of chemical union is restored, e.g. by the passage of a current through the compound formed, chemical decomposition occurs and the original components are again obtained. Davy regarded the primary cause of chemical and electrical effects as possibly the same force; when this force is exerted between masses of matter, electrical phenomena, he said, result; when it is exerted between the smallest particles of bodies chemical phenomena result. Thus in his *Elements of Chemical Philosophy*[3] Davy says,

"Electrical effects are exhibited by the same bodies when acting as masses, which produce chemical phenomena when acting by their particles; it is not therefore improbable that the primary cause of both may be the same, and that the same arrangements of matter, or the same attracting powers, which place bodies in the relations of positive and negative, i.e. which render them attractive of each other electrically, and capable of communicating attractive powers to other matter, may likewise render their particles attractive, and enable them to combine, when they have full freedom of motion." "That the decomposition of the chemical agents is connected with the energies of the pile, is evident from all the experiments that have been made; as yet no sound objection has been urged against the theory that the contact of the metals destroys the electrical equilibrium, and that the chemical changes restore it; and, in

[1] 'On some chemical agencies of electricity,' p. 1.

[2] *Collected Works*, vol. IV. (see also Ladenburg's *Entwickelungsgeschichte der Chemie*, pp. 75—81).

[3] Pp. 119—120, and p. 125.

consequence, that the action exists as long as the decompositions continue."[1]

47 At once a brilliant theoriser and a thorough-going experimenter, Davy did not attempt to found a general scheme of chemical classification on his electro-chemical work. This was however done by Berzelius, who developed a consistent and definite, although narrow, theory which for a time seemed to explain all chemical phenomena.

All chemical actions were regarded by Berzelius as brought about by electrical force[2]. "*Die Elektricität...scheint die erste Thätigkeits-Ursache in der ganzen, uns umgebenden Natur zu sein.*" Electrical actions, according to Berzelius, were not to be described as consequences of contact, or of mutual action, between heterogeneous bodies. Each elementary atom, he held, is endowed with two kinds of electricity, it has two electric poles; but these poles differ in strength, so that each atom considered as a whole is positively *or* negatively electrified; in some elementary atoms positive electricity predominates and gives a positive character to the whole atom; in others negative electricity overpowers the positive. When a positively electrified atom attracts a negatively electrified atom, opposite electricities neutralise one another, but the electricities formerly masked in the separate atoms now come into play, and so the new group of atoms, as a whole, exhibits positive or negative electricity, in virtue of which it is capable of chemically combining with other atoms or groups of atoms. But as the stronger poles are first neutralised, it follows that the more complex a compound is, the less polarity does it exhibit, and hence the less readily does it combine with other substances. Berzelius moreover regarded the quantity of electricity on either pole as to some extent variable with variations of temperature. By the Berzelian theory

[1] It is interesting to observe how similar this view, stated by Davy in the beginning of the present century, is to the latest views regarding the connexion of chemical and electrical forces. Compare especially Helmholtz's 'Faraday Lecture.' (*C. S. Journal*, **Trans.** for **1881**, 277 *et seq.*: *see particularly* pp. 300—302.) [See *post*, Book II.]

[2] *Lehrbuch* (1st Ed.), III. part I. p. 77.

atoms are regarded as essentially unipolar; one polarity so predominates over the other that each atom acts as a positively *or* negatively electrified whole.

The electro-chemical properties of oxidised compounds, Berzelius taught, depend chiefly on the unipolarity of the electro-positive radicles they contain. Of two oxides, that which contains the more electro-negative radicle is generally itself electro-negative; thus sulphuric acid (regarded as SO_3) is electro-negative to all metallic oxides, because sulphur is itself electro-negative to all metals: on the other hand the oxides of potassium and sodium are electro-positive to all other oxides (excepting those of cæsium and rubidium) because potassium and sodium are themselves electro-positive to all other elements[1] (except cæsium and rubidium).

Polarity and chemical affinity are closely connected in the system of Berzelius: the 'specific unipolarity'[2] however does not alone determine the greater or less affinity of one atom for another. Some atoms have a more intense polarity than others and therefore exhibit a greater striving (*Bestreben*) to neutralise the electricity divided between their poles, in other words, have a greater affinity for a given substance than other atoms.

Chemical affinity appears to have been regarded by Berzelius as nearly synonymous with intensity of atomic polarity[3]. Thus, oxygen combines with sulphur rather than with lead, although oxygen and sulphur have the same unipolarity (viz. negative); but, the Berzelian view asserts, the positive pole of the sulphur atom neutralises more negative electricity on the oxygen atom than can be neutralised by the positive pole of the lead atom.

[1] An important deduction made from these considerations is, that as oxygen occurs both in markedly electro-positive and electro-negative compounds, and as acids are as a group electro-negative, oxygen cannot be *the* acidifying element, as Lavoisier said it was.

[2] *Specifische Unipolarität.* Berzelius, *loc. cit.* p. 73.

[3] This might perhaps be regarded as equivalent to the modern conception of higher and lower potential; as if one atom might have a smaller electrical charge but at a higher potential than another, and would therefore exhibit greater chemical affinity than the other.

Double decompositions were readily explained in terms of this theory:

"Every chemical action," says Berzelius[1], "is an electrical phenomenon depending on the electrical polarity of the particles; everything that appears to be due to the action of affinity is caused by the possession by some bodies of an electrical polarity stronger than that of others. If the compound AB is decomposed by the substance C which has a greater affinity for A than B has, then C must possess a more intense electrical polarity than B; on this account there results more complete neutralisation between A and C than between A and B.... If two bodies, AB and CD, so react as to produce two new bodies, AD and BC, it follows that the electrical polarities are better neutralised in the latter pair of bodies than in the former."

48 On the basis of this conception Berzelius raised the structure of the dualistic chemistry, which asserted that every compound, whether simple or complex, must be constituted of two parts, of which one is positively, and the other negatively, electrified.

The doctrine of dualism is thus introduced by Berzelius[2]:

"If these electro-chemical conceptions are just, it follows that every chemical compound is dependent on two opposing forces, positive and negative electricity, and on these alone; and that every compound must be composed of two parts held together by their mutual electro-chemical reactions. Therefore it follows that every compound body, whatever be the number of its constituents, can be separated into two parts, whereof one is positively and the other negatively electrified. Thus, for example, sodium sulphate is put together, not from sulphur, oxygen, and sodium, but from sulphuric acid and soda, which again can themselves be separated into positive and negative constituents. So also alum cannot be regarded as immediately built up from its elements, but must rather be looked on as the product of a reaction between sulphate of alumina and sulphate of potash, the former acting as a negative, the latter as a positive element."[3]

In support of his theory Berzelius appealed to the facts of electrolysis. A solution of sodium sulphate containing a little blue vegetable colouring matter is electrolysed; the colouring matter is reddened around the positive electrode and rendered

[1] *Lehrbuch* (1st Ed.), III. part I. p. 77.

[2] *Ibid.* p. 79.

[3] See also Berzelius, *Theorie des proportions chimiques, et de l'influence chimique de l'électricité dans la nature inorganique*; 3rd Ed. Paris, 1835. Also, for a condensed account of the electro-chemical theory of Berzelius, see Ladenburg, *Entwickelungsgeschichte der Chemie*, pp. 89—93.

more distinctly blue around the negative. What can this experiment teach but that the salt is separated by the electric current into alkali and acid? And can the inference be avoided that the salt is composed of, or contains in itself, these two compound radicles, soda (Na_2O), and sulphuric acid (SO_3)? All salts were to be regarded as dualistic structures. Given the composition of a salt, a dualistic formula, or rather a series of formulæ, was at once devised for it. The following formulæ were employed by various dualistic chemists to express the structure of acetic acid:—

(1) $C_4H_6O_3 . H_2O$	(2) $C_4H_6O_4 . H_2$	(3) $C_4H_6O . O_2 . H_2O$
(4) $(C_2H_6)C_2O_3 . H_2O$	(5) $(C_2H_6)C_2O_4 . H_2$	(6) $(C_3H_6O)CO_2 . H_2O$
(7) $C_4H_8 . O_4$	(8) $C_2H_4 . O_2$	(9) $C_4H_6O_2 . H_2O_2$
(10) $C_4H_2 . O_4H_6$		

To choose the proper formula from such a chaos was a task possible only for one whose foible was omniscience. That formula which had the weight of authority on its side was accepted as correct.

49 Lavoisier had regarded oxygen as the 'acidifying principle.' Hydrochloric acid was undoubtedly an acid substance; therefore, in accordance with the dictum of Lavoisier, it contained oxygen. Davy's study of this compound, and of its analogue hydriodic acid, nevertheless established the fact that an acid can exist which contains no oxygen. The further fact, that so many of the oxides—then called acids—exhibited acidic properties only in presence of water, led Davy to the belief that very many acids are compounds of hydrogen. Shaking off the trammels of that older philosophy which regarded the introduction of undefined '*principles*' as affording explanations of natural phenomena, Davy said that acids are not characterised by the invariable presence of any one element, but that certain compounds of very diverse elements belong to this group[1].

Dulong[2] in 1815 further advanced Davy's conception of acids by recognising no essential difference between those

[1] For an account of the important work of Davy on the non-oxygenised acids, and the arguments of his opponents, see Ladenburg, *loc. cit.* pp. 81—87.

[2] *Mém. de l'Acad.* 1813—15, p. 198: and *Schweigger's Journal*, **17**. 229.

acids which contain oxygen and those which do not. Lavoisier's hypothesis was not however generally abandoned until many years later.

In 1837—38 Liebig[1], following up Graham's work on phosphoric acid[2], distinctly recognised the existence of 'replaceable hydrogen' in acids, whether oxy-acids or acids containing no oxygen, and defined salts to be compounds belonging to the same class as acids, and formed by putting a metal in the place of an equivalent quantity of hydrogen in acids[3].

This view of the structure of salts was altogether opposed to the dualistic theory of Berzelius.

50 Another severe blow was inflicted on the prevailing theory by Faraday's researches on electrolytic decompositions.

Faraday shewed that the quantities of various elements set free from different electrolytes, by the same electric current, were chemically equivalent to one another: thus for each two parts by weight of hydrogen set free from water, there were obtained 16 parts of oxygen, 78·2 parts of potassium, 63·5 parts of copper from persalts and 127 parts of copper from protosalts. But the affinities of the atoms of the various electrolytes were undoubtedly different in each combination. According to Berzelius, the quantity of electricity collected on any group of atoms is greater, the greater the mutual affinity of these atoms; but Faraday's experiments shewed, that in so far as this electricity was measurable by electrolytic decomposition, (and that at least comparative measurements should be thus obtained followed from the terms of the dualistic theory itself), the quantity of it was in no way dependent on the affinities of the combining atoms[4].

51 A bold and partially successful attempt, such an attempt

[1] *Compt. rend.* **5.** 863 (with Dumas): and *Annalen*, **26.** 113, see especially p. 181.

[2] *Phil. Trans.* for **1833.** 253.

[3] See, in connexion with *acid* generally, Laurent, *Chemical Method*, pp. 39—45.

[4] See Helmholtz, 'The Faraday Lecture.' *C. S. Journal*, **Trans.** for **1881.** pp. 284—6.

as could be made only by a man of preeminent power, had been made by Berzelius to found chemical classification on the study of composition alone, almost wholly divorced from the study of function or power of doing. As his authority became greater Berzelius led chemistry further from the only true path by which she could advance, that namely wherein experiment, and reasoning on experimental data, go hand in hand. And yet no single chemist has enriched the science by the addition of so great a mass of laboriously and accurately determined experimental data as he. The intense concentration of his great intellectual powers upon one view of chemical phenomena led Berzelius to disparage the reasoning of those who sought to view these phenomena from standpoints other than his own.

Among those who recalled chemistry to the true scientific method, Dumas, Laurent, and Gerhardt stand preeminent.

In 1839[1] Dumas described trichloracetic acid, obtained by the action of chlorine on acetic acid. The new compound, although containing chlorine in place of hydrogen, was a monobasic acid and resembled acetic acid in its general reactions. Dumas said there are certain *types* in organic chemistry which are maintained even when a volume of chlorine, bromine, or iodine, is put in the place of an equal volume of hydrogen in the parent substance[2].

Berzelius, and the defenders of the dualistic chemistry, violently opposed the idea that the electrically negative chlorine could be substituted for the positive hydrogen, and the identity of type yet be maintained. In Dumas' succeeding papers[3] the conception of types was more fully developed. All compounds composed of the same number of equivalents of simple substances, combined in a similar manner, and exhibiting broad analogies of properties, were regarded as belonging to the same type. Such compounds were also, as a

[1] *Compt. rend.* **8.** 609: and *Annalen*, **32.** 101.

[2] *Compt. rend.* **8.** 621.

[3] *Annalen*, **33.** 259: **35.** 129 (with Stas), and 289 (with Peligot): or *Compt. rend.* **9.** 813, and **10.** 149.

rule, simply related to one another by reactions of formation and decomposition:—thus acetic and chloracetic acids; chloroform, bromoform, and iodoform; ethylene and its chloro-derivatives, &c.; belonged to the same types, or as Dumas said to the same 'natural families'. Dumas regarded carbonyl chloride as derived from carbonic anhydride by substituting one oxygen by two chlorine atoms; thus COO gives $COCl_2$: this was utterly opposed to the dualistic view, according to which the formula of carbonyl chloride was written $CO.CCl_4$ because every compound *must* be composed of two parts, one of which is electrically positive and the other negative.

52 The new school of chemists naturally opposed the conception of compound radicles, a conception too closely associated with those dualistic theories they were leaving behind to find favour in their sight. But these chemists found that, unless substitution of simple atoms by groups of atoms were regarded as possible, identity of type could not be maintained through groups of compounds undoubtedly belonging to the same natural family.

Inasmuch as the new chemistry based its claims to recognition on an appeal to actual reactions, it was impossible that it should long refuse to recognise the conception of compound, as well as simple, radicles, without proving false to its own method. Liebig and Wöhler, in their researches on oil of bitter almonds, explained the observed reactions of the bodies they obtained by assuming the existence of the compound radicle *benzoyl* ($= C_{14}H_{10}O_2$) in these bodies (see *Annalen*, **3**. 249).

But what are these compound radicles which the chemists who upheld the unitary system were obliged to recognise, equally with their opponents who supported a dualistic theory? Are they definite groups of atoms always existing as such in compound molecules, or are they only convenient methods of expressing and generalising reactions?

As chemistry advanced, compound radicles came to be generally recognised as certain groups of atoms, in compound molecules, which remain undecomposed throughout

a series of reactions undergone by those molecules[1]. Thus we find Kekulé in 1857 citing the case of sulphuric acid, H_2SO_4, which when acted on by zinc gives $ZnSO_4$, and may therefore be said to contain the radicle SO_4; but when acted on by phosphorus pentachloride, the compound SO_2Cl_2 is produced, hence the acid may be said to contain the radicle SO_2.

53 The conception of types was destined to bear much fruit. Let us briefly trace its development.

Liebig and Dumas had regarded salts as substituted metallic derivatives of acids; they had spoken of a quantity of metal as taking the place of an equivalent quantity of hydrogen: Dumas had even ventured to regard the negative chlorine as capable of replacing an equivalent amount of the positive hydrogen. In doing this, these chemists had returned to the old conception—too much forgotten by the Berzelian school—of equivalents as quantities to be determined by the study of reactions; but they had given this conception fresh life by engrafting on to it the notion of natural families or types.

In writing the formulæ of sulphates, selenates, and chromates, as $MO . SO_3$; $MO . SeO_3$; and $MO . CrO_3$; Berzelius had undoubtedly recognised the principle of types; but so long as this principle was dominated by the necessities of the dualistic system it was unfruitful. The idea of the chemically reacting unit as one whole, one structure with parts capable of replacement by other parts without the necessary destruction of the building, gave meaning to what was before but a form of words.

From its earliest beginnings to its present form the theory of types has been interwoven with the atomic theory; without the latter, the former had never had being. If the value of a scientific idea is to be measured by its fruitfulness, then is Dalton's *New System of Chemical Philosophy* the most important work yet produced by any chemist.

[1] See especially Laurent's *Chemical Method*, pp. 276—300 Also Ladenburg, *loc. cit.* 9th and 10th Lectures. The modern development of the conception of compound radicle will be better understood by considering pars. 70—74 in Section 4 of this chapter.

Now if the reacting unit of any substance is possessed of a definite atomic structure, only those bodies can be said to belong to the same type, or natural family, whose reacting units are built on a similar atomic plan: but our only method of discovering similarity of structure is by studying reactions; hence only those bodies which are characterised by similarity of chemical function ought to be classified under the same type[1]. And as modification of structure has been recognised as not necessarily implying destruction of type, it follows that those quantities of radicles, simple or compound, are equivalent, which can perform similar functions in similarly constituted compounds.

At last a method of chemical classification has been found by Dumas, Liebig, Gerhardt, and Laurent, which when more fully developed will reconcile those who regard composition as all important, with those for whom function is supreme; which will preserve the fundamental conception of equivalent, but interpret it in terms of the wider theory of atoms; and which will recognise the connexion, while yet emphasising the importance of the difference, between the atom of Dalton and the molecule of Avogadro.

But in its development the theory of types must necessarily be largely modified. Classification by types cannot be final in a science which has advanced so far towards becoming an abstract science as chemistry.

"By the classification of any series of objects is meant the actual, or ideal, arrangement together of those which are like and the separation of those which are unlike; the purpose of this arrangement being, primarily, to disclose the correlations or laws of union of properties or circumstances, and, secondarily, to facilitate the operations of the mind in clearly conceiving and retaining in the memory the 'character of the objects in question'."[2]

Those 'properties or circumstances' which are correlated must be such as are really characteristic of the objects classified, they must be essential properties of these objects, not mere surface appearances; they must be capable of accurate

[1] See especially Laurent's *Chemical Method*, pp. 298—300.

[2] W. Stanley Jevons (modifying the words of Huxley), *Principles of Science*, 2. p. 348.

definition, and at the same time of fairly easy recognition; and that property, or properties, chosen as the mark of a class must belong to all the members of that class.

But the properties of a type are necessarily somewhat vague: properties regarded by one observer as essentially belonging to the type may by another be regarded as accidental; a given substance may possess so many of the properties of the type as at one time suffices to ensure its admission into the class, but at a future time new properties may be discovered which necessitate the removal of the substance to a class whose type shews considerable divergence from that under which the substance was originally placed.

The very elasticity, and even vagueness, of the theory of types ensured it an important place in the development of chemical science.

SECTION III. *Equivalency of atoms.*

54 Dualism had reigned supreme, but only because it was despotic; when the rebellion, headed by Dumas, once got a footing the fate of the older theory was sealed. The new system succeeded because it was not too systematic.

In attempting to preserve unity of type through large series of compounds, the builders of modern chemistry were obliged to make free use of the conception of compound radicles as substituting simple radicles; they thus became familiarised with the general notion of each radicle possessing a definite substituting power.

In 1852 Frankland[1] extended this conception to the atoms of the elementary bodies; in 1855 Odling[2] introduced the use of dashes placed over the atomic symbols to express what he called 'the replaceable, or representative, or substitu-

[1] *Phil. Trans.* **142**. 417, see especially p. 440.

[2] *C. S. Journal*, **7**. 1. (The recognition of two 'replaceable values' for the iron atom, and other atoms, shews the close connexion between the theory then coming into existence and the older theory of equivalents.)

tion value' of these atoms, he also recognised that an elementary atom may have more than one 'replaceable value'. Odling applied this fruitful conception to the formulæ of many salts, especially the phosphates, and succeeded in shewing analogies until then overlooked.

The inherent fascination of the idea of the compound radicle may be realised, by considering that in less than twenty years after Dumas' discovery of the chloracetic acids, a discovery which marks the beginning of the revolt against the compound radicles of dualism, Kekulé[1], and independently of him Couper[2], (in papers of the greatest importance) found it necessary to recall chemists to the consideration of elementary atoms as being the true units by the combinations of which all compound molecules are built up, and by whose properties those of the compounds are determined. Couper criticised Gerhardt's development of types, objecting to the vagueness of the idea as a basis for classification; and especially opposing Gerhardt's opinion that the molecular constitution of bodies can never be ascertained by chemists. "Would it not be rational," says Couper, "in accepting this veto to renounce chemical research altogether?" This dictum of Gerhardt is to be traced, in Couper's opinion, to the overdue employment of compound radicles, to forgetting that these can have no properties which are not "a direct consequence of the properties of the individual elements of which they are made up," and hence to endowing these radicles with some "unknown and ultimate power which it is impossible to explain." Returning then to a study of the elements, Couper finds chemical affinity as a property inherent in, and common to, them all; he distinguishes 'affinity of kind' and 'affinity of degree;' applying the latter to carbon, he cites the oxides CO and CO_2 (in his notation C_2O_2 and C_2O_4), the former expressing the first, the latter the second and last, degree: CO_2 is "the ultimate affinity, or combining unit, for carbon."

Kekulé in 1857, and more especially in a paper published

[1] *Annalen* (1857), **104.** 129.

[2] *Phil. Mag.* (1858) [4], **16.** 104.

in March 1858[1], a paper the importance of which can hardly be overrated, distinguishes more clearly than Couper 'affinity of kind' from 'affinity of degree'; or rather he distinguishes chemical affinity from what he calls the '*basicity of atoms*'; both conceptions being needed, he says, for the explanation of chemical combinations. Kekulé clearly distinguishes, and this distinction has been too much forgotten in recent developments of chemical theory, between equivalent weights of elements, and equivalency (or basicity) of elementary atoms; he shews that the new theory deals with definite entities, called atoms, having defined properties, and not with 'unit weights,' and that it is these atoms which he proposes to compare as to their substituting power for the hydrogen atom. Having shewn that one atom of carbon, so far as our knowledge goes, is never combined with more than four atoms of hydrogen in a compound molecule, Kekulé also shews that two atoms of carbon do not bind to themselves more than six atoms of hydrogen, three atoms of carbon not more than eight atoms of hydrogen, and so on.

The *tetravalency* of the carbon atom, and the power which two, or more, atoms of carbon possess of binding themselves together in a molecule, are enunciated by Kekulé in this paper, which forms the foundation stone of the modern hypothesis of 'atom-linking.'[2]

Kekulé and Couper insisted, that if a definite conception of the connexions between the properties and the structure of compounds is to be obtained, it must be based on the study of the combining powers of the elementary atoms: 'The whole is simply a derivative of its parts,' said Couper.

55 An hypothesis which shall attempt to explain the atomic structure of compound molecules, must, in the present state of knowledge, be based on the consideration of gaseous bodies. We do not know how to determine the relative

[1] *Annalen*, **106**. 129.

[2] In comparing Couper's paper with Kekulé's it may be well to notice how Couper attempts to trace a close connexion between the *basicity of atoms* and chemical affinity; his statements are here much vaguer than Kekulé's, yet this dynamical method of regarding 'valency' at the very outset of the theory is important.

weights of the molecules of solid or liquid substances; indeed the term molecule is used with a strictly definite meaning only when applied to gases. We have reason to believe that the ultimate structure of a mass of a solid or liquid is much more complex than that of a mass of a gaseous substance; no generalisations have yet been made regarding the molecular phenomena of solids or liquids comparable with those which—under the names of the laws of Boyle, Charles, and Avogadro—have been made regarding the molecular phenomena of gases. We must recognise the limits within which an hypothesis regarding atomic structure can assist advance; if it be pushed too far it will become, with some a dogma, with others a thing to be scorned.

Consider these four molecular formulæ HCl, H_2O, H_3N, H_4Si. It is seen that one atom of chlorine is combined with one atom of hydrogen in the molecule HCl, that one atom of oxygen is combined with two atoms of hydrogen in the molecule H_2O, that one atom of nitrogen is combined with three atoms of hydrogen in the molecule H_3N, and that one atom of silicon is combined with four atoms of hydrogen in the molecule H_4Si. Considering the molecular formulæ ClH, Cl_2Hg, Cl_3Bi, and Cl_4Sn, it is seen that one atom of hydrogen is combined with one atom of chlorine, one atom of mercury with two atoms of chlorine, one atom of bismuth with three atoms of chlorine, and one atom of tin with four atoms of chlorine, in these compound molecules.

These facts may be expressed by saying that the atoms of oxygen and mercury are *divalent*, the atoms of nitrogen and bismuth are *trivalent*, and the atoms of silicon and tin are *tetravalent;* i.e. so far as the data at present before us are concerned, the atom of oxygen, and that of mercury, combines with two atoms of hydrogen or of chlorine; the atom of nitrogen, and that of bismuth, combines with three atoms of hydrogen or of chlorine; the atom of silicon, and that of tin, combines with four atoms of hydrogen or of chlorine, to form compound molecules.

56 But these terms *monovalent*, *divalent*, &c., *atoms* must be more strictly defined.

Let us begin by attempting to define the expression, *a monovalent atom.* Let those atoms which combine each with one, and not more than one, atom of hydrogen to form gaseous molecules, be placed together and called monovalent atoms. Then the atoms of *hydrogen, chlorine, bromine, iodine,* and probably *fluorine,* are monovalent; the evidence is the existence of the gaseous molecules HH, HCl, HBr, HI, and HF[1], and the non-existence of any gaseous molecules composed of a single atom of hydrogen, chlorine, bromine, iodine (or ? fluorine), and more than one atom of hydrogen. The term monovalent strictly implies that all the atoms to which it is applied are equivalent, or of equal value in exchange. It is important to observe that as regards combination with one atom of hydrogen to produce gaseous molecules, the atoms of chlorine, bromine, iodine, and probably fluorine, are equivalent; but that it is quite possible that these atoms may not be equivalent, or of equal value in exchange, in other respects.

If it is assumed that an atom which combines with not more than two atoms of chlorine, bromine, iodine, or fluorine, is equivalent to another atom which combines with not more than two atoms of hydrogen, then we arrive at the definition of a *divalent atom* as an atom which combines with not more than two monovalent atoms (i e. atoms of hydrogen, chlorine, bromine, iodine or fluorine) to form gaseous molecules. Similarly, definitions of *trivalent, tetravalent,* &c. *atoms* are found. Applying these definitions to the data contained in the table on pp. 39—43 we arrive at the following classification of atoms.

[1] Mallet [*Amer. Chem. Journal* **3** 189] has shewn that at low temperatures the molecule of hydrofluoric acid must be represented by the formula H_2F_2; at higher temperatures however the formula HF represents the molecule of this gas. It is possible that hydrofluoric acid is a 'molecular compound' at low temperatures (see Section **5** of the present chapter): determinations of the spec. gravity of this gas for a considerable range of temperature and pressure would throw light on this question.

STANDARD MONOVALENT ATOMS; H, F, Cl, Br, I.

I. *Monovalent atoms;* i.e.

atoms which combine with *one* standard monovalent atom to form gaseous molecules .. ..K, Rb, Ag, Cs, **Hg**, Tl.

II. *Divalent atoms;* i.e.

atoms which combine with *two* standard monovalent atoms to form gaseous molecules .....O, S, Se, **Te**, Be, Cd, Zn, **Hg**, **Sn**, **Pb**, Mn.

III. *Trivalent atoms;* i.e.

atoms which combine with *three* standard monovalent atoms to form gaseous molecules .....B, N, Al, **P**, Cr, As, Sb, Bi, In.

IV. *Tetravalent atoms;* i.e.

atoms which combine with *four* standard monovalent atoms to form gaseous molecules...C, Si, Ti, Ge, Zr, V, **Sn**, **Te**, Th, U, **Pb** (s. p. 128).

V. *Pentavalent atoms;* i.e.

atoms which combine with *five* standard monovalent atoms to form gaseous molecules.....**P**, Nb, Ta, Mo, **W**.

VI. *Hexavalent atoms;* i.e.

atoms which combine with *six* standard monovalent atoms to form gaseous molecules .....**W**.

The data on which this classification of atoms rests are presented in the following list of formulae which shew the compositions of all gaseous molecules composed of one of the standard monovalent atoms combined with a single atom of any other element:—

KI, RbCl, RbI, AgCl, CsCl, CsI, HgCl, TlCl; $BeCl_2$, $BeBr_2$, OH_2, OCl_2, SH_2, $MnCl_2$, SeH_2, TeH_2, $TeCl_2$, $CdBr_2$, $ZnCl_2$, $HgCl_2$, $HgBr_2$, HgI_2, $SnCl_2$, $PbCl_2$; BF_3, BCl_3, BBr_3, NH_3, $AlCl_3$, PH_3, PCl_3, $CrCl_3$, AsH_3, $AsCl_3$, AsI_3, $SbCl_3$, SbI_3, $BiCl_3$, $InCl_3$; CH_4, CCl_4, SiF_4, $SiCl_4$, SiI_4, $GeCl_4$, GeI_4, $TiCl_4$, $ZrCl_4$, VCl_4, $SnCl_4$, $SnBr_4$, $TeCl_4$, $ThCl_4$, UBr_4, UCl_4; PF_5, $NbCl_5$, $TaCl_5$, $MoCl_5$, WCl_5; WCl_6.

When it is said that one atom is combined with a certain number of standard monovalent atoms, direct interaction between these atoms in the molecule is assumed. Thus the statement that one atom of bismuth is combined with three

monovalent atoms of chlorine in the gaseous molecule $BiCl_3$ implies, that in this molecule there is direct action and reaction of some kind between the atom of bismuth and each of the atoms of chlorine. It might be that the atom of bismuth interacts directly with one, or two, atoms of chlorine and only indirectly with the other atoms; but considering that one atom of chlorine is never found combined with more than a single atom of hydrogen, bromine, or iodine, in gaseous molecules composed of any two of these elements, considering, that is to say, that the atom of chlorine is by definition monovalent, the simplest hypothesis is that the atom of bismuth interacts directly with each of the chlorine atoms in the gaseous molecule $BiCl_3$, in other words, that the atom of bismuth is trivalent in this molecule.

The groups of atoms, methyl CH_3, and ethyl C_2H_5, may be regarded as monovalent, inasmuch as each combines with one and not more than one of the standard monovalent atoms to form gaseous molecules[1]. If the formulæ of those gaseous molecules which are composed of a single atom of an element combined with one of the groups of atoms methyl or ethyl are tabulated, we find that the atom of lead is tetravalent as well as divalent[2].

The table on p. 127 contains 37 elements (besides the five standard monovalent elements); the atoms of six of these are found each in two classes. The atom of mercury is monovalent and divalent, the atoms of tellurium, tin, and lead are divalent and tetravalent, the atom of phosphorus is trivalent and pentavalent, and the atom of tungsten is pentavalent and hexavalent. This variation in the valency of certain atoms is not surprising when we recall the fact that an element has frequently more than one equivalent weight, and we consider that the object of the classification of atoms in accordance with their valencies is to place together those atoms which are equivalent, that is of equal value in exchange.

[1] These molecules are $(CH_3)H$, $(CH_3)F$, $(CH_3)Cl$, $(CH_3)Br$, $(CH_3)I$, $(C_2H_5)H$, $(C_2H_5)Cl$, $(C_2H_5)Br$, $(C_2H_5)I$.

[2] The molecules in question are these;—$Hg(CH_3)_2$, $Hg(C_2H_5)_2$, $Zn(CH_3)_2$, $B(CH_3)_3$, $Sb(C_2H_5)_3$, $Si(C_2H_5)_4$, $Sn(C_2H_5)_4$, $Pb(CH_3)_4$.

57 We have now gained definitions of the terms *monovalent, divalent, trivalent,* &c. as applied to atoms. The atoms of hydrogen, chlorine, bromine, iodine, (and fluorine) are equivalent in this respect that each combines with one and only one atom of hydrogen to form gaseous molecules; these atoms are therefore taken as the standard monovalent atoms.

The valency of any other atom is determined by finding the number of standard monovalent atoms with which it combines to form gaseous molecules, the maximum valency being measured by the maximum number of these standard monovalent atoms. It is certain that some atoms combine now with one number, and now with another number, of standard monovalent atoms, to form gaseous molecules.

The valency of the atom of an element cannot be accurately determined except at least one gasifiable compound has been obtained composed of a single atom of the element in question combined with standard monovalent atoms, and with such atoms only. Thus the valencies of the atoms of aluminium, iron, copper, and gallium cannot be definitely determined from considering the compositions of the following gaseous molecules;—Al_2Br_6, Al_2I_6, Fe_2Cl_6, Cu_2Cl_2, Ga_2Cl_6.

We might now define the valency of an atom to be the maximum number of atoms of hydrogen, fluorine, chlorine, bromine, or iodine, with which the specified atom combines to form gaseous molecules; but when we apply this definition we find it too limited. An examination of the compositions of the gaseous molecules tabulated on p. 127 leads to the notion of a limit to the number of atoms between which direct interaction occurs in gaseous molecules. This conception may be put into a definite form of words, thus; each atom in a gaseous molecule can directly interact with a limited number of other atoms. From this conception the definition of valency easily follows: *the valency of an atom is a number which expresses the maximum number of other atoms between which and the specified atom there is direct inter-*

action in any gaseous molecule. This definition furnishes an excellent working hypothesis in all attempts to learn anything of the arrangement of the parts of molecules.

But while the definition of valency of an atom is widened, we must, I think, always determine the valency of any specified atom by considering the compositions of gaseous molecules composed only of that atom and the standard monovalent atoms, hydrogen, fluorine, chlorine, bromine, and iodine. If a specified atom combines with not more than n standard monovalent atoms, then we conclude that this atom will not directly interact in any gaseous molecule with more than n atoms of any element. The greater the number of gaseous molecules composed of the specified atom and atoms of hydrogen, fluorine, &c. which have been examined, the greater is the probability that the value of n expresses the true maximum valency of the atom in question. Thus, suppose that the gaseous molecules $SnCl_4$ and $SnBr_4$ were unknown, the existence of the molecule $SnCl_2$ would lead us to place the atom of tin in the class of divalent atoms.

As only six of the 37 atoms whose valencies have been accurately determined (excluding the standard monovalent atoms) shew variations of valency, we may provisionally regard the value found for the valency of an atom from the composition of even a single molecule composed of that atom and any of the standard monovalent atoms as the true valency of the specified atom. At any rate we must make use of this value in all discussions regarding the arrangement of the parts of molecules into which this atom enters so long as no direct proof is forthcoming that the value is erroneous; and the only direct proof is the formation and analysis of gaseous molecules composed of the specified atom and a number of standard monovalent atoms different from the number present in the gaseous molecule on the composition of which the value originally adopted for the valency of the atom in question was based. If we allow ourselves to vary the valencies of atoms without cogent proof endless confusion arises, and the applications

of the hypothesis of valency become merely amusing exercises of fancy.

When therefore it is said in this book that the atom of a certain element is *n* valent, the statement is to be understood as asserting, (1) that one or more gaseous molecules are known composed of a single atom of the specified element combined with *n* atoms of hydrogen, fluorine, chlorine, bromine, or iodine; (2) that no gaseous molecule is known composed of a single atom of the specified element and more than *n* atoms of hydrogen, fluorine, &c.; and (3) that in discussions regarding the arrangement of the parts of molecules of which the specified atom forms a constituent, we shall assume that direct interaction occurs between the specified atom and not more than *n* other atoms of any kind.

58 Such a statement as 'the atom of phosphorus is trivalent in the molecule PCl_3' or 'the atom of carbon is trivalent in the molecule C_2H_4' asserts that the atom named directly interacts in the specified molecule with three other atoms; such statements do not assert that the maximum valency of the specified atom is defined by its actual valency in the particular molecule referred to. Such a statement as 'the atom of arsenic is trivalent' implies that the maximum valency of this atom is three.

59 The atoms of hydrogen, fluorine, chlorine, bromine, and iodine were placed in one class and said to be equivalent, because each combines with a single atom of hydrogen to form gaseous molecules. The atoms of 37 other elements were then arranged in classes, and the members of each class were said to be equivalent because they all combine with the same number of atoms of hydrogen, or fluorine, or chlorine, or bromine, or iodine, to form gaseous molecules. The conception of equivalency has evidently been widened; an atom of hydrogen is regarded as equivalent to an atom of chlorine not only as regards the combination of each with hydrogen atoms, but also as regards the combination of each with certain other atoms. Then the notion of equivalency was yet further widened, and it was said that all atoms which are equivalent in respect that they combine with *n*

atoms of hydrogen, fluorine &c. are also equivalent in respect that they directly interact with *n* atoms of any kind in gaseous molecules. The words *equivalent to* have been used with an ever widening meaning. It might be, and it has very often been, urged that to say that an atom is divalent is the same thing as to say that the atom is equivalent to two monovalent atoms. Thus, to say that the atom of oxygen is divalent, it may be argued, is an assertion that one atom of oxygen is equivalent to two atoms of hydrogen, fluorine, &c. If we are careful to recall the exact meaning of the words *equivalent to* in this statement, then, it seems to me, that no valid objection can be brought against the statement. Now the words *equivalent to* here mean, *combines with the same number of standard monovalent atoms as;* no other kind of equivalency between one atom of oxygen and two atoms of hydrogen, &c. is asserted. But the limitation of the meaning of the term equivalent in connexion with the valencies of atoms has been too much forgotten. Thus, it has been argued that because an atom of oxygen is divalent, and because the gaseous molecules CO and CO_2 exist, therefore the atom of carbon is divalent in the molecule CO and tetravalent in the molecule CO_2. To say this appears to me to be using a phrase which has no accurate meaning.

60 As there has been much discussion regarding such phrases as this, it behoves us to consider some of them more closely. The valency of an atom is generally expressed by a Roman numeral placed over the symbol of the element, thus C^{IV}, P^{III}; or by lines proceeding from the symbol, thus $-\overset{|}{\underset{|}{C}}-$, $-\overset{|}{\underset{|}{P}}-$. It required but a short time from the introduction of this notation for chemists to forget that these lines are only a form of language. From speaking of the valency of an atom, they soon came to speak of each line as *a valency*, or *a unit of affinity*, and to assert that such or such an atom has four (or three or two &c.) units of affinity or valencies. Then they went a step farther, and asserted that in the molecule CO two of the four valencies or units of affinity of the tetravalent carbon atom are satisfied by the two valencies

of the divalent oxygen atom, and that in the molecule CO_2 all the affinities of the carbon atom are satisfied by the four valencies of the two oxygen atoms. These assertions were embodied in the symbols $C=O$ and $O=C=O$. Similarly, the symbols $H_2=C=C=H_2$ and $H-C\equiv C-H$ were used to represent the distributions of the units of affinity, or the valencies, of the atoms of carbon and hydrogen in the molecules C_2H_4 and C_2H_2. Then such phrases as 'carbon atoms linked by double and treble bonds' and 'doubly and singly linked carbon atoms' were employed.

61 What definite meanings can be given to such expressions and such symbols?

(1) The statement[1] that an atom of carbon has four valencies or four units of affinity cannot mean that the force of affinity of a carbon atom is divided into four parts within that atom, for 'force' has no meaning apart from two or more reacting bodies: force is a name given by one of the parties to a transaction, but a transaction involves at least two transacting parties. The force between a carbon atom and another atom must vary with external conditions, probably with the distance, the mass, and the chemical nature, (a vague term but perhaps as good as can be given at present) of *both* atoms.

(2) The carbon atom has four equivalencies, or four units of affinity. This cannot mean that four parts of the carbon atom are chemically active, and the other parts inactive: such a hypothesis leads at present to contradictions (see appendix to Section **4**); moreover in the present state of knowledge it is inadvisable to hazard hypotheses as to the inner structure of atoms in order to explain chemical phenomena. Atoms may not be homogeneous, but at present they are the ultimate particles to be considered in chemical changes.

(3) The expression under consideration cannot mean that the chemical energy of a carbon atom is divided, or is

[1] A paper of the greatest importance entitled 'Ueber die Vertheilung der Atome in der Molekel,' by W. Lossen, appeared in *Annalen*, **204**. 265. I have made free use of this paper in the present chapter. (See also Claus, *Ber.* **14**. 432; and Lossen, *ibid.* 760.)

always divisible, into four parts. What is to be the unit of chemical work? the mass of matter fixed by a given atom? where then is the equivalency between one atom of oxygen with the mass 16 and two atoms of chlorine with the mass 71? Let a carbon atom combine with four hydrogen atoms, the total chemical energy of the atoms disappears; let a carbon atom combine with two atoms of oxygen, the total chemical energy of the atoms again disappears: but if the carbon atom possesses four 'units of affinity,' the oxygen atom two 'units of affinity.' and the hydrogen atom one 'unit of affinity,' the heats of formation of the two compound molecules ought to be equal; assuming, of course, that the heat produced when the molecules CH_4 and CO_2 are formed from atoms of carbon and hydrogen, and carbon and oxygen, respectively, measures the total loss of chemical energy which occurs in these processes. But the differences between the heats of formation of carbon compounds shew that the expression 'the carbon atom has four units of affinity' cannot mean that the chemical energy of the carbon atom is divisible into four parts, unless indeed the unit of affinity is variable, and is varied for each combination of carbon with other atoms[1].

(4) The carbon atom has four equivalencies. Can this mean that the atom exerts force in four directions? A so-called 'valency' is then a direction. But there is no force exerted till the mutual atomic transaction begins; the carbon atom considered alone has therefore no 'valencies.' Take the molecule CO; force is exerted by the carbon on the oxygen atom; the remaining 'valencies' are sometimes said to be 'mutually satisfied,' i.e. on the present hypothesis, the carbon atom in the molecule CO exerts force in two directions on itself; but here again we have the hypothesis of the non-homogeneity of the carbon atom, and the existence of active and inactive parts in that atom.

(5) In the vibration of a carbon atom there are four points, at each of which mutual action can occur between this atom and another atom. On this supposition, a 'double

[1] For a view analogous to this see appendix to Section 4 of the present chapter, par. 98.

link' would mean that mutual action occurs between the two atoms thus linked at two of these positions; e.g. the formula O = C = O would mean that in performing a vibration the carbon atom acts twice on, and is twice acted on by, each oxygen atom. But if so, surely a 'double link' would imply molecular stability, whereas it frequently means the reverse[1].

62 But although we cannot form a clear physical conception of the meaning of the phrase 'the carbon atom has four bonds,' and although such formulæ as C = O, O = C = O, $H_2C=CH_2$, and HC ≡ CH, which spring from the notion of atomic bonds, fail to call up in the mind clear images of the things they are meant to represent, nevertheless it may be urged that inasmuch as the properties of such molecules as CO, CO_2, C_2H_4, and C_2H_2, shew that the chemical functions of the atoms of carbon vary in different molecules all of which are composed of carbon and hydrogen atoms only or of carbon and oxygen atoms only, it is convenient to express such variations of function in our nomenclature and notation, and that the expressions 'singly, doubly, and trebly, linked carbon atoms,' and the symbols C − C, C = C, and C ≡ C, are convenient for this purpose.

The importance of expressing undoubted chemical facts in simple terms and of representing these facts in consistent

[1] A view different from any of the preceding has been suggested by Pickering (*C. S. Proc.* **1885.** 122), and also by Armstrong (*Proc. R. S.* **1886.** 268; *Nature*, **35.** 570); but the view appears to me to involve the use of the term *valency* as synonymous with *affinity of atoms*, and therefore to call for discussion rather in the chapter on affinity than in the present place. In his *Ansichten über die organische Chemie* (part I., pp. 2—5), van't Hoff regards the chemical interactions of atoms as a consequence of gravitation. He shews that if the form of an atom is not spherical the intensity of the attraction of that atom for other atoms must be marked by a definite number of maximum points on the surface of the atom, which maxima depend on the form of the atom, and may have different values. The number of these maxima is regarded by van't Hoff as expressing the valency of the atom. As the atom vibrates its form will undergo change; hence the valency of an atom may vary with variations in the state of motion of the atom, and these variations will be conditioned by temperature, nearness to other atoms, &c. On this view, a combination of atoms, that is a molecule, must possess a certain valency, which is conditioned by the special arrangement of its parts, but is not necessarily the same as the valency of any of these parts. On the subject of 'double bonds' see also appendix to Section 4 of this chapter.

formulæ is admitted by all chemists. Those chemists who oppose the use of formulæ and terms based on the hypothesis of atomic bonds assert, and I think rightly assert, that the facts supposed to be expressed by single, double, and treble linkings are more simply and as forcibly expressed by formulæ arising out of the three fundamental notions of atomic valency; which are (1) that each atom in a molecule directly interacts with a limited number of other atoms; (2) that the maximum number of atoms with which any specified atom directly interacts is measured by the maximum number of atoms of hydrogen, fluorine, chlorine, bromine, or iodine, with which the atom in question combines to form a gaseous molecule; and (3) that an atom may, and frequently does, directly interact with a smaller number of other atoms than is expressed by its maximum valency. Instead of saying, 'the two carbon atoms in the molecule of ethane (C_2H_6) are singly linked, the two carbon atoms in the molecule of ethylene (C_2H_4) are doubly linked, and in the molecule of acetylene (C_2H_2) the two carbon atoms are trebly linked,' these chemists say, 'the molecule of ethane contains a pair of tetravalent carbon atoms, the molecule of ethylene contains a pair of trivalent carbon atoms, and the molecule of acetylene contains a pair of divalent carbon atoms'; and instead of the symbols $H_2C=CH_2$ and $HC\equiv CH$, they use the symbols H_2C-CH_2 and $HC-CH$. All that is expressed or suggested by the first pair of formulæ is expressed and suggested by the second, and the latter have the great advantage of being based on a definite and self-consistent hypothesis of atomic valency, whereas the former rest to a great extent only on words and phrases.

The expressions 'single, double, and treble linkings,' 'mutual satisfaction of units of affinity,' and the like, imply the possession of knowledge which at present we do not possess.

The notion of units of affinity, or valencies[1], or bonds, has been carried too far. It appears at first sight to give

[1] It is important to distinguish between the expression '*valency*' and '*a* valency.'

a dynamical explanation of the structure of molecules, but it has forgotten the two-sidedness of atomic transactions; it apparently affords a means of measuring atomic forces, but it has used a unit, undefined except as a quantity changeable at pleasure; it appears to simplify chemical formulæ, but it has really made them harder to understand by grafting on to the definite conception of atom the vague and unnecessary notion of 'bond.'

63 The valencies of the atoms of about three-fifths of the elements can be regarded as fairly well established. The data required for determining the valency of an elementary atom are, the analysis, and determination of the molecular weight, of more than one gasifiable compound, the molecule of each of which compounds is composed of a single atom of the specified element combined with monovalent atoms only, that is combined with atoms of hydrogen, chlorine, bromine, iodine, or fluorine, only.

Many non-gasifiable compounds containing monovalent atoms combined with atoms of a single other element are known (e.g. many metallic haloid compounds): if the reacting weights of these solid compounds, as deduced by the aid of considerations such as those sketched on pp. 78—85, are assumed to be the true relative weights of the molecules of these compounds; and if those generalisations which have been made concerning the arrangement of atoms in gaseous molecules are assumed to hold good for the reacting weights of solids also; then the valency of many elementary atoms not included in the table on p. 127 can be determined. Thus, if we assume that the general formula MX represents the atomic structure of the molecules of the solid haloid salts of the alkali metals, (M = K, Na, Li, &c. and X = F, Cl, Br, or I) then the atoms of these metals are most probably monovalent. Most of the generally accepted formulæ for salts of alkali metals may be written with the atoms of these metals represented as each in direct combination with only one other atom; but whenever this arrangement has become somewhat unsatisfactory chemists have not hesitated to assume that the atoms of the alkali

metals may be tri- penta- or even heptavalent, i.e. may each act on, and be acted on by, 3, 5, or 7 other atoms. So with other elements; from a consideration of solid or liquid compounds only no trustworthy conclusions as to the valencies of the atoms in the molecules of these compounds can be deduced. It is so easy, after making the two fundamental assumptions stated above, to make an indefinite number of further assumptions; it becomes so pleasant to manipulate formulæ on paper, that it is certainly better, in the present state of knowledge, to determine the valencies of atoms altogether from the study of gaseous molecules. It is very probable that the valency of the elementary atoms varies periodically with variations in the relative weights of these atoms: if this general statement is thoroughly established, the exact nature of the periodic function is determined, and the true atomic weights of all the elements are fixed, we shall have in the *Periodic Law* a most important method for determining atomic valencies. But a great deal of work must be done before this 'law' can be applied otherwise than generally and tentatively to questions of valency (see chap. III. par. 114).

SECTION IV. *Allotropy and Isomerism.*

64 Having gained the conception of a molecule as composed of atoms each directly interacting with a definite number of other atoms, we at once regard the molecule as a structure; we recognise what Frankland in 1852 happily called 'limited molecular mobility.' A structure involves arrangement of parts and subordination of less to more important parts; it supposes the existence of definite actions for fulfilling which the structure is adapted; in a word, structure means correlation of properties with material configuration[1].

[1] When 'arrangement of atoms in the molecule' is spoken of, or when a similar phrase is used, it is to be taken as implying only a rough approximation to a knowledge of atomic arrangements. Structural formulæ sum up facts of formation and decomposition, and, assuming the fundamental positions of the molecular and atomic theory, and also the hypothesis of valency, these formulæ exhibit, in a rough and general way, connexions between these facts and the directions of the mutual interactions of the atoms in the molecules of the compounds

And when we consider the properties of individual molecules the justness of thus regarding each as a definite atomic structure becomes more apparent. We find many compound molecules composed of the same number of the same atoms and yet exhibiting markedly different chemical and physical properties, i.e. we find the phenomenon of *Isomerism:* how can we account for this except by assuming (1) that each molecule has a definite atomic structure, and (2) that the same atoms may be differently arranged in different molecules?

65 A knowledge of the atomic configurations of series of molecules, supposing this to be gained, must be supplemented by a knowledge of the way in which the energy of each molecule varies with variations in the configuration and motion of its constituent atoms, before a complete knowledge of the dynamical properties of these molecules is possible. But chemistry is yet far from this goal; she is obliged to be content with a very partial and sometimes very vague knowledge concerning the atomic configurations of a few molecules; she has hardly entered on the second part of her task.

66 Granting then that variations in the properties (chemical and physical) of molecules accompany variations in the configurations of the atoms which build up these molecules, it is conceivable that the latter variations may consist in

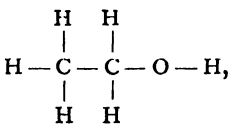
(1) variations in the relative positions of the atoms,

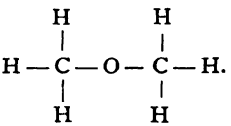
or (2) variations in the distances between the atoms, their relative positions being constant.

To illustrate this point let us take the molecule C_2H_6O. More than one compound exists the molecules of which have the atomic composition expressed by this formula. On the first assumption, viz. that variation of properties is to be correlated with variations in the relative positions of the atoms in the molecule, the atoms being represented as arranged all in the same plane, we find that there are two possible arrangements of two carbon, six hydrogen, and one oxygen,

formulated, the atoms being represented in the formulæ as situated all in the same plane. No attempt is made in these formulæ to express quantitative measurements of atomic interactions.

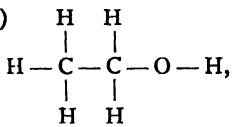
atoms (assuming the valency of the carbon, hydrogen, and oxygen atom to be 4, 1, and 2 respectively), viz.;

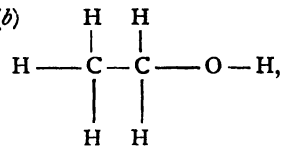
(*a*)


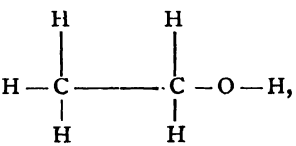
(*b*)


Hence, on the first assumption, two compounds each having the composition expressed by the empirical formula C_2H_6O may exist.

But if we make the second assumption, viz. that variation of properties is to be correlated with variations in the distances between the atoms in the molecule, the relative positions of these atoms remaining unchanged, we may have an apparently unlimited number of compounds of the formula C_2H_6O; such compounds might perhaps be represented in this way:—

(*a*)


(*b*)


(*c*)


and so on.

Now as only two compounds having the composition C_2H_6O are known to exist, we have a presumption in favour of the first supposition: much stress cannot however be laid on this argument. Moreover if the second of the two suppositions is correct, then any molecule composed of two atoms should be capable of existing in more than one modification; in other words, every diatomic molecule should be capable of shewing isomerism. But there is no certainly-established instance of isomerism exhibited by a molecule composed of less than three atoms; therefore, as the assumption that variations of properties exhibited by compounds having the

same composition and the same molecular weight are connected with variations in the relative positions of the atoms composing the molecules of these compounds suffices to explain the vast majority of well-authenticated cases of isomerism among gaseous molecules, we conclude that it is better, at any rate at present, to build the general theory of isomerism on this hypothesis[1].

67 But before more fully considering this subject, it will be well to glance at the allied phenomena of *allotropy* and *polymerism*.

The table on p. 45 shews that of the sixteen elements whose molecular weights have been determined by the help of Avogadro's law, six, viz. oxygen, sulphur, selenion, iodine, phosphorus, and arsenic (probably bromine also), possess a smaller molecular weight at high than at lower temperatures:—the number of atoms in the molecule of oxygen at temperatures below about 300° and under special conditions is 3, at temperatures above 300° it is 2; the molecule of sulphur at temperatures not much higher than the boiling point of that element is composed of 6 atoms, and at somewhat higher temperatures of 2 atoms; the number of atoms in the molecule of selenion varies from 3 to 2, in the molecule of iodine (and probably also in that of bromine) from 2 to 1, and in the molecules of phosphorus and arsenic from 4 to 2, according to temperature. We know that the properties of the triatomic molecule O_3 differ much from those which characterise the diatomic molecule O_2; no experiments have been made to compare the properties of the hexatomic with those of the diatomic molecules of sulphur, of the triatomic with the diatomic molecules of selenion, of the diatomic with the monatomic molecules of iodine, or of the tetratomic with the diatomic molecules of phosphorus or arsenic.

Of the 15 or 16 nonmetallic elements, phosphorus and

[1] The supposition that isomerism may be due to variations in the distances between atoms the relative positions of which remain unchanged, appears to be opposed to the results of physical experiments which are in agreement with deductions made from the kinetic theory of gases. See Lossen, *Annalen*, **204**, p. 269.

arsenic, boron, carbon and silicon—besides sulphur and selenion—exhibit marked variations in physical and chemical properties when in the solid state. We are not justified in unconditionally asserting that these variations of properties accompany differences in the atomic configurations of the molecules, or differences in the numbers of atoms in the molecules, of red and yellow phosphorus, or of octahedral and prismatic sulphur, &c. When the differences in properties are chiefly physical (e.g. differences in crystalline form, in specific gravity, in melting points, &c.), they very probably may be correlated with differences in the molecular, rather than in the atomic, configurations of the various modifications of the element in question [1].

Be this however as it may, the differences experimentally shewn to exist between the properties of the molecules of gaseous oxygen and ozone are explicable in terms of the molecular theory only by admitting that the properties of a molecule are dependent not only on the nature but also on the number of the atoms which compose it [2].

68 The names *allotropy* and *polymerism* are applied to analogous phenomena exhibited by elements and compounds respectively [3]. In the preceding paragraph we have had

[1] See Section 5 of present chapter.

[2] It ought to be noted that change from one allotropic form to another is accompanied by production or disappearance of heat; see *post*, chap. IV., par. 125. There are some interesting observations bearing on the subject of allotropy by W. Spring in the *Berichte* [see especially 16. 1002—3]. Spring finds that when an element which exhibits allotropy is subjected to great pressure, that modification which has the greatest specific gravity is produced. Yellow phosphorus is changed into red by compression: red phosphorus and sulphur do not combine until heated to 260°, i.e. to the temperature at which red is changed to yellow phosphorus; red phosphorus does not combine with sulphur when the two are subjected to a pressure of 6500 atmospheres, at which pressure many metallic sulphides are produced. Hence Spring concludes that red phosphorus is less chemically energetic than yellow; and generally that the more a solid substance is rendered dense the more is its chemical activity decreased. Red phosphorus he regards as a *polymeride* of yellow phosphorus.

[3] The term *allotropy* is sometimes applied to compounds as well as to elements, to express the existence of two or more forms of the same solid compound; thus arsenious oxide crystallises in two distinct forms, and the change from one of these to the other is sometimes said to be an allotropic change. *Allotropy* as thus applied to compounds is synonymous with *physical isomerism* (*s. post*, par. 101). The

examples of allotropy, let us now consider a few examples of polymerism.

If two molecules exist consisting of the same elementary atoms but one heavier than the other, the heavier molecule is said, in certain cases, to be a 'polymeric modification' or a 'polymeride' of the other: thus $C_{10}H_{20}$ is a polymeride of C_5H_{10}, $C_{15}H_{24}$ is a polymeride of $C_{10}H_{16}$, $H_3C_3N_3O_3$ is a polymeride of HCNO, $C_6H_{12}O_3$ is a polymeride of C_2H_4O. Glucose, $xC_6H_{12}O_6$, is not however regarded as a polymeride of acetic acid, $C_2H_4O_2$: the name is restricted to those molecules whose mass is a multiple of that of other molecules, and which are obtained by simple reactions from these other molecules. Thus ethaldehyde, C_2H_4O, is easily polymerised (e.g. by the action of a very little hydrochloric or sulphuric acid) with formation of parethaldehyde, $C_6H_{12}O_3$: but the latter body is not directly obtainable from ethylene oxide, although the molecule of this compound, like that of ethaldehyde, is composed of 2 atoms of carbon, 4 of hydrogen, and 1 of oxygen; therefore parethaldehyde is not called a polymeride of ethylene oxide.

But few examples of undoubted polymerism are furnished by compounds of the elements other than carbon: one of the most marked cases is the molecule N_2O_4 which is a polymeride of NO_2; another instance is furnished by the molecules Sn_2Cl_4 and $SnCl_2$.

69 Let us now turn to the subject of *isomerism*. This term is applied to the existence of molecules characterised by different properties but composed of the same number of the same atoms.

Isomeric compounds are generally said to be *metameric* when they belong to different chemical types. This statement does not of course furnish a definition of metameric compounds; but it is sufficient. Various hydrocarbons, all possessed of the general properties of paraffins but each differing in some properties, chemical and physical, from the others, are represented by the formula C_6H_{14}: various hydro-

art. **Allotropy** in the new edition of *Watts's Dictionary* should be read by the student.

carbons, all benzenes, but each characterised by its own special properties, are represented by the formula C_8H_{10}: the different paraffins (C_6H_{14}) or the different benzenes (C_8H_{10}) are said to be *isomerides* one of the other. But although two molecules are represented by the formula C_2H_6O yet these belong to very different types or groups of compounds, one is a primary alcohol, the other is an ether; so again allylic alcohol and dimethyl ketone have both the formula C_3H_6O, but these bodies are altogether distinct in their chemical properties: such compounds are said to be *metameric*. *Metamerides* are thus seen to be a sub-class included in the larger class of isomeric compounds.

A few inorganic compounds exhibit phenomena which may be explained by supposing the existence of isomeric molecules, but it is only when we study the compounds of carbon that we are obliged to admit that molecules may be composed of the same numbers of the same atoms but differ in chemical and physical properties.

70 The hypothesis of atomic valency having led to the recognition of the molecule as a structure may be carried further; it may guide us in determining the probable relative structures of isomeric molecules (see note to p. 138).

If it be granted that isomerism is correlated with different relative positions of atoms, but not with different distances between atoms in the same relative positions in the molecule, (see p. 139) it follows that a molecule composed of not more than two atoms cannot exhibit isomerism[1].

The maximum number of monovalent atoms which can be combined with polyvalent atoms in a molecule is found by the formula[2]

$$n_1 = n_3 + 2n_4 + 3n_5 + 4n_6 + 2,$$

where n_1, n_3, n_4, &c. represent the numbers of monovalent, trivalent, tetravalent, &c. atoms in the molecule. In any molecule in which the value of n_1 agrees with that deduced by this formula each polyvalent atom must necessarily directly

[1] Such formulæ as O=N– and =N–O– are really at present the same

[2] See Lothar Meyer, *Die Modernen Theorien der Chemie* (4th Ed.), p. 218 *et seq.*, or English Edition [*Modern Theories of Chemistry*], p. 198 *et seq.*, of which pages free use has been made in these paragraphs.

interact with the maximum number of monovalent atoms. Such molecules are said to be *saturated;* they cannot directly combine with monovalent atoms. Examples of saturated molecules are furnished by C_2H_6, C_3H_8, C_2H_5Cl, $C_3H_6Cl_2$, &c. But in the molecules C_2H_4, C_2H_2, C_6H_6, and in many other molecules, the number of monovalent atoms is less than that expressed by the formula just given. In these molecules each polyvalent atom directly interacts with less than the maximum number of monovalent atoms. Such molecules are said to be *unsaturated.* Unsaturated molecules are generally able to combine directly with monovalent atoms.

The language in which the facts of isomerism are generally expressed speaks of some of the polyvalent atoms in unsaturated molecules as being 'linked by double or treble bonds'; the language which springs from the view of valency adopted in this book (the view is essentially that of Lossen) speaks of some of the polyvalent atoms in unsaturated molecules as exhibiting in these molecules less than their maximum valency.

Thus to take the unsaturated molecules C_2H_4 and C_2H_2: the expression in common use is 'the carbon atoms in the molecule C_2H_4 are joined by a double bond, and in the molecule C_2H_2 by a treble bond'; and this expression is embodied in the formulæ $H_2C=CH_2$ and $HC\equiv CH$: the expression used by the upholders of Lossen's conception of atomic valency is 'the carbon atoms in the molecule C_2H_4 are trivalent, and in the molecule C_2H_2 the carbon atoms are divalent'; and this expression is embodied in the formulæ H_2C-CH_2 and $HC-CH$. The expressions 'a pair of doubly linked carbon atoms' and 'a pair of trebly linked carbon atoms' are respectively synonymous with the expressions 'a pair of trivalent carbon atoms' and 'a pair of divalent carbon atoms': each term used in the latter expressions has an accurate meaning defined once for all; the meanings given to the terms 'doubly linked' and 'trebly linked' atoms depend upon the views of the chemist who employs them.

71 The number of ways in which the atoms comprising a complex molecule may be arranged, in accordance with the

limitations imposed by the hypothesis of atomic valency, is evidently very great; to determine the maximum number of possible isomerides of a given formula is a purely mathematical problem[1]. At present we seem justified in concluding that many atomic configurations which are mathematically possible are physically impossible; this is equivalent to saying that the stability of molecules does not depend solely on the valencies of their constituent atoms. To determine which of the possible configurations of a given number of atoms are stable; to generalise the connexions undoubtedly existing between molecular structure and stability, and also between this structure and the functions of the molecule or of parts thereof; this is the task that chemists are now elaborating.

72 The molecular formula of a compound sometimes of itself gives us a considerable amount of information regarding the structure of the molecule of that compound. Thus we appear justified, at present, in making the following assertions: (1) molecules composed of monovalent atoms only cannot exhibit isomerism; (2) molecules composed of a single polyvalent atom united with monovalent atoms only cannot exhibit isomerism; (3) isomerism cannot be exhibited by molecules composed of two polyvalent atoms united with monovalent atoms, provided the latter are all atoms of the same element, or all but one atoms of the same element, when the two polyvalent atoms are themselves atoms of the same element.

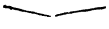
73 Any molecule composed of more than two atoms and not belonging to one of the classes above defined may exhibit isomerism. The possible variations of structure even in molecules composed of a small number of atoms may be large. Thus N_2O may have any of the structures

(1) $\begin{matrix} N-N \\ \diagdown O \diagup \end{matrix}$, or (2) $N-N-O$, or (3) $N-O-N$;

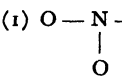
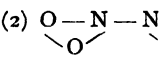
[1] Prof. Cayley, *Brit. Ass. Reports* for 1875. 257, examined the relations between the number of carbon atoms in the molecules of paraffins and the number of isomeric modifications of each molecule allowed by the hypothesis of valency; thus

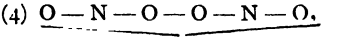
number of carbon atoms in molecule of paraffin,	1.	4.	7.	10.	12. 13.
number of possible isomerides	1.	2.	9.	75.	357. 799.

neither the nitrogen nor the oxygen atom can directly interact with *more* than two atoms, i.e. neither can be more than divalent[1]. NO can be regarded only as N — O. NO_2 *may* be

(1) O — N — O, or (2)  or (3) N — O — O.

N_2O_4 *may* have many structures; e.g.

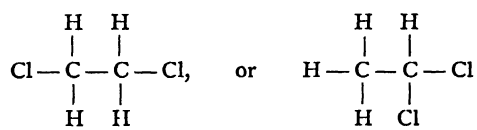
(1)  or (2) 

or (3) O — N — O — O — N — O, or (4) 

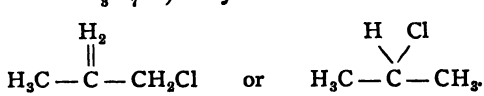
or (5) N — O — O — O — O — N, or (6) N — N — O — O — O — O, &c.

The compounds of carbon present the best field for the study of isomerism[2].

It has been already stated that a molecule composed of two carbon (tetravalent) atoms united with five monovalent atoms of one element and one monovalent atom of another element, (i.e. a molecule of the form C_2X_5X) cannot exhibit isomerism. If however there are four monad atoms of one kind, and two of another kind, in the molecule (if the form of the molecule is represented by the symbol $C_2X_4X_2$) isomerism becomes possible; thus $C_2H_4Cl_2$ may have the structure



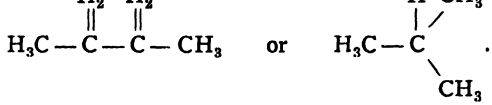
(or more shortly, $ClH_2C - CH_2Cl$ and $H_3C - CHCl_2$). But when three carbon atoms combine with monovalent atoms, the existence in the molecule thus produced of a single monad atom different in kind from the other monad atoms renders isomerism possible; thus C_3H_7Cl (which belongs to the general form C_3X_7X) may have the structure



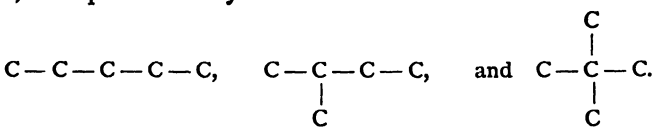
[1] Lossen's nomenclature and notation are used here and generally throughout the rest of this book.

[2] The subject of the constitution of compounds is considered very fully and clearly in the 3rd edition of Remsen's *Theoretical Chemistry*.

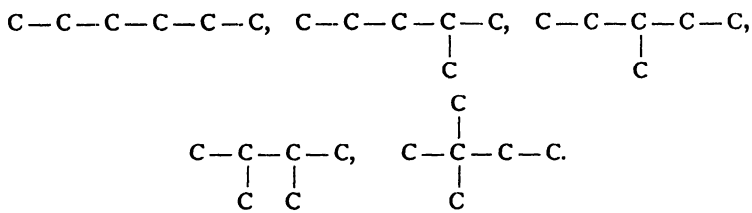
So also four molecules $C_3H_6Cl_2$, five molecules $C_3H_5Cl_3$, six $C_3H_4Cl_4$[1], five $C_3H_3Cl_5$, &c. may exist. Molecules composed of four, or more than four, atoms of carbon combined with monovalent atoms may exhibit isomerism even when all the monad atoms are of one kind, (i.e. molecules of the general form C_4X_{10}); thus C_4H_{10} may have the structure



Molecules composed of five carbon atoms combined with other atoms may have the carbon atoms arranged in three ways, as represented by the formulæ

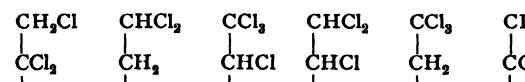


When six carbon atoms are present in the molecule these atoms may be arranged in five ways, viz.



When eight carbon atoms are present, they may be arranged in 18 different ways, &c. The maximum number of monovalent atoms which can be combined with any of these arrangements of carbon atoms is found by the formula $n_1 = 2n_4 + 2$ where n_4 = number of carbon atoms[2]. But all the carbon atoms in a molecule are not necessarily tetravalent in that molecule (in the ordinary nomenclature some of

[1] Viz.



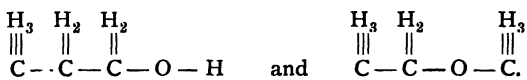
[2] See Lothar Meyer, *loc. cit.* pp. 240—242.

the carbon atoms may be doubly or trebly linked to one another, or there may exist 'free affinities'). Now the general formula given on p. 144, viz.

$$n_1 = n_3 + 2n_4 + \ldots\ldots 2$$

shews that the maximum number of monad atoms in such a molecule is dependent only on the number of trivalent and tetravalent, and is independent of the number of divalent, carbon atoms in the molecule. But in applying this formula it is assumed that the number of carbon atoms which are actually trivalent, and of those which are actually tetravalent, in any given molecule, can be determined. It is better to represent the molecule of a carbon compound, if possible, as containing only tetravalent carbon atoms: in many cases however this cannot be done; in any case the reactions of the compound must be studied before a formula is given to it.

Let us suppose we are required to assign formulæ to compound molecules containing carbon, hydrogen, and oxygen atoms. When the equation $n_1 = 2n_4 + 2$ is satisfied, the structural formula assigned to the molecule must evidently contain only tetravalent carbon atoms; several such formulæ may however be possible; thus for the molecule C_3H_8O two structural formulæ fulfil the conditions required:—



In accordance with generalisations which have been made correlating structure and properties the first of these formulæ belongs to a primary alcohol, the second belongs to a mixed ether: two and only two compounds having the composition C_3H_8O are known; one exhibits the properties of a primary alcohol, the other those of a mixed ether.

When however $n_1 < 2n_4 + 2$, and divalent atoms are also present in the molecule, the formula may contain only tetravalent carbon atoms, or it may contain tetravalent, and also di- or trivalent, carbon atoms. Thus in C_3H_8O $n_1 = 2n_4$;

two structural formulæ are possible for this molecule wherein each carbon atom is tetravalent, viz.

(1) $H_2C-CH_2-CH_2$ (O) and (2) $H_3C-CH-CH_2$ (O).

Each of these is the formula of an ether; in propylene oxide we have an ether the properties of which shew that it is probably described by the first of these formulæ. Six structural formulæ are possible for the molecule C_3H_6O, provided some of the carbon atoms may be tri- or divalent. Three compounds having this formula (besides propylene oxide) are known; of these, one is a ketone, i.e. belongs to a class of compounds the molecules of which are generally regarded as containing a carbon and an oxygen atom in direct union; another is an aldehyde, i.e. belongs to a class of compounds the molecules of which are regarded as containing a carbon atom in direct combination with one oxygen and one hydrogen atom; and the third is an alcohol, probably a primary alcohol. The six possible formulæ are

(1)	(2)	(3)	(4)	(5)	(6)
CH_3	CH_3	CH_2	CH_3	CH_2	CH_3
|	|	|	|	|	|
$C-O$	CH_2	CH	CH_2	C	CH
|	|	|	|	|	|
CH_3	$H-C-O$	CH_2	$C-O-H$	CH_2	CH
		|		|	|
		$O-H$		$O-H$	$O-H$

The first and second formulæ contain each one trivalent carbon atom and the oxygen atom is monovalent in both, the fourth and fifth contain each one divalent carbon atom, and the third and sixth each two trivalent carbon atoms. Formulæ (1) and (2) are appropriated by dimethyl ketone and propaldehyde respectively; of the remaining four, (3) and (5) represent allylic alcohol as a primary, (6) as a secondary, and (4) as a tertiary, alcohol. Judging from the general reactions of allylic alcohol this compound is probably a primary alcohol. Formula (3) is preferable to (5), because the latter would lead us to expect acetic acid (H_3C-CO_2H) as one of the products of oxidation of allylic alcohol; inasmuch as

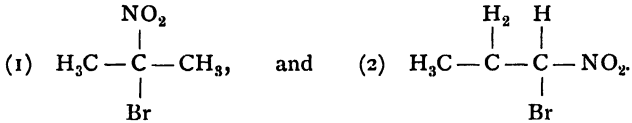
acetic acid is not produced in this oxidation, formula (3) more probably expresses the structure of the molecule of allylic alcohol than any other possible formula.

74 In these examples of the method adopted for determining the structural formula of a compound several generalisations concerning the connexion of structure with properties have been assumed. For instance, it has been assumed that if a given compound exhibits aldehydic properties the structural formula of the molecule is to be written as containing the atomic group CHO; but it has also been assumed that two structures are possible for this group, one in which the carbon atom interacts directly with the oxygen and the hydrogen atoms (H−C−O), and the other in which the carbon atom directly interacts with the oxygen atom only (C−O−H); further, the first of these structures is assumed to be correlated with the group of properties connoted by the word 'aldehydic,' and the second with the properties connoted by the expression 'tertiary alcoholic.' When therefore a new carbon compound is discovered, it is necessary to determine, as far as possible, to what group of compounds it belongs; the existence of a certain atomic group (or groups) in the molecule of the compound may then generally be predicated, and the number of possible structural formulæ may thus be considerably diminished. But the classification of the carbon compounds is certainly not yet complete; hence arise two difficulties; (1) a new compound may belong to a class no other member of which has been previously examined, in which case no class-group can be assigned to the formula of the new compound; or (2) a compound may be prepared whose properties indicate that it belongs to one of the known classes, and yet the atomic group which generally marks this class may not be present in the molecule of this particular compound. The following cases may be taken as illustrations of these difficulties.

(1) It was known that the interaction of nitrous acid with carbon compounds the molecules of which contained the group NH_2 (amido-derivatives) resulted in the production of compounds differing from the original by containing OH

in place of NH_2; but when nitrous acid acted on certain amido-derivatives of benzene, compound molecules containing one nitrogen atom more and two hydrogen atoms less than the original molecule were obtained. The reaction appeared to be abnormal. Several of the new compounds were prepared, their properties were studied, and the existence of a new class of carbon compounds was recognised, the relations of which to other classes could be summarised in formulæ containing the characteristic group $-N_2-$.

(2) As the result of long and varied experience the generalisation has been made that the molecules of very many carbon acids contain the characteristic group $H-O-C-O$; but from time to time compounds have been prepared exhibiting acidic properties, but possessed of a molecular structure from which the characteristic group is absent. Thus C_3H_8 yields $C_3H_7NO_2$, and from this compound two isomerides $C_3H_6BrNO_2$ are obtained, one of which is a monobasic acid, while the other does not shew acidic properties; the possible formulæ for these isomerides are



From a consideration of the general properties of the two isomerides and their relations to other compounds the second formula is assigned to the acid. Hence we are obliged to conclude that although most known carbon acids are characterised by the atomic group $H-O-C-O$, yet a carbon compound in the molecule of which this group is not present may nevertheless be a true acid.

A very instructive example of the difficulties to be overcome before a general structural formula can be assigned to a group of carbon compounds, is afforded by the investigations which have been and are being made into the constitution of the quinones; and also into the constitution of the compounds allied to indigo[1].

[1] See Armstrong and Groves, *Organic Chemistry*, pp. 812, 813. Also art. "Indigogruppe" in Ladenburg's *Handwörterbuch der Chemie*, Bd. 5, p. 248.

These examples (and others might easily be added) shew how undesirable it is to regard the present system of classification of carbon compounds as final. As facts are accumulated the atomic grouping which was regarded as a class-group sometimes becomes the group of a larger class, sub-classes being formed each characterised by its special group and yet each containing the class-group. Thus, from the analogy between metallic hydroxides and alcohols, and for other reasons, the group O – H was assigned to alcohols (e.g. $C_2H_5.OH$, $C_3H_7.OH$, &c., &c.); but it became evident that a sub-division of this great class was required; facts were amassed and formulæ devised to generalise these facts, until most chemists are now agreed that the molecules of those alcohols called 'primary' (which yield certain definite products when oxidised, &c.) contain the atomic group H – O – CH_2, the molecules of those called 'secondary' (and which yield other but also definite products when oxidised) contain the group H – O – C – H, and the molecules of those called 'tertiary' (which yield a third distinct set of products when oxidised) contain the group C – O – H.

Each of these 'alcoholic groups' itself contains the group O – H; but the 'acid group' H – O – C – O also contains this group; now we know that the function performed by hydrogen in an alcoholic molecule is not the same as that performed by hydrogen in an acid molecule; e.g. all, or some, of the hydrogen in the latter, but none of that in the former, is replaceable by metal when the compound is acted on by a metallic carbonate; hence we infer that the function discharged by a given atom in a molecule depends not only on the nature of that atom, but also on the nature of the atoms with which it is directly, and indirectly, connected in the molecule.

In all the alcoholic groups (viz. H_2C – OH, HC – OH, and C – OH) an atom of hydrogen is directly connected with an oxygen atom which is again directly connected with an atom of carbon, which directly interacts with either hydrogen atoms *and* atoms belonging to the other part of the molecule—always either carbon or hydrogen atoms—or

only the latter. In the acid group (O – C – OH) the carbon atom with which the hydrogen atom is indirectly connected (through an atom of oxygen) is itself directly connected with an oxygen atom, as well as with an atom, or atoms, belonging to the other part of the molecule. Now oxygen is a markedly electro-negative element; from the facts enumerated and from other similar facts, the generalisation has been made, that when an atom of hydrogen is in direct connexion with an atom of carbon which also directly binds negative atoms, or negative groups of atoms, that hydrogen is, as a rule, 'replaceable by metal' &c.; i.e. that hydrogen fulfils the function of 'acidic hydrogen.'[1]

75 In thus trying to use the hypothesis of valency as a guide towards determining the structures of isomeric molecules, we have found it on the whole advantageous to limit the application of this hypothesis in various ways.

I. The hypothesis is applied in strictness only to the molecules of bodies in the gaseous state.

II. The valency of an atom of any specified element is defined as a number which expresses the maximum number of other atoms between which and the given atom there is direct action and reaction in a molecule; this number is determined by the study of certain defined classes of molecules, viz. molecules composed of a single atom of the specified element combined with atoms of hydrogen, fluorine, chlorine, bromine, or iodine.

III. Isomerism is regarded as correlated with varying

[1] I am aware that such expressions as are used in these paragraphs, 'a carbon atom is directly connected with, or directly binds to itself, an atom of hydrogen,' &c., are very easily misunderstood; they appear, at first sight, to convey much more precise information than they really do convey. I have more than once insisted on the importance of clearly remembering that these and similar expressions are attempts to summarise facts concerning the reactions of compounds in the language of a special theory of the structure of compounds. Nor should it be forgotten that, granting the fundamental hypotheses of the molecular and atomic theory, and also granting that each atom can directly interact with a limited number of other atoms in a molecule, we are obliged to regard the atoms which form any molecule as performing constant but regulated movements, and not, as might be supposed by a careless or superficial reader of the atomic explanation of isomerism, as in absolutely fixed positions within the molecule.

relative positions of the atoms, not with variations in the distances between identically arranged atoms, forming a molecule.

IV. The atoms which form a molecule are regarded as arranged in the same plane; no attempt is made to connect the facts of isomerism with the arrangement of the atoms in different dimensions in space.

Applying the hypothesis as thus limited, and for the most part to compounds of carbon, we found that the structural formulæ of classes of carbon compounds can be generalised so far as to admit of the assertion that the molecules of the members of any one class are characterised by the presence of a special atomic group which may be called the class-group: and hence that the first step in assigning a structural formula to a new compound is to determine the class to which it belongs by comparing the reactions of this compound with those of known substances belonging to various classes; having done this, we then eliminate from the possible structural formulæ those which do not contain the characteristic group of the class in which our compound is placed. Finally, we choose from the remaining formulæ that one which best summarises the reactions of the compound molecule under consideration and its relations to other molecules.

We found that a wide knowledge of the characters of classes of compounds is required on the part of him who would employ this method with success, and also that the chemist has constantly to be on his guard against drawing too rigid conclusions. A new compound may represent a new class, hence a new class-group has to be determined by comparing the reactions of the new compound with those of others the classification of which is fairly settled, and also by seeking to obtain other representatives of the new class. The discovery and study of new compounds apparently belonging to a known class may lead to a revision of the general formula assigned to the class, and perhaps to a division of the class into sub-classes each characterised by its own group.

76 The application of the hypothesis of valency to determine the most probable of many possible formulæ is evidently a matter of no little difficulty. Certain generalisations are usually adopted as guides in interpreting the results of the study of the chemical properties of molecules. The principal generalisations are these.

(1) Those atoms which are obtained as an undecomposed group in reactions resulting in the splitting up of a compound are present in the molecule of that compound as a group of directly combined atoms.

(2) When a group of atoms passes from one compound molecule to another, the relative arrangement of these atoms, as a rule, is not altered.

(3) When an atom, or group of atoms, replaces another atom or group of atoms of equal valency with itself, the replacing atom, or group, occupies (as a rule) the same position relatively to the other atoms in the molecule as was occupied by the atom, or group of atoms, which it has replaced[1]; or it may be better to say, the relations of the replacing atom, or group, to the rest of the molecule are generally the same as those of the atom, or group of atoms, which it has replaced.

77 Many of the reactions given on pp. 149—154, as illustrative of methods for assigning structural formulæ to given compounds also serve as illustrations of the use of these generalisations; one or two further illustrations will be given here.

Two isomerides each having the composition C_2H_6O are theoretically possible; viz.

(1) $H_3C-\overset{H_2}{\overset{\|}{C}}-O-H$ and (2) $H_3C-O-CH_3$.

Two compounds having this formula are known. One of these (alcohol) interacts with potassium or sodium thus,

$$(a)\quad C_2H_6O+K=C_2H_5KO+H;$$

potassium (or sodium) does not react with the substance thus

[1] L. Meyer, *loc. cit.* pp. 252 *et seq.* (English Ed. pp. 230—31) slightly modified.

formed: alcohol interacts with phosphorus pentachloride thus,

$$(b)\quad C_2H_6O + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

The second isomeride (methyl ether) does not interact with potassium or sodium but reacts with phosphorus pentachloride thus,

$$C_2H_6O + PCl_5 = 2CH_3Cl + POCl_3.$$

The first formula generalises the reactions of alcohol, the second generalises the reactions of methyl ether: thus

$$(a)\quad H_3C - CH_2 - OH + K = H_3C - CH_2 - OK + H;$$

one, and only one, hydrogen atom is represented in the formula as indirectly bound (through an oxygen atom) to a carbon atom;

$$(b)\quad H_3C - CH_2 - OH + PCl_5 = H_3C - CH_2 - Cl + POCl_3 + HCl;$$

the group OH is replaced by the atom Cl, which being of equal valency is regarded as occupying the place in the molecule relatively to the other atoms formerly occupied by the group OH.

The second formula $H_3C - O - CH_3$ assigned to methyl ether represents all the hydrogen atoms as directly reacting with atoms of carbon, it represents them as having all the same function; hence either none, or all, will be replaced by the action of potassium. But the second formula represents the atom of oxygen as in direct union with atoms of carbon only; if the oxygen atom should be replaced by two monovalent atoms, e.g. by two atoms of chlorine, the molecule could no longer hold together but would separate into two molecules, each having the structure $Cl - CH_3$; this is what happens when methyl ether is acted on by phosphorus pentachloride.

When the molecule $HO - CH_2 - CH_3$ is oxidised it loses two atoms of hydrogen, producing C_2H_4O, which is then changed, by taking up one atom of oxygen, into the monobasic acid $C_2H_4O_2$. Probably the simplest way in which these changes can be represented in structural formulæ is

(1) $\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ OH \end{matrix} - H_2 = \begin{matrix} CH_3 \\ | \\ C \\ || \\ OH \end{matrix}$ (2) $\begin{matrix} CH_3 \\ | \\ C \\ | \\ OH \end{matrix} + O = \begin{matrix} CH_3 \\ | \\ C-O. \\ | \\ OH \end{matrix}$

Now are the properties of the acid molecule $C_2H_4O_2$ such as we should expect if we assumed it to have the formula $H_3C-CO-OH$? Two important reactions of the compound in question are these:—

(1) By reacting with phosphorus pentachloride it yields C_2H_3OCl, and this does not interact with the same reagent;

(2) When the sodium salt of this acid is heated with caustic soda it is decomposed thus,

$$C_2H_3NaO_2 + NaHO = Na_2CO_3 + CH_4.$$

These reactions are expressed by the formula $\begin{matrix} O-C-CH_3 \\ | \\ OH \end{matrix}$ which is therefore adopted as the structural formula for acetic acid[1].

Now let us turn to the compound C_2H_4O, intermediate between alcohol and acetic acid. Is this molecule well represented by the formula $H_3C-C-OH$ provisionally assigned to it? When the compound in question interacts with phosphorus pentachloride it yields $C_2H_4Cl_2$, and not C_2H_3Cl as might be expected if the formula $H_3C-C-OH$ were correct. From synthetical and analytical reactions, $C_2H_4Cl_2$ may be shewn to be best represented by the structural formula $Cl_2=CH-CH_3$; assuming this formula, and remembering that the reaction to be explained, viz. formation of $C_2H_4Cl_2$ from C_2H_4O, consists in the replacement of one divalent oxygen atom by two monovalent chlorine atoms, we apply generalisation (3) par. 76, and conclude that the structure of

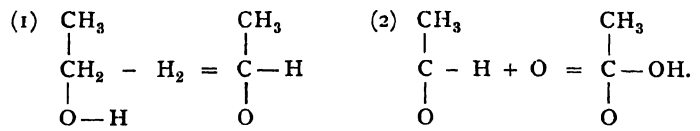
[1] Thus,

(1) $\begin{matrix} CH_3 \\ | \\ C-O \\ | \\ OH \end{matrix} + PCl_5 = \begin{matrix} CH_3 \\ | \\ C-O \\ | \\ Cl \end{matrix} + \&c.$ (2) $\begin{matrix} CH_3 \\ | \\ C-O \\ | \\ ONa \end{matrix} + Na-OH = \begin{matrix} CH_3 \\ | \\ H \end{matrix} + Na_2CO_3.$

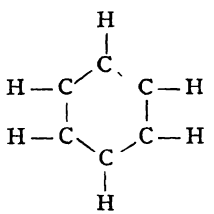
One of the carbon atoms in the original molecule remains associated with 3 atoms of hydrogen throughout both processes of change, hence we conclude that the molecule of acetic acid contains the group CH_3.

the molecule C_2H_4O is best represented by the formula $O-CH-CH_3$.

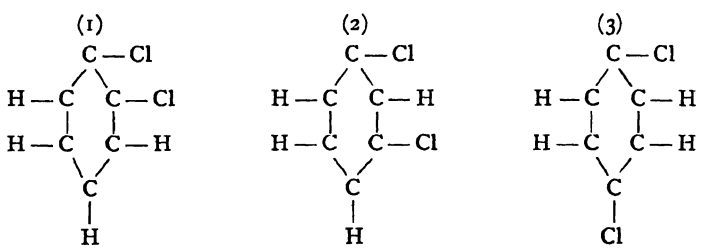
The oxidation of alcohol is then best represented thus in structural formulæ:—



Another and somewhat more complex illustration, taken from the so-called 'aromatic' (or better 'benzenoid') carbon compounds, will serve to shew that the generalisations stated in par. 76, although widely applicable, must yet be used with great caution. Assuming the generally adopted structural formula for the molecule of benzene[1] (C_6H_6), viz.[2]



the existence of three, and only three, isomeric dichloro- or dibromo- &c. benzenes, becomes possible, viz.



[1] See Armstrong and Groves, *Organic Chemistry*, pp. 260—63; also pp. 270—74. See also *post*, par. 81.

[2] The fact that this formula is generally used rather than the more complex formula originally proposed by Kekulé with alternate 'doubly' and 'singly-linked' carbon atoms, and that most chemists are content meanwhile to overlook the contradiction involved in employing such a formula and yet using the language of 'bonds,' is indicative of the unsatisfactory nature of this language when rigidly applied.

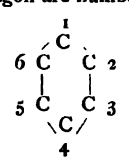
In (1) both chlorine atoms are in direct connexion with carbon atoms which are directly bound to one another; in (2) one carbon atom intervenes, and in (3) two carbon atoms intervene, between the atoms of carbon which directly interact with the chlorine atoms.

These three isomeric compounds[1] are usually distinguished as 1 : 2, 1 : 3, and 1 : 4, dichlorobenzene; it is evident that 1 : 6 = 1 : 2, and 1 : 5 = 1 : 3. Each of these dichlorobenzenes when acted on by chlorine yields one or more isomeric trichlorobenzenes ($C_6H_3Cl_3$). Körner has formulated a simple method of proving that 1 : 2 dichlorobenzene can yield two, 1 : 3 can yield three, and 1 : 4 can yield only one, trichlorobenzene[2].

Now if the generalisations we are considering are applicable to the benzenoid hydrocarbons, it follows that any di-derivative of benzene—$C_6H_4X_2$ where X is a monovalent atom or group of atoms—which, by a simple series of reactions can be obtained from, or can be converted into, 1 : 2 dichloro- (or dibromo- or dinitro-) benzene, must be itself a 1 : 2 derivative; i.e. the two X groups or atoms must be in direct interaction with carbon atoms between which there is direct mutual action within the molecule. A similar conclusion is drawn regarding the structure of those compounds of the formula $C_6H_4X_2$ which can be obtained from or reduced to 1 : 3, or 1 : 4, dichloro dibromo or dinitro-benzene.

Thus 1 : 3 dinitrobenzene, by the action of zinc and hydrochloric acid, yields nitramidobenzene $C_6H_4NO_2NH_2$; by the further action of nascent hydrogen this yields diamidobenzene $C_6H_4(NH_2)_2$; and diamidobenzene, by the

[1] The carbon atoms in the hexagon are numbered thus:—



[2] 1 : 2 yields 1 : 2 : 3, and 1 : 2 : 4, (1 : 2 : 3 = 1 : 2 : 6, and 1 : 2 : 5 = 1 : 2 : 4) 1 : 3 yields 1 : 2 : 3, and 1 : 3 : 4 (which = 1 : 3 : 6), and 1 : 3 : 5. 1 : 4 yields 1 2 : 4 (which = 1 : 3 : 4 = 1 : 4 : 5 = 1 : 4 : 6). See Armstrong and Groves, *loc. cit.* pp. 267—8.

'diazo reaction'[1] (or 'Griess' reaction'), yields bromohydroxybenzene $C_6H_4Br.OH$; this bromohydroxybenzene is therefore assumed to be a 1 : 3 derivative of benzene. Now when this body is fused with caustic potash it yields one of the three isomeric dihydroxybenzenes $C_6H_4(OH)_2$; in accordance with generalisation (3) par 76 this dihydroxybenzene ought to be regarded as a 1 : 3 derivative. But 1 : 4 bromohydroxybenzene—obtained by a method similar to that sketched above from 1 : 4 dinitrobenzene—yields, by fusion with potash, the same dihydroxybenzene as just mentioned; hence this dihydroxybenzene is now shewn to be probably a 1 : 4 derivative of benzene. Again, this same dihydroxybenzene is the sole product of the fusion with potash at a high temperature of 1 : 4 iodohydroxybenzene $C_6H_4I.OH$; but when this iodohydroxybenzene is fused with potash at 165° none of the dihydroxybenzene already mentioned is obtained but only one of the dihydroxybenzenes isomeric with it[2].

Another example, shewing how necessary it is to apply such generalisations as those under consideration only in a tentative manner, is furnished by some reactions of 1 : 4 nitrobromobenzene $C_6H_4NO_2Br$. By the action of alcoholic ammonia on this compound nitramidobenzene $C_6H_4NO_2NH_2$ is produced; that this nitramidobenzene is, as we should expect, a 1 : 4 derivative of benzene, can be proved by trustworthy evidence. But if the same 1 : 4 $C_6H_4NO_2Br$ is acted on by potassium cyanide, and the product of this action, C_6H_4CNBr, is boiled with dilute acid, bromobenzoic acid, $C_6H_4Br(CO_2H)$, is obtained, and the reactions of this acid prove beyond doubt that it is a 1 : 3, and not as we should expect a 1 : 4, derivative of benzene. Similarly the product of the action of potassium cyanide followed by that of dilute acid on 1 : 3 $C_6H_4NO_2Br$ is 1 : 2 bromobenzoic acid, $C_6H_4Br(CO_2H)$, and not, as a strict application of the statement in par. 76 would lead us to expect, the 1 : 3 derivative.

[1] For an account of these 'diazo-reactions,' which are much used in the synthesis of benzene derivatives, see Armstrong and Groves, *loc. cit.* pp. 298—9.

[2] See, for more details, Armstrong and Groves, *loc. cit.* pp. 521—2.

And finally, when 1 : 2 $C_6H_4NO_2Br$ is subjected to the action of potassium cyanide[1] no replacement of NO_2 by CN occurs[2].

78 The application of the hypothesis of valency to the phenomena of isomerism has rendered more definite that general conception of the molecule as a structure which arose so soon as it was recognised that each atom in a molecule could directly interact with a limited number of other atoms. Analyses of reactions, and comparisons of classes of reactions, have led to the adoption of certain rules which, when applied with caution, have proved of very considerable service in researches on molecular structure. These researches have served to emphasise the fundamental connexion which exists between composition and properties, between function and quality of material: but chemistry is not now contented with connecting the reactions of compounds with their elementary compositions, or even with the atomic compositions of their molecules, she attempts, and is gradually succeeding in the attempt, to connect certain definite arrangements of atoms in molecules with certain definite properties and actions of these molecules.

79 In his remarkable paper published in 1858, Kekulé recognised that the function performed by an atom in any molecule depends on the nature of the other atoms, as well as on the nature of the given atom, and also on the arrangement of all the atoms. Since 1858 the nature of the dependence in question has been more fully elucidated; and although it cannot be said that we have at present much knowledge, capable of being generalised in statements at once accurate and wide, of the connexions between the functions of parts of molecules and the atomic compositions and structures of these molecules, yet we are certainly gathering facts which will doubtless prove the basis for far-reaching generalisations.

[1] In Armstrong and Groves, *loc. cit.* pp. 334—6, will be found an account of the action of potassium cyanide on benzene derivatives; this action, although abnormal, may be expressed by a tolerably simple generalisation.

[2] Further examples of the point under discussion will be found in the change of normal propyl to isopropyl, by (1) the action of Al_2Br_6 [see Kekulé, *Ber.* **12.** 2279], or (2) the action of zinc dust [see Jacobsen, *Ber.* **12.** 1512]: also in the change of $C_nH_{2n+1}CN$ to $C_nH_{2n+1}NC$ by the action of heat: and also in the action of reducing agents on phenanthraquinone (see Japp, *C. S. Journal*, **Trans.** for **1883. 13, note**].

Numerous illustrations have already been given of the existence of a connexion of some kind between the functions of parts of a molecule and the composition, using this term in its widest sense, of the whole molecule. But the existence of such a connexion is so important that I shall devote a paragraph to its illustration.

The relation to be illustrated is that between the function performed by an atom, or atomic group, in a molecule,

and { I. the nature, and arrangement relatively to the given atom (or group), of the other atoms; II. the general relative arrangement of all the parts; } of the molecule.

80 I. That the function performed by an atom of hydrogen in a molecule varies according to the nature and arrangement relatively to the hydrogen of the other atoms, has already been shewn (see par. 74, pp. 151—154). Hydrogen which is associated with negative atoms or groups is as a rule 'replaceable by metals,' in other words, performs acidic functions in the molecule. Thus of the two compounds, potassium-nitropropane and bromonitropropane, the latter is much more decidedly acidic than the former: if the formulæ are compared,



it is seen that, in the markedly acidic compound the carbon atom with which the sixth atom of hydrogen is represented as directly connected is itself directly bound to the negative group NO_2 and to the negative atom Br; but that in the less acidic compound this carbon atom is represented as directly bound to the negative group NO_2 and to the positive atom K.

Again Cl_3C-H is not an acid, but $(NO_2)_3C-H$ is; the influence of the very negative NO_2 group seems to be impressed through the carbon atom on the hydrogen atom of the molecule.

In these cases the atom of 'acidic hydrogen' is represented as *directly* bound to a carbon atom within the binding-sphere of which come negative atoms or groups. But the case of the nitrolic acids, assuming the usually accepted formula $(C_nH_{2n+1})—C(-NO_2)$ to be correct, shews that

$$\begin{array}{l} \\ | \\ N-OH \end{array}$$

an atom of hydrogen which is *indirectly* bound to carbon itself binding negative groups may react as acidic hydrogen. Glyoxaline and tribromoglyoxaline also furnish examples in point; each of these molecules contains one atom of acidic hydrogen[1].

A portion of the hydrogen in monohydric alcohols is replaceable by metal, but only by the very positive metals; e.g. $C_2H_5.OH + K = C_2H_5OK + H$; but by the introduction of an atom of sulphur into the molecule in place of oxygen a thio-alcohol is obtained which readily exchanges hydrogen even for comparatively negative metals[2], e.g.

$$2C_2H_5SH + HgO = (C_2H_5S)_2Hg + H_2O.$$

Again, the experiments of R. Meyer appear to prove that an atom of hydrogen in the molecule of a carbon compound can be replaced by the group OH, by the action of oxidising agents, only when the carbon atom with which the hydrogen is directly connected does not directly bind any other hydrogen atoms; thus isobutyric acid is oxidised by potassium permanganate to isohydroxybutyric acid, but normal butyric acid yields acetic, oxalic, carbonic, and other acids, under the same conditions.

[In structural formulæ; $H_3C—CH_2—CH_2—C(=O)(OH)$ does not yield a hydroxy-acid; but $HO—C(CH_3)_2—CO_2H$ yields $HO—C(CH_3)_2—COH$.]

[1] The most probable formulæ are,

$$CH—CH—CH—NH \quad (\backslash N) \qquad CBr—CBr—CBr—NH \quad (\backslash N/)$$

(see Armstrong and Groves, *loc. cit.* p. 769). Some reactions of water are consistent with the statement that one of the hydrogen atoms performs the functions of acidic hydrogen; e.g.

$$HOH + CH_3ONa = CH_3OH + NaOH.$$

[2] For details concerning these reactions see Armstrong and Groves, *loc. cit.*, pp. 660—1.

81 II. A good illustration of the influence exerted by the arrangement of all the atoms in a molecule on the functions of one, or some, of these atoms, is afforded by a comparative study of the two groups of carbon compounds, more especially the hydrocarbons, generally known as 'fatty' (or 'paraffinoid') and 'aromatic' (or 'benzenoid') respectively[1]: a few, but only a few, of the more important points will be briefly stated.

Comparing the interaction between concentrated nitric or sulphuric acid and a paraffin, e.g. C_2H_6, with the interaction of the same acid with a benzene, e.g. C_6H_6, it is noticed that while one or more hydrogen atoms in the molecule of the latter are readily replaced by the groups NO_2 or SO_3H, the acids are without action on the former hydrocarbon. When the homologues of benzene are oxidised, they generally yield quinones, the molecule of any one of which contains the same number of carbon atoms as the parent hydrocarbon but has two atoms of oxygen in place of two atoms of hydrogen in the original molecule. When the paraffinoid hydrocarbons on the other hand are oxidised they do not yield derivatives analogous to the quinones, but rather afford mixtures of acids the molecule of each of which contains fewer carbon atoms than were present in the original hydrocarbon molecule.

When chlorine reacts with the molecule of a paraffinoid hydrocarbon containing only tetravalent[2] carbon atoms it produces chloro-substitution derivatives containing tetravalent carbon atoms, the whole of the hydrogen in the hydrocarbon being eventually replaced by chlorine; the further action of chlorine then frequently results in a separation of the molecule into two or more molecules, each containing a smaller number of carbon atoms than the original molecule. When however chlorine reacts with the molecule of a paraffinoid hydrocarbon containing two or more trivalent[3] carbon atoms it generally combines with it and so produces a molecule containing tetravalent carbon atoms, which then reacts with

[1] See Armstrong and Groves, *loc. cit.* pp. 391—402.

[2] In ordinary nomenclature it would be said 'singly-linked carbon atoms.'

[3] In ordinary nomenclature it would be said 'doubly-linked carbon atoms.'

chlorine as hydrocarbons with tetravalent carbon atoms usually do. Thus when propane, $H_3C-CH_2-CH_3$, reacts with chlorine, chloro-derivatives $H_3C-CH_2-CH_2Cl$, $H_3C-CH_2-CHCl_2$, &c. and finally octochloropropane $Cl_3C-CCl_2-CCl_3$, are produced; and when this octochloropropane is caused to interact with iodine chloride, two compounds, viz. Cl_3C-CCl_3 and CCl_4, are formed. On the other hand when propylene, $H_2C-CH_2-CH_2$, the molecule of which contains two trivalent atoms of carbon, reacts with chlorine propylene chloride, $ClH_2C-CH_2-CH_2Cl$, is produced; and this compound, which contains only tetravalent carbon atoms in its molecule, is decomposed by the action of iodine chloride, first into C_3Cl_8, and then into C_2Cl_6 and CCl_4.

The interaction of chlorine with the hydrocarbon benzene, C_6H_6, finally results in the formation of hexachloro-benzene C_6Cl_6, in which, it may be safely asserted from the formula and from a study of the properties of the compound, the carbon atoms directly interact with the same number of atoms as in the original C_6H_6 molecule. So far then benzene behaves like a paraffin: but ICl has no action on C_6Cl_6; the molecule refuses to separate into parts; the six atoms of carbon are apparently more firmly joined together, and form a more stable group, than the carbon atoms in the molecule of a paraffin.

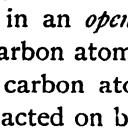
The functions both of the hydrogen and the carbon atoms in the molecules of a benzene and of a paraffin—say in C_6H_6 and in C_6H_{14}—evidently depend to some extent on the general arrangement of all the atoms in these molecules.

The arrangement of carbon atoms supposed to characterise the molecule of a fatty hydrocarbon, e.g. a paraffin, is usually spoken of as an arrangement in '*an open chain;*' while that supposed to characterise the molecule of an aromatic hydrocarbon, e.g. a benzene, is called '*a closed ring.*'[1] If the inter-

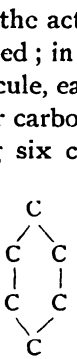
[1] Ring-formed molecules resemble unsaturated molecules in that they can directly combine with monovalent atoms without loss of any of their constituent atoms, e.g. benzene forms $C_6H_6Cl_6$; but they resemble saturated molecules in that the assumption of monovalent atoms is possible only when preceded by

action between atom and atom be supposed to begin at one of the carbon atoms, then in a *closed ring* molecule it returns to that atom; in other words each carbon atom acts on, and is acted on by, at least two other carbon atoms in the molecule: but in an *open chain* molecule the action does not return to the carbon atom at which it started; in other words, there are two carbon atoms in the molecule, each of which acts on, and is acted on by, only one other carbon atom.

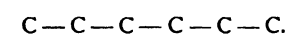
The *ring-formed* molecule containing six carbon atoms may be represented thus :—



or thus



and the *open chain* molecule thus :—



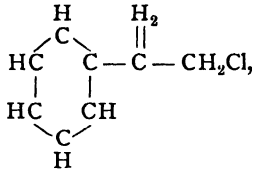
As the six carbon atoms in the molecule of benzene appear to form a very stable group, they are sometimes spoken of as the '*six-carbon-nucleus*' of the molecule. Now if the monochloro-derivative of xylene, C_8H_{10}, produced by the reaction of chlorine with that hydrocarbon when cold is compared with the monochloro-derivative produced by the reaction of chlorine with the same hydrocarbon when hot, it is found that the latter readily exchanges its chlorine atom for the group OH with production of an alcohol, $C_8H_9(OH)$, but that the chlorine atom in the former can scarcely be replaced by other radicles. If we assume the ordinarily accepted structural formulæ for the two isomeric monochloroxylenes we at once see how profoundly the functions

a redistribution of the mutual actions between some of the polyvalent atoms. (*Lossen.*)

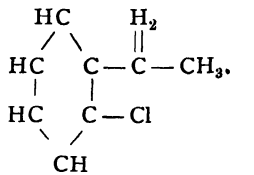
The number of molecules produced in any reaction wherein only saturated molecules take part is equal to or greater than the number of molecules taking part in the reaction: when the number produced in any reaction is smaller than the number of molecules originally taking part in the reaction, at least one of the reacting molecules must be either unsaturated or ring-formed. (*Lossen.*)

It is evident that a ring-formed molecule must contain at least three polyvalent atoms, and that for such molecules $n_1 < n_3 + 2n_4 + \&c. \ldots + 2$.

of the chlorine atoms depend on the relative arrangement of all the atoms in the molecule. The formulæ in question are (*a*) monochloroxylene from *hot* xylene



(*b*) monochloroxylene from *cold* xylene



The chlorine atom in (*a*) is said to be in '*the side chain*,' and in (*b*) in the '*central nucleus*.' In the hydrocarbon C_8H_{10} we have the properties both of a paraffin and a benzene; part of the molecule, the six-carbon-nucleus, behaves as a benzenoid group; the other part, the side chain C_2H_5, as a paraffinoid group.

A comparison of some of the reactions of metallic hydroxides, alcohols, and phenols, will serve to illustrate the dependence of the functions of part of a molecule at once on the nature, and arrangement relatively to this part, of the other atoms, and also on the general arrangement of all the atoms, in the molecule.

The interactions of acids with metallic hydroxides and alcohols result in the formation of salts:—

$$\text{e.g.} \begin{cases} Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O \\ CH_3(OH) + HCl = CH_3.Cl + H_2O. \end{cases}$$

But phenols do not yield analogous products by their reactions with acids. Alcohols and some metallic hydroxides, e.g. $Zn(OH)_2$ and $Al_2(OH)_6$, yield unstable metallic derivatives by reacting with markedly positive metals or their hydroxides; phenols however yield much more stable metallic derivatives by reacting with the same metals, or their hydroxides. The hydrogen atom (or atoms) which is indirectly connected,

through oxygen, with the metal or hydrocarbon-radicle of the molecules of alcohols, certain metallic hydroxides, and phenols evidently fulfils more or less acidic or basic functions according to the nature of the other part of the molecule. When that other part is a strongly positive metallic atom (or atoms) the hydrogen is basic; when the metallic atom (or atoms) is not markedly positive the hydrogen as a rule is at once basic and acidic in function; when the nonhydroxylic part of the molecule is composed of carbon and hydrogen atoms arranged in an 'open chain' the hydrogen appears to be more or less analogous to the hydrogen of metallic hydroxides; and when the carbon and hydrogen of the nonhydroxylic part of the molecule are arranged in a 'closed ring' the hydrogen appears to be more distinctly acidic in function[1].

The following facts and generalisations concerning the action of reagents on various benzene derivatives afford further examples of the influence exerted by the relative position, and nature of the parts, of a molecule, and the general arrangement of all the atoms in a molecule, on reactions wherein atoms, or atomic groups, in the molecule are substituted by other atoms or groups.

In the production of certain di-substituted derivatives of benzene C_6H_4XX', from mono-substituted derivatives C_6H_5X, it is found that whether the di-derivative shall belong to the 1 : 2, 1 : 3, or 1 : 4 series[2], depends on the nature of the atom or atomic group X in C_6H_5X, and also on the nature of the atom or group X' in C_6H_4XX'. When $X = Cl$, Br, I, OH, CH_3, CH_2Cl, $CHCl_2$, CCl_3, or NH_2, and $X' = Cl$, Br, I, NO_2, or SO_3H, the di-derivative C_6H_4XX' generally belongs to the 1 : 4 series: when $X = NO_2$, SO_3H, CN, CHO, $COCH_3$, or CO_2H, and $X' = Cl$, Br, I, NO_2, or SO_3H, then C_6H_4XX' generally belongs to the 1 : 3 series[3].

When derivatives of benzene containing paraffinoid radicles as 'side chains' are oxidised they yield mono-, di-, tri-, &c.,

[1] See Armstrong and Groves, *loc. cit.* p. 566.

[2] See par. 77, p. 160, for an explanation of this notation.

[3] See table in Armstrong and Groves, *loc. cit.* p. 337: also Armstrong, *C. S. Journal*, **Trans.** for **1887**. 258.

$C_6H_2 . (NH_2) . (NO_2)_2 . OH$ combines with HCl, but the product is not very stable; the same molecule however readily exchanges an atom of hydrogen for metal by the action of alkaline carbonates, thus forming well-marked stable metallic derivatives, e.g. $C_6H_2(NH_2)(NO_2)_2ONa$. If however two NH_2 groups and one NO_2 group are introduced in place of three hydrogen atoms in the phenol molecule, the product $C_6H_2(NH_2)_2(NO_2)OH$ is distinctly basic, combining readily with HCl, but yielding only unstable metallic derivatives.

83 Not only is the general chemical stability of a molecule dependent, in part, on the balance of functions of the atoms and atomic groups in the molecule, but many of the properties generally called physical are correlated with a similar balance of parts. Thus Witt[1] has shewn that there exists a definite connexion between the tinctorial properties of many derivatives of azobenzene, $C_6H_5-N_2-C_6H_5$, and the atomic composition and structure of these molecules. By introducing the group NH_2 in place of hydrogen in the azobenzene molecule salt-forming molecules are produced, possessed of considerable dyeing properties; if negative groups, as OH, HSO_3, &c. are introduced into the molecule the products are also strongly coloured; but the best dyes are formed by compounds which are neither markedly basic or acidic. Thus $C_6H_5-N_2-C_6H_4(NH_2)$ dyes a light yellow, but the colour is very fugitive; the colour of $(NH_2)C_6H_4-N_2-C_6H_3(NH_2)_2$ is too dull; but when an azotised or a di-azotised base is combined with a negative phenolic or naphtholic group, good dyes are usually obtained; e.g. $C_6H_5-N_2-C_{10}H_5(SO_3H)(OH)$ or $C_6H_5-N_2-C_6H_4-N_2-C_6H_4OH$.

84 We have already learned (pars. 32—34) that a general relation exists between the crystalline form of a compound and the number and arrangement of the atoms in the molecule of that compound. Groth[2], and others, have shewn that the

[1] *C. S. Journal*, **Trans.** for **1879.** 179 and 357: also Hartley, *C. S. Journal*, **Trans.** for **1887.** 152.

[2] *Pogg. Ann.* **141.** 31. See also C. Hintze, *Pogg. Ann.* **Ergzbd. 6.** 195; C. Bodewig, *Pogg. Ann.* **158.** 239; P. Friedlander, *Zeitschr. Krystall.* **3.** 168;

substitution of Cl, Br, NO_2, or OH &c., for hydrogen in the molecules of benzene derivatives is accompanied by definite changes in the crystalline forms of the compounds. The relations existing between crystalline form and chemical structure, so far as the latter is modified by processes of substitution, are called by Groth *morphotropic* relations. The change of crystalline form in any given case depends on (1) the chemical nature of the parent substance; (2) the crystalline system to which it belongs; (3) the chemical nature of the substituting atom (or group); and (4) the chemical nature of the product of the reaction, using the expression 'chemical nature' in its widest sense as including the conceptions of atomic composition and atomic structure.

When the parent substance belongs to a crystalline system in which the relations of the axes are not invariable, substitution of Cl, Br, &c., generally only produces changes in these relations, without total changes to other systems; but if the parent substance belongs to the regular system, the substituted product is found to belong to one of the other five systems.

Groth's researches lead to the following generalisations concerning the derivatives of benzene:—

(1) Substitution of H by OH or NO_2, is accompanied by changes in the relations of the axes, but not by changes from one system to another.

(2) Substitution of H by Cl or Br, is accompanied by changes from one crystalline system to another, less symmetrical, system; but further substitution by the same atoms is sometimes accompanied by a return to a more symmetrical system.

(3) Substitution of H by CH_3 is also accompanied by marked changes in crystalline symmetry.

(4) Chemically similar derivatives of benzene belonging to a *para* [1 : 4] series shew greater crystallographic analogies with one another than with the members of a *meta* [1 : 3] or an *ortho* [1 : 2] series.

and the article 'Isomorphie' in the *Neues Handwörterbuch der Chemie*, **3.** especially pp. 854—9; also 'Isomorphie' in Ladenburg's *Handwörterbuch der Chemie*, **5.** pp. 401—5.

The general conclusion to be drawn from these facts is, that, in some compounds at any rate, crystalline form is more or less closely connected with the nature and arrangement, as well as with the number, of the atoms and groups of atoms in the compound molecules.

85 Very many measurements have been made of the quantities of heat which are produced or disappear during processes of chemical change. This subject will be considered more fully in a future chapter[1]; at present I wish to insist on the fact that the data of thermal chemistry establish an undoubted connexion between the thermal changes which accompany chemical reactions and the nature and arrangement of the atoms, and groups of atoms, forming the molecules which take part in these reactions. Especial reference must be made here to the experiments of J. Thomsen[2], from which the conclusion can be drawn that the change from a material system of isolated atoms—say x carbon atoms, x' hydrogen atoms, and x'' oxygen atoms—to a molecular system in which these atoms are combined so that all the carbon atoms are tetravalent (i.e. each acts on and is acted on by four other atoms) and all the oxygen atoms are divalent, is attended with the loss to the system of a quantity of energy different from that which accompanies the change from the same system of isolated atoms to a molecular system in which some, say $(x-2)$, carbon atoms are trivalent, and some, say $(x''-1)$, oxygen atoms are monovalent.

86 The measurements which have been made of the quantities of heat that are produced or disappear during similar chemical changes undergone by isomeric compounds shew that in many cases at any rate the quantity of energy associated with one isomeride is different from that associated with another. Thus, the heat produced during the complete combustion of dipropargyl (C_6H_6) is about 850,000 gram-units, while that produced during the combustion of the isomeric molecule

[1] See Chapter IV. Section 1.

[2] *Ber.* **13.** 1321; *Journal fur prakt. Chemie.* **23.** 157 and 163; and *Zeitschr. f. physikal. Chemie.* **1,** 369. See also *post*, chap. IV., par. 134.

benzene is about 800,000 gram-units; hence the amount of energy associated with the arrangement of six atoms of carbon and six atoms of hydrogen in the molecule of benzene is less than that associated with the arrangement of the same numbers of the same atoms in the molecule of dipropargyl. But in the molecule of benzene each carbon atom is at least trivalent (and possibly tetravalent), while in that of dipropargyl some of the carbon atoms are certainly divalent[1]: hence, it might apparently be concluded, that more energy is degraded in the formation, from atoms of carbon and hydrogen, of a molecule in which all the carbon atoms act as tri- or tetravalent atoms, than of an isomeric molecule in which some of the carbons act as divalent atoms. But it must be remembered that in the benzene molecule each carbon atom directly interacts with not more than one atom of hydrogen, and with at least two other atoms of carbon; whereas in the molecule of dipropargyl it is very probable that two of the carbon atoms directly interact each with a single other carbon atom, and also that some of the atoms of carbon interact each with two atoms of hydrogen. Hence, if we may provisionally draw a general conclusion from the very limited data before us, it might be inferred that the differences between the quantities of energy associated with different isomeric atomic systems depend, among other conditions, on

(1) whether each atom directly interacts with the maximum number of other atoms; in other words, on the actual valencies of the atoms in the molecules; and

(2) on the nature of the atoms between which direct interaction occurs; in other words, on the distribution of the interatomic reactions.

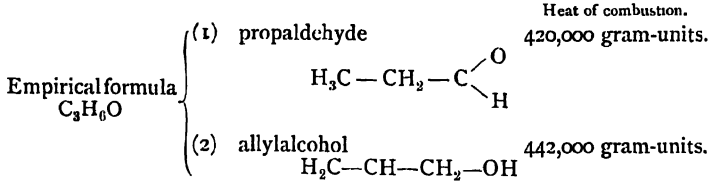
87 The following data, in addition to the numbers already given for the heats of combustion of benzene and dipro-

[1] The usually adopted formula for the dipropargyl molecule is

$$HC{-}C{-}CH_2{-}CH_2{-}C{-}CH,$$

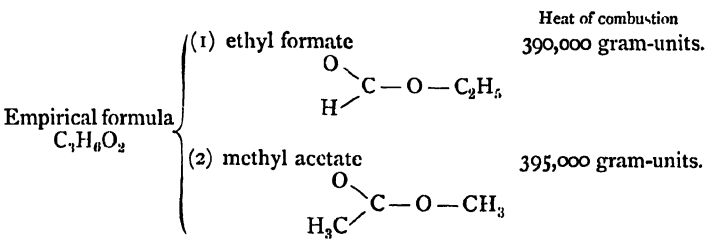
which contains 2 tetra- and 4 divalent carbon atoms.

pargyl, serve to illustrate the existence of a relation between the quantities of energy, and the valencies of the atoms, in isomeric molecules.



Assuming the correctness of these structural formulæ, it is seen that the propaldehyde molecule contains two tetra- and one trivalent carbon atoms, and also one monovalent oxygen atom, whereas the molecule of allylic alcohol contains two tri- and one tetravalent carbon atoms, and also one divalent oxygen atom.

88 The data of thermal chemistry furnish more numerous examples of the existence of a connexion between greater or less molecular energy and the distribution of the atomic interactions in isomeric molecules.



If the structural formulæ given are correct, then in each of these molecules we have two tetra- and one trivalent carbon atoms, and one mono- and one divalent oxygen atoms; but the trivalent carbon atom in ethyl formate interacts directly with two oxygen and one hydrogen atoms, and in methyl acetate with two oxygen and one carbon atoms: inspection of the formulæ will disclose other differences in the distribution of the atomic interactions.

Alcohol and methylic oxide afford another example of the relation we are discussing :—

		Heat of combustion
Empirical formula C_2H_6O	(1) alcohol, H_3C-CH_2-OH	330,000 gram-units.
	(2) methylic oxide $H_3C-O-CH_3$	344,000 gram-units.

We have here two molecules each containing a pair of tetravalent carbon atoms, one divalent oxygen atom, and six monovalent hydrogen atoms, but in one of the molecules each carbon atom directly interacts with three hydrogen and one oxygen atoms, while in the other the arrangement of the atomic interactions is less symmetrical.

Other examples are afforded by the following groups of compounds :—

		Heat of combustion
I. Empirical formula C_3H_6O	(1) allyl alcohol..... $CH_2.CH.CH_2OH$	443,000 gram-units.
	(2) propaldehyde ..... $CH_3.CH_2.CHO$	426,000 „ „
	(3) acetone ..... $CH_3.CO.CH_3$	424,000 „ „
II. Empirical formula $C_2H_4O_2$	(1) methyl formate ..... $H.COOCH_3$	252,000 „ „
	(2) acetic acid . ..... $CH_3.COOH$	210,000 „ „
III. Empirical formula $C_4H_8O_2$	(1) ethyl acetate ..... $CH_3.CO.OCH_2.CH_3$	554,000 „ „
	(2) butyric acid .... $CH(CH_3)_2.COOH$	497,000 „ „
IV. Empirical formula $C_7H_6O_3$	(1) 1 : 4 hydroxybenzoic acid, $C_6H_4(OH)CO_2H$	752,000 „ „
	(2) 1 : 3 „ „	754,000 „ „
	(3) 1 : 2 „ „	759,000 „ „

89 The data are not sufficient to warrant any precise statement as to the relations between greater or smaller quantities of energy and molecular structure. It is possible that the case of benzene and dipropargyl is typical, and that of two

isomeric molecules one of which belongs to the class of ring-formed and the other to that of open-chain molecules, the former always contains relatively less energy than the latter. It is also possible that of two isomeric carbon compounds the molecules of which belong to the open-chain class, and in which $n_1 < 2n_4 + \dots 2$, that containing the greater number of tetravalent carbon atoms contains the smaller quantity of energy, provided that the distribution of the atomic interactions is the same, or nearly the same, in the two molecules. Or again it may be that when the actual valencies of the atoms in two or more isomeric molecules are the same, that molecule in which the atomic interactions are distributed so as to produce the greatest degree of symmetry is marked by the smallest amount of energy[1]. But we have as yet no accurate knowledge which may enable us to test the applicability of these suggestions.

Even if it could be asserted (as seems possible in a few cases) that this isomeride contains relatively less energy than that, and is therefore more stable, the question would arise, what do we mean by stability? For although of two molecules one may be the more stable as stability is measured by thermal changes, it may nevertheless be impossible to say that this molecule is possessed of greater *chemical stability* than the other. But a discussion of the meaning and application of the expression chemical stability, requiring as it does a knowledge of the facts and theories of chemical affinity, will find a fitter place in that part of this book which deals with chemical kinetics[2].

Inasmuch as variations in the physical properties of material systems accompany variations in the energies of these systems, it follows, if the two very general assumptions made on p. 175 concerning the connexion between the energy and the structure of isomeric molecules are granted, that physical phenomena, other than thermal, may be expected to exhibit variations in isomeric molecules.

[1] This view is put forward tentatively by Carnelley, *Phil. Mag.* [5] **13**. 180. The data given on p. 177 for alcohol and methylic oxide are not in keeping with this suggestion.

[2] See Book II.

An attempt will be made in a future chapter to summarise the more important physical phenomena between which and molecular structure in general there is an established connexion (Chapter IV.). Here I would only remark that the researches of various chemists on the 'specific volumes' of liquid compounds seem to shew that the influence of any atom on the 'specific volume' of a compound molecule is dependent, not only on the nature and the actual valency of that atom, but also on the nature of the other atom, or atoms, between which and the given atom there is direct interaction. It is also probable that while the influence exerted by a polyvalent atom on the 'molecular refraction' of isomeric carbon-containing molecules is to a large extent dependent on the actual valency of that atom, nevertheless this influence is also sometimes connected with the nature of the other atoms between which and the given atom there is direct interaction in the molecule (*s.* Chapter IV. Sect. 2).

90. Much is to be expected from researches into the phenomena which occupy the border-land between chemistry and physics. If the knowledge chemists already have of the structure of molecules, meagre though that knowledge be, can be supplemented by definite dynamical conceptions, obtainable in part by the methods of thermal chemistry, then we may hope that chemistry will enter on a new stage of advance as a branch of the science of matter and motion. It seems to me that a most important step will be made by abandoning the vague conception of atomic valency which finds expression in such phrases as 'single and double bonds,' 'satisfaction of one, two, or more valencies,' and the like; with this will go all those quasi-dynamical expressions, the offspring of loose and slipshod ways of thinking, which have gathered round that strange anomaly, a 'unit of affinity,' employed as a variable standard for measuring nothing.

If it is decided that the valency of an atom expresses the maximum number of other atoms between which and the given atom there is direct interaction in any molecule, and if it is agreed to measure this valency by the maximum number of monovalent atoms (i.e. atoms of hydrogen, fluorine,

chlorine, bromine, or iodine) which combine with the specified atom to form a molecule, then we are put in possession of a definite conception which may be applied to actually occurring phenomena, and the application of which will gradually lead to more precise knowledge regarding the distribution of the atomic interactions in various molecules. But at the same time that we are classifying molecules in accordance with the valencies of their constituent atoms and the distribution of the interactions of these atoms, i.e. in accordance with their structure, we are also becoming more impressed with the inadequacy of this classification; we see a vast field opening for investigation, we see that measurements of losses or gains of energy are required, and that determinations of many physical constants are called for. We begin, I think, to perceive that this knowledge, when gained, will supplement and not supplant that which is already possessed by us, and that it will do this by leading to an exact knowledge of the way in which the variations in the energies of molecules are connected with changes in the configurations and motions of the atoms which constitute these molecules.

91 Granting that the definition of valency given by Lossen furnishes a better working hypothesis than any other, we must nevertheless admit that several compounds present phenomena which seem to find no explanation in terms of the hypothesis of isomerism which arises out of the notion of valency, if that hypothesis is limited as was done in par. 75. If the best studied examples of these exceptional compounds are classified[1] it will, I think, be apparent; that structural formulæ in keeping with reactions may be assigned to some of the isomeric compounds mentioned provided we cease to regard the conventional method of expressing valency by one or more straight lines, as affording any quantitative measurements, even relative measurements, of atomic interactions; that some cases of unexplained isomerism[2] are probably

[1] See especially the article **Isomerism** in Watts's *Dictionary* [1st Ed.], *Suppl.* III. (1881).

[2] That optical properties are not always dependent on the structure of the

illustrations of modifications in properties being correlated with variations in mutual actions between groups of molecules rather than between the atoms constituting each molecule; and that the remaining cases are true residual phenomena, at present inexplicable in terms of the generally accepted hypothesis but not therefore of necessity destructive of this hypothesis.

92 One of the limitations almost universally placed on the application of the molecular and atomic theory to explain the facts of isomerism consists in simplifying the phenomena to be explained by assuming that the atoms which form a molecule are arranged in one plane.

Chemists have always recognised that a complete mechanical conception of the atomic structure of a molecule was impossible unless the conception included the spatial arrangement of the atoms which form the molecule. Attempts have been made from time to time to formulate such a conception. van't Hoff[1], following Le Bel[2], in 1875 tried to gain a definite notion of the spatial arrangement of the atoms forming the molecules of certain carbon compounds. Considering the molecule CRRRR, where each R represents a different monovalent atom or atomic group, van't Hoff supposed the carbon atom to be placed at the centre of a regular tetrahedron and each monovalent radicle to be placed at one of the summits; two different tetrahedra would thus result, bearing to each other the relation of an object to its reflected image, and incapable of being superposed in whatever position they may be placed.

The more immediate object of this conception was to connect the power of rotating the plane of polarisation of a ray of light possessed by certain compounds of carbon with the atomic structure of the molecules of these compounds (for more details *s.* Chap. IV. par. 416). Wislicenus has

molecule is shewn by the ease with which optically active amylic alcohol and valeric acid are converted into the inactive alcohol, and acid, without change of chemical properties. See Armstrong and Groves, *Organic Chemistry*, p. 449.

[1] *La Chimie dans l'Espace.*

[2] *Bull. Soc. Chim.* **22.** 337; **23.** 395.

recently extended the notions of van't Hoff and Le Bel regarding the spatial arrangement of atoms; he has endeavoured to shew that the greater number, if not all, of the well-established facts of isomerism which lie outside of the ordinary hypothesis find an explanation in terms of the geometrical conception of the molecule suggested by van't Hoff[1].

93 Although atomic valencies can be accurately determined only by the examination of a certain class of gaseous molecules, yet we may carry over the general conception of limited direct atomic interactions from gaseous molecules and apply it to the reacting atomic aggregates of solid and liquid compounds. This is done by Wislicenus. Most of the phenomena to be explained are exhibited by compounds of carbon which cannot be gasified without decomposition. Wislicenus assumes that in the molecules or atomic aggregates of these compounds no carbon atom can directly interact with more than four other atoms.

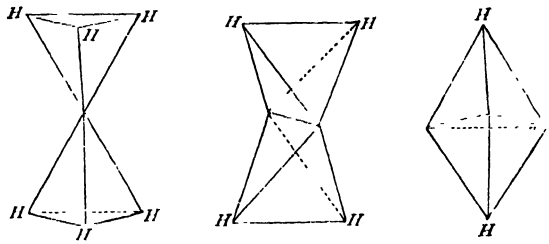
The geometrical conception which Wislicenus forms of the molecule of a carbon compound is that each carbon atom is situated at the centre of a regular tetrahedron, and that each can directly interact with four other atoms or radicles situated relatively to the carbon atom as the four summits of a regular tetrahedron are situated relatively to the centre. A molecule containing a pair of tetravalent ('singly linked') carbon atoms of the general form C_2a_6, where a = a monovalent atom or radicle, is represented by two tetrahedra with one pair of common summits; a molecule containing a pair of trivalent ('doubly linked') carbon atoms—C_2a_4—is represented by two tetrahedra with two pairs of common summits; and a molecule containing a pair of divalent ('trebly linked') carbon atoms —C_2a_2—is represented by two tetrahedra with three pairs of common summits. Figures 1, 2, and 3 represent these geometrical conceptions.

In a molecule of the composition $C_2a_2b_2$, where a_2 repre-

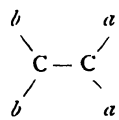
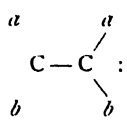
[1] **Über die raümliche Anordnung der Atome in organischen Molekulen und ihre Bestimmung in geometrischen-isomeren ungesättigten Verbindungen.** *Konigl. Sachsischen Gesellschaft der Wissenschaften* (*math-physische Classe*) Bd. **14.** 1.

sents two identical monovalent atoms or radicles, and b_2 represents two monovalent atoms different from a, chemical iso-

Fig. 1. Fig. 2. Fig. 3.

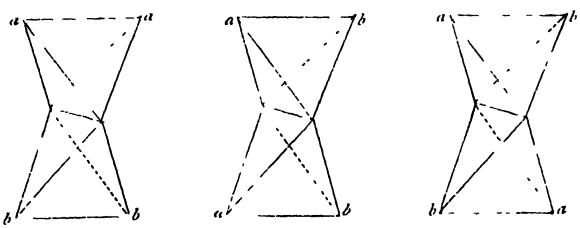


merism may arise because of different arrangements of the atoms; thus we may have

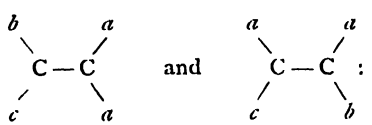
(1)  or (2) 

but the second of these isomerides may exist in two forms which are geometrically different although structurally the same, and either of these geometrical isomerides will bear to the other the relation of an object to its image. The three forms of $C_2a_2b_2$ are represented in figs. 4, 5, and 6.

Fig. 4. Fig. 5. Fig. 6.



Similarly a molecule of the composition C_2a_2bc may shew chemical isomerism;



but the second isomeride may also exhibit geometrical isomerism. A molecule of the form C_2abcd may exist in three isomeric modifications, each of which may exist in two geometrically different forms. Figs. 7 to 15 represent these isomerides.

Fig. 7.

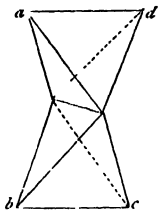


Fig. 8.

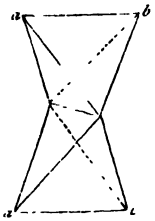


Fig. 9.

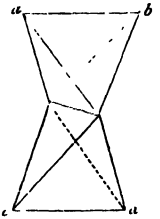


Fig. 10.

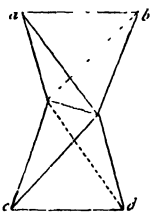


Fig. 11.

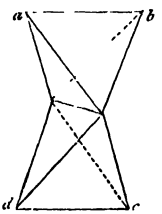


Fig. 12.

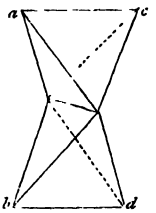


Fig. 13.

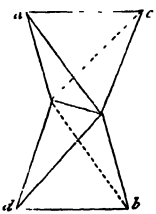


Fig. 14.

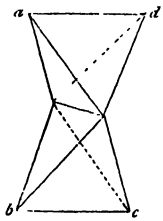
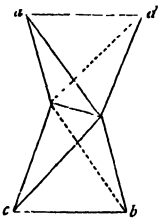


Fig. 15.



The terms *axially symmetric* and *plane-symmetric* are used to distinguish geometrical isomerides of the composition $C_2a_2b_2$. A molecule the configuration of which is shewn in fig. 16 is called by Wislicenus *axially symmetric*, because the atoms *a* and *b* are represented as arranged symmetrically about an axis passing between the two pairs of common

summits; the geometrically isomeric molecule shewn in fig. 17 is called *plane-symmetric* because the atoms *a* and *b* are

Fig. 16.

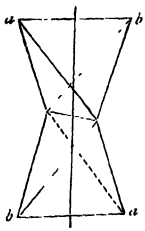
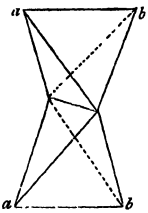


Fig. 17.



represented as arranged symmetrically about a plane passing through the two pairs of common summits.

94 Wislicenus developes these conceptions chiefly for molecules containing two carbon atoms. When the molecule contains a pair of divalent ('trebly linked') carbon atoms geometrical isomerism cannot occur; when the molecule contains a pair of trivalent ('doubly linked') carbon atoms geometrical isomerism may occur in the manner illustrated in the preceding paragraph; when the molecule contains a pair of tetravalent ('singly linked') carbon atoms geometrical isomerism may occur by the rotation of one part of the molecule relatively to the other. This last kind of isomerism is illustrated by figs. 18 and 19. The cause of this rotation of one part

Fig. 18.

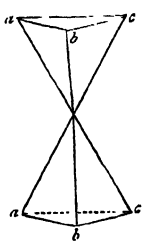
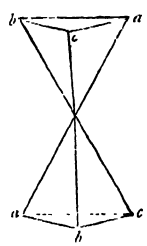


Fig. 19.



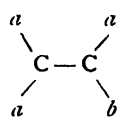
of a molecule containing a pair of tetravalent carbon atoms is supposed by Wislicenus to be the affinities[1] of the atoms

[1] The term affinity is here used to express the unknown property of atoms by reason of which they chemically interact.

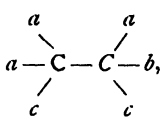
other than carbon; the configuration of the molecule tends to become that in which the atoms with the largest affinities are situated nearest to each other.

But besides the affinities of the atoms, heat will probably produce rotation of the parts of a molecule containing only tetravalent carbon atoms. The most stable atomic configuration will be that caused by the mutual atomic affinities; but besides this, some configurations will probably exist, and will likely increase in number as temperature rises, which configurations are caused by the action of heat; at high temperatures therefore a given compound will probably be composed for the greater part of molecules the atomic configuration of which is determined by the atomic affinities, but other and less stable configurations will also be present.

If a molecule containing a pair of divalent ('trebly linked') carbon atoms combines with two monovalent atoms of the same kind, or of different kinds, only one geometrical isomeride can be produced. If a molecule containing a pair of trivalent ('doubly linked') carbon atoms, one or both of which atoms is in direct union with two monovalent atoms of the same kind, combines with two new atoms two geometrical isomerides may be produced; in some cases the isomerides so produced will contain an *asymmetric* carbon atom, i.e. an atom in direct union with four different atoms or groups. Thus if the original molecule is of the form



and the new molecule is of the form



the italicised *C* represents an *asymmetric* carbonation. In such a case the compound thus produced should exhibit optical

[1] See Chap. IV. par. 146.

activity, if the hypothesis of van't Hoff is adopted (*s.* Chap. IV.) But such reactions are sometimes known to produce compounds which do not shew optical activity. Wislicenus supposes that in these cases the two geometrical isomerides are produced in equal quantities, and that as one is dextrorotatory and the other lævorotatory the compound as a whole is optically inactive. The foregoing statements are rendered clearer by examining figs. 20 to 27.

Fig. 20. Fig. 21. Fig. 22. Fig. 23.

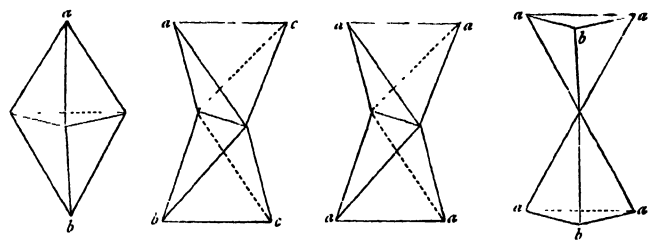
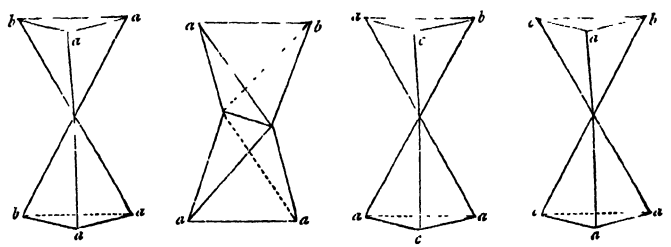


Fig. 24. Fig. 25. Fig. 26. Fig. 27.



95 Wislicenus developes these conceptions and applies them to many cases of isomerism which do not find an explanation in terms of the hypothesis of valency when it is limited by the condition that the atoms which form a molecule must be represented as arranged in a single plane.

Thus to take the cases of fumaric and maleic acids, $C_2H_2(CO_2H)_2$. Fumaric acid is probably the axially symmetric, and maleic acid the plane-symmetric, isomeride; figs. 28 and 29 represent these compounds. When malic acid $C_2H_3(OH)(CO_2H)_2$ is heated to about 150° water is separated and fumaric acid is formed; this change is represented in

figs. 30 and 31. But at 170°—180° malic acid is partly changed to maleic anhydride; if we suppose that rise of

Fig. 28.

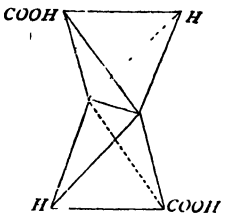


Fig. 29.

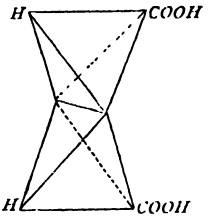


Fig. 30.

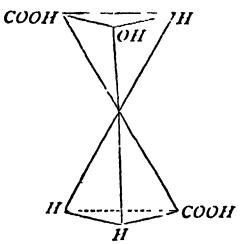
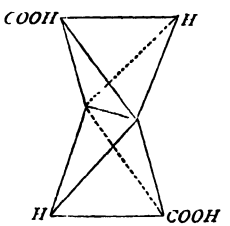


Fig. 31.



temperature causes rotation of the parts of the molecule of malic acid with the production of a geometrical form less stable than the original form, and that water is then separated from this less stable form, we can explain the production of maleic anhydride along with fumaric acid by heating malic acid. Figs. 32 and 33 (taken with fig. 30) represent this process.

Fig. 32.

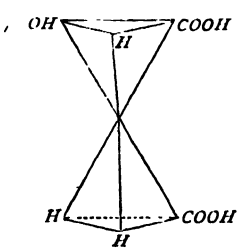
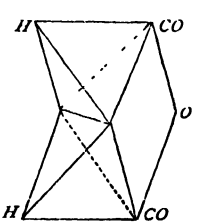


Fig. 33.



Maleic acid is changed almost wholly to fumaric acid by interacting with hydrochloric or hydrobromic acid. Wis-

licenus supposes that an additive compound is produced, that rotation of the parts of this molecule then occurs caused by the affinities of the atoms H and Br and the group COOH, and that HBr is then split off; the mechanism of the change as thus imagined is shewn in figs. 34 to 37.

Fig. 34.

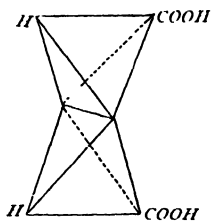


Fig. 35.

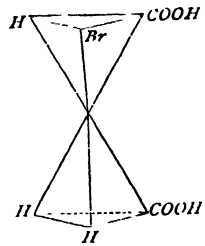


Fig. 36.

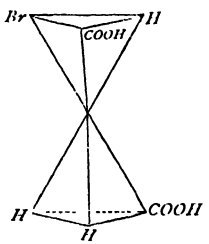
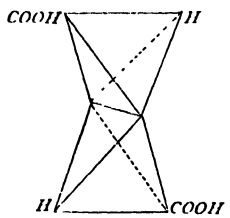


Fig. 37.



Fumaric acid combines with bromine forming dibromosuccinic acid, which when boiled with water yields hydrobromic and bromomaleic acids. Maleic acid combines with bromine forming isodibromosuccinic acid, and this when boiled with water yields hydrobromic and bromofumaric acids. These changes are easily explained in terms of Wislicenus' conception, by supposing that in each case an additive compound is formed, that the atomic affinities then cause rotation of the parts of the molecules, and that hydrobromic acid is then split off. Figs. 38 to 45 represent the changes.

Other reactions of fumaric and maleic acid are considered and explained by Wislicenus. The only reaction of these acids which is inexplicable in terms of the geometrical hypothesis of isomerism is that of bromine with acetylene di-

carboxylic acid, $C_2(CO_2H)_2$, whereby dibromofumaric acid is said to be produced. The geometrical hypothesis requires

Fig. 38.

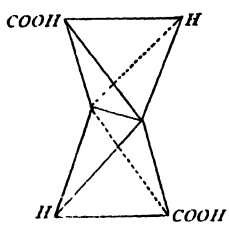


Fig. 39.

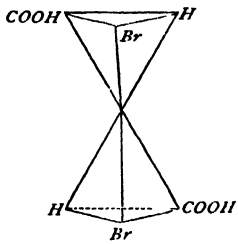


Fig. 40.

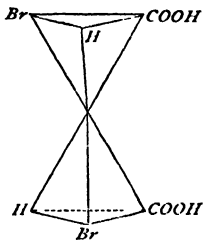


Fig. 41.

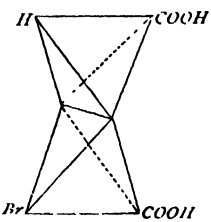


Fig. 42.

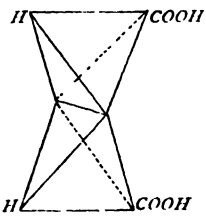


Fig. 43.

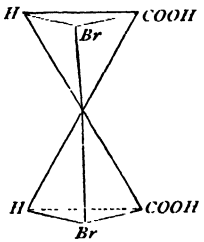


Fig. 44.

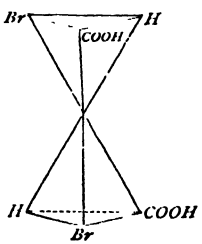
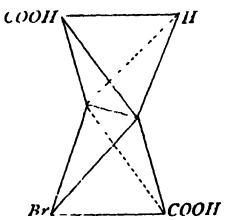


Fig. 45.



the production of dibromomaleic acid. But Wislicenus' experiments have proved that hydrobromic acid is always produced in this reaction, and that if care is taken to limit the yield of this acid as much as possible, some dibromomaleic acid is produced. The production of dibromofumaric acid is easily explained by the interaction of the hydrobromic and bromomaleic acids produced in the principle reaction.

There can be no doubt as to the ingenuity of the extension of van't Hoff's geometrical conception made by Wislicenus. One point which appears to me to be gained by this hypothesis is the possibility of keeping separate the two conceptions of atomic valency and atomic affinity, and of using both in explaining the configurations and chemical properties of molecules.

96 We have thus found that to trace the connexions between the compositions and the properties of changing material systems has always been regarded as the fundamental problem of chemistry. Attention has sometimes been almost confined to the composition of substances forming such systems, at other times the properties of the systems and their components have been regarded as chiefly important. We found that as chemistry advanced it became necessary to know more than the mere elementary composition of bodies; having gained the atom and the molecule, chemists were soon convinced that the arrangement of the same atoms might vary, and that properties might therefore be correlated not only with atomic composition but also with atomic configuration. We traced this conception through the dualism of Berzelius and the unitary system of Dumas, Laurent, Gerhardt and others, through the hypothesis of compound radicles and that of types, to the time when Frankland and Kekulé gave it greater precision by arranging the elementary atoms in groups according to the maximum number of other atoms with which each was found to combine.

But we saw that the expression equivalency, or valency, of atoms gradually came to be used in a loose and inexact manner. We found that the comparison of monovalent with divalent, &c. atoms, when unchecked by accurate dynamical knowledge, led to the belief that the terms in question expressed in some vague way quantitative measurements of interatomic forces, and to the conclusion that, inasmuch as one divalent atom could directly bind to itself two other atoms, while one monovalent atom could directly interact with only a single other atom, in a molecule, therefore the divalent atom was capable of exerting twice as much force

as the monovalent atom. The latter part of the foregoing sentence may I think be taken as fairly representative of the loose and slipshod way in which dynamical language has too often been used in chemistry.

We found that attempts were made to build a general conception of atomic valency on a shifting quasi-dynamical foundation; but the account given in this section of Lossen's criticisms of the expressions 'a bond,' 'a valency,' 'a unity of affinity,' &c. has I think been sufficient to shew how inexact, while apparently precise, and how narrow, while apparently far-reaching, the conception in question really is.

The objections raised against the atomic theory in recent years by some chemists, who nevertheless made free use of the essentially atomic conceptions of modern chemistry, led, it seems to me, to a looseness of thinking about atoms, molecules, and equivalents, which has done no little harm. *Parts by weight* were spoken of as if the expression were synonymous with *atom; equivalents* were regarded as acting and reacting with one another; there appeared to be a possibility of chemistry retracing her steps to the time when no precise meaning was attached to any of the terms *atom, molecule, combining weight, equivalent*, but each was used as nearly synonymous with the others. From the possibility of such retrogression we have been saved by the general advance of physical science. As the molecular theory of matter became more precise and its applications more far-reaching, it was impossible for chemists to employ conceptions essentially molecular and atomic and at the same time to express chemical changes in a notation based on the notions of a pre-molecular era. It became necessary to choose definitely between the atom and the equivalent, and the great body of chemists has certainly chosen the former.

But as soon as attempts to found a conception of chemical actions on the basis of equivalents were abandoned, it was seen that the conception of equivalency might be retained and applied to the elementary atoms. To keep distinct the conceptions implied in the terms equivalent and atom, and at the same time to arrange the atoms in equivalent groups, is

one of the problems of modern chemistry. On this distinction and on this resemblance is based the molecular explanation of isomerism. We have found that the study of isomerism has done much to render precise the conception of the molecule as a structure with properties dependent on the nature, the number, and the arrangement, of the constituent atoms.

We endeavoured to subdivide the conception expressed in the words 'arrangement of atoms in a molecule' into parts, and to demonstrate by illustrations the existence of a connexion between each of these parts and the properties of the molecule. These illustrations led to clearer notions concerning the valencies of atoms, and the meaning of structural formulæ: these formulæ we regarded as expressing the actual valencies of the atoms in the molecule, i.e. the number of atoms directly acting on and acted on by each atom, and as expressing also the distribution of the atomic interactions, i.e. the nature of the atoms in direct mutual connexion; but we tried not to attach any quantitative meaning to the symbols used for expressing atomic valencies and the distributions of atomic interactions. We also glanced at the geometrical conception by which van't Hoff and Wislicenus have sought to picture the connexion between the properties of isomeric molecules and the configurations of the atoms which form these molecules.

The hypothesis of valency as thus used leads to dynamical conceptions but regards these as outside its sphere: it points the way along which progress will be made. Attempts must be made to apply thermal, optical, and other physical, methods of research to the investigation of chemical problems; thus we may hope to gain clear and precise knowledge regarding the connexion between the structure and the stability of molecules, in so far as the latter is measured by variations in the quantities of energy associated with different molecules.

APPENDIX TO SECTION IV.

To have given a detailed account of Lossen's criticisms of the generally accepted views regarding 'valencies' or 'units of affinity' in the text of the section on isomerism, would have involved too great an interruption of the main argument of that section. But as Lossen's

criticisms seem to me of great importance I propose to give some account of them here.

The many and varied hypotheses concerning valency set forth by chemists of acknowledged authority may be divided, says Lossen, into three groups :—

I. Those hypotheses which regard 'an affinity' as a definite quantity of matter, or as an action of some kind proceeding from a definite quantity of matter.

II. Those which regard 'an affinity' as a part of an atom, or at least as something connected with a part of an atom.

III. Those which regard the 'affinities' of an atom as definite forms of motion of the atom.

I. Erlenmeyer[1] has developed the conception of '*Affinivalencies*.' He states, as a rule without exceptions, that "in all chemical combinations a constant quantity of one element always attracts a constant quantity of another." These constant quantities are the 'affinivalencies' of the elements: one affinivalency of element *a* always binds to itself one affinivalency of element *b*. The affinivalency of carbon = 3, of oxygen = 8. Now in CO_2 we have 3 parts by weight of carbon combined with 8 of oxygen, but in CO the same amount of carbon with only 4 parts by weight of oxygen; Erlenmeyer's general law does not therefore always hold good. If it be said that a constant quantity of one element *attracts* (not combines with) a constant quantity of another, then, as in CO_2 6 parts by weight of carbon attract 16 of oxygen, we must suppose that in CO 16 parts by weight of oxygen are attracted by 6 of carbon, and that the remaining 6 of carbon have no attractive action on the oxygen.

Atoms and relative quantities of matter are compared by Erlenmeyer; but *relative* quantities do not attract each other. In the molecule CO there is one atom of carbon and one atom of oxygen, and these atoms attract one another; half an atom cannot attract because it has no existence. The hypothesis that an atom is non-homogeneous, although indivisible, might be made, but is not made, by Erlenmeyer. If an equivalent is regarded as a constant quantity, this quantity attracts sometimes one, sometimes two (or more) equivalents of other elements. The molecule CH_4 is composed of one atom of carbon and four atoms of hydrogen, we may say that 3 parts by weight of carbon here attract 1 part by weight of hydrogen; so in CCl_4 it may be said that 3 parts of carbon attract 35·5 parts of chlorine. But in CH_3Cl 12 parts of carbon attract 3 parts of hydrogen *and* 35·5 parts of chlorine; in place of 12 parts of carbon we may, if we choose, say 9+3 parts, just as we might say that 7+5=12, or $\sqrt{144}=12$; but we cannot say that 9 parts

[1] For references to the work of the various chemists mentioned, see Lossen, *Annalen*, **204.** 265 *et seq.*

of carbon attract 3 parts of hydrogen and the remaining 3 parts of carbon attract the 35·5 parts of chlorine. If we suppose the carbon atom to be perfectly homogeneous, then the whole atom interacts with the chlorine atom and with each of the hydrogen atoms; if we suppose that the atom of carbon is possessed of a structure, it remains to explain in what respect one part of the atom differs from the other parts: but *a part of an atom* is not the same thing as *a fraction of the relative weight of an atom.*

Hofmann speaks of 'an affinity' as a force proceeding from a constant mass of an element, which mass he regards as the equivalent and defines as 'the minimum atom-binding quantity' of the element. He nevertheless uses an equivalent as a varying quantity. By an arbitrary choice of certain values for the equivalents of the elements it is possible that the number obtained by dividing the atomic weight by the equivalent weight of any element should be the same as the number expressing the maximum number of hydrogen atoms which can be bound by one atom of the given element.

L. Meyer also speaks of the action of quantities by weight of one element on atoms of another element. In one place he defines equivalent quantities of elements as those quantities which are able to bind to themselves, directly and without the intervention of a third substance, equal quantities of other substances. We should expect 16 parts by weight of oxygen to be equivalent to 12 parts by weight of carbon, and to 14 parts by weight of nitrogen, because 16 parts of oxygen directly bind 16 of oxygen in O_2, 14 of nitrogen in NO, and 12 of carbon in CO; but Meyer supposes two free affinities in the last named molecule, i.e. he supposes that $\frac{1}{2}^2$ parts of carbon bind 16 parts of oxygen, although the molecule CO contains one indivisible atom of carbon and one indivisible atom of oxygen.

Those hypotheses in which 'affinities' are regarded as constant weights of matter, or as actions proceeding from constant weights, arise, according to Lossen, from not sufficiently marking the distinction between the equivalent and the atom. Equivalent, or combining, weights are relative weights of divisible masses; atomic weights are relative weights of indivisible masses. If the atomic hypothesis is adopted we must regard atomic weights as relative weights of mutually reacting bodies; but equivalent weights, in so far as they differ from atomic weights, are relative weights of imagined sums, or fractions, of these bodies. Bodies whose relative weights are equal to these equivalent weights do not mutually react in molecules. To find equivalents, parts by weight should be compared with parts by weight, or atoms with atoms.

II. Besides the hypothesis of 'affinivalencies' already referred to, Erlenmeyer also speaks of mutual actions between atoms as occurring at certain points of these atoms. This may mean either that contact

(not of course absolute contact) between the reacting atoms is made at these points, or that mutual atomic action occurs only when these attracting points coincide. The attracting points must be considered as qualitatively different from the rest of the atoms. The form of polyvalent atoms must be such that several points of one can touch the same number of points of another: the positions of the points must be such that when some of these points are in contact it is not necessary that all should be in contact. To fulfil these conditions without supposing the form of the atoms, or at any rate the positions of the points, changeable, is exceedingly difficult. This hypothesis of Erlenmeyer tends to foster the notion of an attractive force proceeding from different parts of elementary atoms; Kekulé's graphic formulæ do not, probably, imply this conception, but these formulæ may be, and have been, used as if this conception were true.

A qualitative difference between parts of an atom can only mean that some parts are chemically active while others are chemically inactive. If the inactive parts are composed of imponderable matter then each n-valent atom must be made up of n atoms; we thus arrive at atomic weights different from those on which the science of chemistry at present rests. If the inactive parts consist of ponderable matter, then in the case of action between different atoms we have action through the ether, but in the case of action between parts of the same atom we have action through ponderable chemically inactive matter. In either case it appears that the notion of atom must be very different from that at present adopted, and, it would seem, necessarily adopted if facts are to be explained.

But it may be supposed that the active parts of the atom are in a different electrical condition from the inactive parts. If electricity be a form of motion, then some parts of an indivisible atom must be supposed in motion while others are not; if electricity be a fluid, then we have a material difference, arising from the partial fixation of this fluid, between the active and inactive parts of the atom. Both of these hypotheses are opposed to the fundamental conception of atom[1].

Michaelis has supposed that the attractive force of an atom is exerted in certain fixed directions only. On this hypothesis a straight line joining two atoms which are directly bound together may be regarded as expressing the direction of the mutually exerted force; an n-valent atom has n such directions. If this atom is directly bound to fewer than n atoms, say to $n-x$ atoms, then the mutual action is exerted in $n-x$ directions. Lossen expresses his general agreement with this interpretation of the hypothesis of Michaelis. But if that chemist sup-

[1] This criticism is rather weak: we know too little as to what electricity is to hazard such criticism as this; besides, Helmholtz has shewn that there is probably a close and definite connexion between the valency of an atom and the electrical charges on that atom; see Book II.

poses that to every atom, regarded as a point, there are *always* attached a fixed number of such 'lines of force,' then it is asked 'on what does the atom act when it is bound to less than its maximum number of other atoms?'

The objection urged to van't Hoff's form of the hypothesis now being discussed, is, that by this chemist the 'affinities' of an atom are imagined as arranged in a definite form in space; but as we cannot define an 'affinity,' much less can we assign geometrical figures to the arrangement of these 'affinities'[1].

III. L. Meyer supposes that there is one position at which a monovalent atom during its vibration can combine with another atom to form a stable compound, that there are two positions at which a divalent atom can combine with another atom, and so on. In the molecule NH_3 we have one trivalent and three monovalent atoms; the nitrogen atom swings through three positions at each of which it can take up one hydrogen atom. In the molecule OH_2 the divalent oxygen atom swings through two such positions. In the molecule NO it appears as if the three positions of possible combination passed through by the triad nitrogen atom must also be touched by the path of the diad oxygen atom, but if so the oxygen atom may, in some circumstances, be trivalent.

The results of O. E. Meyer's physical and dynamical investigation of the forms of molecules are not in harmony with this view of L. Meyer. The form of a molecule would appear to be dependent more on the number of the constituent atoms than on the valencies of these atoms; but on L. Meyer's hypothesis the nature of the path of the atoms swinging in the molecule must condition the form of the molecule, and the nature of this path is itself conditioned by the valencies of the atoms.

Kekulé has advanced hypotheses as to the motion of atoms within molecules, but these hypotheses are not sufficiently definite to admit of detailed criticism. Lossen however objects to applying to the motion of atoms within molecules the conceptions which arise from a study of the motion of molecules in a confining vessel. If the atoms composing a mass of hydrogen molecules undergo mutual collisions, why, when they have separated a certain distance from one another, is the direction of their motion changed until a second collision occurs? There is no confining molecular wall answering to the sides of a containing vessel. If it be supposed that the atoms in molecule *a* enter into collision with the atoms in molecule *b* or *c*, then this is equivalent to asserting that a mass of hydrogen is composed not of diatomic, but of monatomic molecules[2].

[1] Van't Hoff's hypothesis as recently developed by Wislicenus is discussed in pars. 92 to 95.

[2] Here again, I think Lossen carries his criticism too far. The methods of molecular enquiry are necessarily statistical; a mass of hydrogen may contain

Among the various developments of the bond-hypothesis of valency not mentioned in the text, is that which concerns itself with the question whether all the bonds of a polyvalent atom are of equal value, or whether one may be 'stronger' than another. If the criticism applied to the subject of bonds generally is just, it follows, I think, that the question alluded to is meaningless; but as it has been hotly disputed about it may be well briefly to consider it here.

It is assumed in the bond-hypothesis that the so-called affinities of atoms attract or satisfy one another, and hence those affinities of one atom which are not satisfied by affinities of another must be satisfied by other affinities of the atom itself. No molecule, it is sometimes said, can contain an odd number of atoms of uneven valency. This outcome[1] of Gerhardt's 'law of even numbers' (see *ante*, chap. I. p. 84) is however contradicted by the existence of the molecules I, NO, NO_2, ClO_2, WCl_5, VCl_4 or $VOCl_3$, and cannot therefore be accepted as a statement of facts, unless indeed the valency of an atom is a number susceptible of arbitrary variation. That the maximum valency of each atom is fixed is generally admitted. One school however holds that (e. g.) a tetrad atom is always tetrad; another school asserts that a tetrad may function as a diad atom. The followers of the first school maintain that in the molecule CO, for instance, the carbon atom is tetravalent, but two of its affinities are mutually satisfied; the opponents of this view say that in CO the carbon atom is divalent, and that the other pair of bonds is latent. The dispute has been wholly a battle about words. Whether the two bonds are latent, or are mutually satisfied, as Lossen remarks, '*zwei und zwei geben doch immer vier.*'

But if always existent, are the bonds always of equal value? Are the two pairs of bonds which hold the two oxygen atoms to the carbon atom in the molecule CO_2 equal in value to twice the pair of bonds by which one oxygen atom is held to a carbon atom in the molecule CO?

Now if we wish to compare things we must have a standard; but I think sufficient facts have been enumerated to shew that no standard exists in terms of which the expression 'value of a bond' may be stated. Even if the valency of an atom is regarded as expressing the total number of parts into which the chemical energy of that atom is divisible, this must mean that the energy is divisible when there is mutual action between the given atom and other atoms in a molecule. Thus, assume for a moment that the chemical energy of an atom of carbon is divisible into four parts, it does not follow that each part represents a fourth of the whole energy, or always represents the same portion of

many free atoms (or monatomic molecules) and yet for all practical purposes behave as if composed entirely of diatomic molecules.

[1] The statement is sometimes put in this form; 'the sum of the valencies, or affinities, of the atoms in any molecule is always an even number.'

that energy. To take an illustration; in the stable molecule CO we must suppose, on this hypothesis, that the whole of the chemical energy of the carbon atom is employed in the transaction symbolised by the formula C – O; again, in the molecule O – C – S the whole of the energy of the carbon atom is employed, but the energy represented by O – C is probably different from that represented by C – S, and the sum of these is probably different from that represented by the expression O – C – O. The results of thermal measurements made by Thomson (see par. 84, also *post*, par. 134) render it fairly certain that the quantity of energy which changes form during the process symbolically expressed as 'linking a pair of carbon atoms by a double bond' bears no simple relation to the quantity of energy which changes form when 'a pair of carbon atoms is linked by a single bond.' The number of possible ways in which the energy is distributed is, on this hypothesis, measured by the valency of the atom; the amount of the energy employed in any atomic transaction depends on the nature of the atom or atoms between which and the given atom there is mutual intramolecular action[1].

Even if we adopt this, the most dynamical, view of valency that can be adopted with any safety, the controversy concerning equal and unequal bonds is seen to be a mere logomachy[2].

SECTION V. *Molecular Compounds.*

97 In the preceding sections we have learned that some compounds can be gasified without decomposition while others are separated by heat into two or more constituent parts.

The conception expressed in the term molecule can be applied in strictness to the former compounds only, and the fundamental notions regarding the structure of molecules must be gained by the study of such gasifiable compounds.

[1] For a fuller working out of this way of regarding valency see Claus, *Ber.* **14**. 432.

[2] It is sometimes said that the hydrogen atoms in the molecule of benzene are of equal value, but when one of these atoms is replaced by a radicle the remaining five are of different values relatively to the radicle introduced into the molecule. To make such a statement as this, it seems to me, is to employ the term value in too loose and vague a way. All the hydrogen atoms in a molecule of a mono-derivative of benzene are monovalent, and therefore of equal value so far as 'proportion in exchange' for chlorine, bromine &c. goes. What appears to be meant by the statement in question is, that more than one mono-derivative (chloro- bromo-.....or generally X – derivative) can be obtained from the molecule C_6H_5X; but this is simply a special illustration of the general proposition that the properties of compounds are not wholly dependent on the valencies of their constituent atoms.

But, it may be asked, is there a distinction of kind, or only one of degree, between those compounds which can be gasified, and those which separate into parts when they are heated? This question has been provocative of much discussion. Kekulé[1] and others have employed the term *atomic compounds* to express those compounds which can be vaporised without decomposition, and they have contrasted these with *molecular compounds*, meaning thereby those compounds which separate into two or more parts when heated.

This division of compounds has played an important part in the development of the hypothesis of valency. Kekulé has always insisted that facts regarding atomic compounds can alone be employed as data for finding the valencies of elementary atoms; his opponents have retorted by demanding a definition of molecular as opposed to atomic compounds, and by shewing that every proposed definition fails when applied to actual phenomena.

But it is not so much as it concerns the hypothesis of valency that the distinction implied in the words atomic and molecular compounds ought, I think, to be insisted on; if the arguments put forward in the preceding section are of any value, we must agree to confine what may be called the non-geometrical hypothesis of valency to gaseous compounds. There are however many and varied phenomena, all more or less belonging to the borderland between chemistry and physics, which may conveniently be considered under the heading of molecular compounds.

98 And I would begin by admitting that no strict definition of molecular, as opposed to atomic, compounds, can be given, which shall enable us to assign every disputed case to its proper class. A substance may yield a vapour which is chemically homogeneous below a certain temperature but heterogeneous above this temperature; we cannot fix a limiting temperature for each group of compounds and say, that those which yield vapours homogeneous above this temperature are atomic, while those in the vapour of which dissociation begins below the temperature-limit are molecular.

[1] See his *Lehrbuch*, Vol. I. pp. 142, 145, 443, &c.: also *Compt. rend.* 58. 510.

I would again urge the importance of remembering that when we say that a gas consists of molecules of this or that composition, we refer and can refer only to the average composition of the gas; many molecules may be dissociated into two or more chemically different kinds of matter, other molecules may be aggregated into complex groups. Even in an elementary gas at moderate temperatures some atoms and many groups of molecules may be present at any moment: the values obtained for the specific gravities of gaseous bromine and iodine, and for gaseous nitrogen dioxide, stannous chloride, and acetic acid well illustrate the gradual nature of the passage from one average molecular state to another[1].

99 Some chemists would recognise the existence of molecular compounds in mixtures of two or more liquids, and in solutions of salts, and of gases (e.g. CO_2), in water. In such cases the proportions in which the substances are supposed to be combined are very variable. It cannot be correct to speak of a molecule of the mixture of alcohol and water, or of a molecule of the solution of salt in water, although it may be permissible to regard these liquids as containing groups of molecules of alcohol and water, or of salt and water.

As examples of bodies which seem to hold a place between definite chemical compounds and mere mixtures may be noted the products of the fusion together of sulphur and selenion. Rathke[2] fused together sulphur and selenion, dissolved the fused mass in carbon disulphide, and fractionally precipitated by gradual evaporation; he then redissolved the various precipitates, and again fractionated. The precipitates all consisted of monoclinic crystals composed of sulphur and selenion (neither element exhibiting the properties which characterise it in the free state) but varying in quantitative composition between the limits expressed by the formulæ SeS_4 and Se_4S. Rathke thinks it possible that elements which are chemically very analogous may combine in varying proportions to produce isomorphous bodies.

There are other actions wherein small changes in physical

[1] See par. 99, pp. 203, 206—7.

[2] *Ber.* **18.** 1534. *See* also Lehmann, *Zeitschr. f. physikal. Chemie*, **1.** 15.

conditions suffice to cause changes in the relative quantities of substances combined in definite proportions; for instance, when the substance containing water and sodium phosphate in the proportion $Na_2HPO_4 : 12H_2O$ is heated, it very readily loses water and becomes $Na_2HPO_4 . 7H_2O$. If by molecular compound is meant, a loose combination in definite proportions of two or more chemically different kinds of matter so as to produce another kind of matter characterised by fairly definite properties but readily undergoing change, then we may certainly say that $Na_2HPO_4 . 12H_2O$ is a molecular compound.

Once more, compounds exist which are characterised by very definite properties, but which, when heated, undergo gradual change into two or more substances, the original compound being gradually re-formed as the vapours cool. Thus the formula PCl_5 expresses the elementary composition of an undoubted chemical compound; when this solid substance is heated it vaporises, but the vapour can be proved by experiment to contain molecules of PCl_3 and Cl_2, along with undecomposed PCl_5. The following numbers shew the gradual progress of the change which occurs:—

Calculated sp. gr. of gaseous $PCl_5 = 7{\cdot}2$
" " gas consisting of $PCl_3 + Cl_2 = 3{\cdot}6$ } [air = 1]

Temperature.	Sp. gr. of vapour.	Number of molecules decomposed[1] per 100 molecules of PCl_5.
182°	5·08	41·7
190	4·99	44·3
200	4·85	48·5
230	4·30	67·4
250	4·00	80·0
274	3·84	87·5
288	3·67	96·2
300	3·65	97·3

[1] Calculated by means of the formula $p = \frac{100(d-D)}{D}$ where p = number of molecules decomposed, D = observed sp. grav. of gas, d = theoretical sp. grav. of vapour supposing no dissociation to occur. This formula assumes that each molecule separates into two parts: if each molecule separates into a parts, the formula is $p = \frac{100(d-D)}{(a-1)D}$. See Naumann, *Lehr- und Handbuch der Thermochemie*, pp. 114, 115.

The following numbers[1] representing the specific gravities of gaseous nitrogen tetroxide at various temperatures exhibit the gradual dissociation of molecules of N_2O_4 into molecules of NO_2:—

Temperature.	Sp gr. of vapour.	Percentage molecular decomposition.	Increase in percentage decomposition for each rise of 10°.
26·7°	2·65	19 96	6·5
35·4	2·53	25·68	8·1
39·8	2·46	29·23	11·0
49 6	2·27	40·04	12·1
60·2	2·08	52·84	13·0
70·0	1·92	65·57	10·4
80 6	1·86	76·61	8·8
96·0	1·72	84·83	1·8
135·0	1·60	98·69	

As N_2O_4 is dark-red and nearly opaque, and NO_2 is transparent and nearly colourless, the change from one compound to the other can be traced by observing the colour of the heated gas.

A study of the specific gravity of the vapour obtained by heating acetic acid, at different temperatures and pressures, shews that the specific gravity decreases as temperature rises whether pressure be small or great, and that the specific gravity also decreases as pressure falls whether the temperature be high or low; in other words, the vapour of acetic acid becomes specifically heavier by increasing pressure, temperature being constant, or by decreasing temperature, pressure being constant[2]. The most probable molecular explanation of these facts is to suppose that the vapour of acetic acid at low temperatures contains molecules, or molecular groups, the parts of which hold together throughout small temperature-intervals, and that these molecules, or groups,

[1] Naumann, *loc cit.* p. 117.

[2] See Ramsay and Young, *C. S. Journal*, **Trans.** for **1886.** 790 (*s.* also Book II.). Comparing the variations in the specific gravities of the vapours of acetic acid, alcohol, and ether, Ramsay and Young (*Phil. Mag.* (5) **23.** 129) found that the specific gravities of alcohol vapour and ether vapour increase as temperature falls until a certain point is reached beneath which the specific gravities are unchanged. They conclude that the increase in the specific densities of the vapours of alcohol and ether are probably due to the cohesion of the molecules, and not to the formation of groups of molecules.

are heavier than those which compose the vapour of the same acid at temperatures considerably above the boiling point of the compound.

If we define a molecular compound to be one the molecules of which may exist in the gaseous state at low temperatures but are gradually decomposed into less dense molecules of the same kind of matter as temperature rises, then we must regard acetic acid at temperatures not far above its boiling point as a molecular compound.

But if this is so, we evidently have a series of substances, beginning with solutions of salts or gases in water, and proceeding through crystallised solid salts to acetic acid vapour at low temperatures, which connects mechanical mixtures on the one hand with stable gaseous compounds on the other.

It might be urged that we ought not to distinguish between the particles which compose acetic acid vapour at low temperatures and those which form the vapour of the same acid at high temperatures; that if a molecule is 'that small part of a gas the parts of which do not part company during the motion of agitation of the gas,' then the reasoning which compels us to say that the molecule of acetic acid vapour at 220° is represented by the formula $C_2H_4O_2$, likewise compels us to say that at 120° the molecule of this gas is represented by the formula $C_3H_6O_3$ (pressure in each case being 760 mm.). The statement that acetic acid at low temperatures is a molecular compound does not appear to me to go against this reasoning; for this statement only implies that at low temperatures the vapour of this acid is composed of particles, of varying masses—which may be called molecules or molecular groups—but that as temperature rises these all tend to separate into particles whose composition is represented by the formula $C_2H_4O_2$. The particle having the composition $C_2H_4O_2$ is stable throughout so large a range of temperature that we may apply to it and to it only the knowledge we have gained regarding the structure of molecules. It is better not to apply the term molecule to the heavier particles, (1) because they so readily separate into lighter, and comparatively stable,

particles; (2) because what we know of molecular structure has been gained from, and can only be strictly applied to, the study of molecules which are stable throughout a considerable range of temperature; and (3) because by recognising the possibility of the existence in certain vapours of groups of molecules, which are not mere mixtures but on the other hand are not to be classed as true molecules, we have the means of explaining, in a general way, many phenomena which at present cannot be explained by any other equally simple hypothesis which is in keeping with the fundamental conceptions of the molecular theory of matter.

That the existence of molecular groups in a gas at low temperatures is in keeping with this theory can readily be shewn. When two gases are at equal temperatures the *mean* kinetic energy of agitation of the molecules must be the same in both; but although the mean kinetic energy is constant for a given temperature, yet the kinetic energy (and hence the temperature) of many molecules may differ from this mean value. If the temperature of the gas is increased, there is an increase not only of the energy of agitation of the molecules as a whole, but also of the energy due to the internal motions of the parts of each molecule; as the latter energy increases, a point is reached at which the molecule decomposes into its constituent parts, but these may again unite in some other portion of the mass of gas. As temperature continues to rise a point will come at which molecular decompositions and recompositions are equal in unit of time; the temperature at which this state of matters is reached has been called (by Naumann and others) the *decomposition-temperature;* from this point onwards, as temperature rises, the molecular decompositions will exceed the recompositions, until finally there are no recompositions, or these are so few in number that the average state of the gas is fitly described as that of complete decomposition.

Now if we suppose that the vapours coming from certain liquids, especially from dissociable compounds, at, or near to, their boiling points consist to a great extent of molecular aggregations, we may trace the gradual decomposition of

these aggregates into true gaseous molecules, just as we have traced the decomposition of molecules of one kind of matter into those of another kind of matter. Many spectroscopic facts almost necessitate the assumption that groups of molecules may exist, and behave for certain small changes in physical conditions as definite wholes[1].

But it might be asked, why should not all molecules decompose when heated? It is extremely probable that all molecules are capable of being decomposed by heat. The results of Meyer's experiments on iodine vapour shew that the diatomic molecules of this gas are separated into atoms at high temperatures. The following table exhibits the process of change from I_2 to I.

Dissociation of Iodine molecules[2].

	Temp.	Sp. gr. of vapour.	Percentage decomposition.	Rise of temp	Increase in percentage decomposition.	Mean increase in decomposition for 100°.
	448°	8·74				
	680	8·23				
	764	8·28				
	855	8·07	8·6			
				85°	5·9	6·9
	940	7·60	14·5			
				103	10·5	10·2
	1043	7·01	25·0			
				232	25·5	11·0
(approximately)	1275	5·82	50·5			
				115	15·7	13·7
	1390	5·27	66·2			
				78	6·9	8·8
	1468	5·06	73·1			

Somewhat similar results have been obtained with bromine. A fact of much interest is disclosed by studying the specific gravities of gaseous bromine and chlorine at low and at high temperatures; some of the results of such a study are given in the following table[3].

[1] In connexion with this subject see especially the article 'Constitution of bodies,' by Clerk Maxwell, in the *Encyclopædia Britannica*. (9th Ed.) See also 'Report of the B. A. Committee on Spectrum Analysis.' *Brit. Ass. Reports* for 1880, 2581 *et seq.* See especially pp. 284—298. Also the article 'Aggregation, States of' in the new edition of Watts' *Dictionary of Chemistry*.

[2] Naumann, *Ber.* 13. 1050, using the numbers of Crafts and Meier, *do. do.* 868.

[3] Jahns, *Ber.* 15. 1238.

Specific gravities of gaseous Bromine and Chlorine.

Temp. measured in degrees above boiling point of		Specific gravity.		Deviation of sp. gr. from normal, in per centages of latter	
BROMINE.	CHLORINE.	BROMINE.	CHLORINE	BROMINE.	CHLORINE
40°	40°	5·7115	2·4844	3·381	1·397
60	60	5·6809	2·4810	2·872	1·261
80	80	5·6503	2·4776	2·223	1·122
100	100	5·6197	2·4742	1·719	0·984
120	120	5·5891	2·4708	1·650	0·845
160	160	5·5279	2·4641	0·058	0·571
	200		2·4572		0·290
	240		2·4504		0·000

We have here a phenomenon very analogous to that presented by acetic acid; and if an analogous explanation is to be given, we must suppose that bromine vapour at temperatures from 40 to 140 degrees above the boiling point of this substance contains molecular groups which are slowly decomposed as temperature increases; and that the same holds good of chlorine vapour, only that in this case the molecular groups are relatively lighter, but more stable as regards heat, than those of bromine.

A study of the specific gravities of the gases obtained by heating various liquid compounds shews that in very many cases the specific gravity decreases as the temperature rises, and that a constant value is not obtained until the gas has been heated many degrees above the boiling point of the liquid.

Facts have now been recounted sufficient I think to warrant the adoption of the hypothesis that gaseous molecules may hold together in groups, the members of which do not part company throughout more or less extended ranges of temperature and pressure; and if this is so in gases, much more should we expect to find the existence of molecular groups in liquids and solids.

100 The hypothesis, by the application of which we hope to find many groups of facts falling into some kind of order, may be broadly stated as consisting in the recognition of a third order of particles more complex, but less stable, than the molecule, as the molecule is more complex, but less stable, than the atom. This hypothesis affords no definition

of the third order of particles, nor does it always enable us to refer a special case to this, or that, order of particles. It is a general guide and as such only must it be employed.

101 Many salts when in solution undergo changes not so marked as those usually called chemical, and yet too definite to be altogether classed as physical. Thus an aqueous solution of ferric chloride undergoes partial separation into hydrochloric acid and a colloidal form of ferric hydrate; aqueous solutions of various alums are partially separated into their constituents when heated. The direction of many of these changes may be partially reversed by altering the conditions of temperature[1]. Again hydrated cobalt chloride crystallises in a rose-red form ($CO_2Cl_4 . 12H_2O$), while the colour of the dehydrated crystals (CO_2Cl_4) is blue; if an aqueous solution of the red salt is warmed, the colour slowly becomes darker and finally changes to blue, but the rose red colour gradually reappears as the liquid cools. The temperature at which the change from hydrated to dehydrated salt occurs is the lower, the less the amount of water present relatively to that of salt. A crystal of cobalt chloride growing in a blue-coloured solution is seen under the microscope to be surrounded by a film of pink liquid, which indicates the existence round the crystal of a zone of liquid containing relatively less of the salt than the rest of the solution[2].

From the results of Lehmann's microscopic studies[3] on the formation of crystals of hydrated ferrous chloride, cobaltous chloride, and cupric chloride, it appears certain that an aqueous solution of one of these salts from which crystals, now of a more hydrated and now of a less hydrated salt, separate, as temperature varies, does not contain at a fixed temperature only the one hydrate and at another temperature only the other hydrate. As temperature slowly rises the molecular groups tend to fall to pieces and so the liquid becomes poorer in particles of the relatively most hydrated salt; on cooling,

[1] The expresssion 'dissociation of salts in solution' is sometimes applied to these processes. See Book II.

[2] See Lehmann, *Zeitschr. fur Krystallog.* 1. 99.: see also Potilitzin, *Ber.* 17. 276.

[3] *Zeitschr. fur Krystallog.* 1. 100—103.

the conditions are reversed, and the liquid becomes poorer in particles of the least hydrated salt. Lehmann considers the three cases; (1) the liquid is equally saturated for the hydrate rich in water and for that poorer in water; (2) the liquid contains rather more of one hydrate than of the other; (3) the liquid is concentrated as regards one hydrate, but dilute as regards the other. He shews that, as temperature slowly increases, in the first case crystals of both hydrates grow simultaneously and at the same rate until the spheres[1] of the crystals touch, when growth is almost entirely stopped; in the second case both kinds of crystals grow, but for a time one kind grows more quickly than the other, then both grow at the same rate, and then the second kind of crystals grow more rapidly than the first; in the third case those crystals which are present in the liquid in greater quantity grow rapidly, and the others dissolve rapidly, so that the dissolving crystals appear to pass directly into crystals of the other hydrate.

The definite form, solubility, temperature of formation, &c. of each kind of crystal formed in these experiments conducted by Lehmann prevent us from regarding the various crystalline solids as mere mixtures of ice and salt; on the other hand, the extremely small variations in temperature, or in the relative quantities of water and salt, required to cause change from one crystal to another, equally prevent us from attempting to explain the properties of each hydrate as wholly, or almost wholly, conditioned by the mutual interactions of atoms forming the molecule: we seem forced to adopt the hypothesis of molecular compounds.

Several compounds exist each in more than one modification, one form being generally more stable towards heat than the other. A typical case of this kind is presented by antimonious iodide, SbI_3; this compound crystallises in red hexagonal forms which are suddenly changed at 114° to an aggregation of yellow orthorhombic crystals, the original external form of the mass being preserved[2].

[1] Lehmann's term is '*der Hof des Krystalles:*' each crystal, he says, can be seen under the microscope to be surrounded by a liquid film, from which it draws its supplies of solid matter; this is the *Hof* or sphere of the crystal.

[2] J. P. Cooke, *Proc. Amer. Acad. of Arts and Sci.* [2]. 5. 72.

Several carbon compounds (apparently all belonging to the class of benzenoid compounds) exist in more than one form, each modification being characterised by a definite melting point and generally also by a special crystalline form. Thus chlorodinitrobenzene, $C_6H_3Cl(NO_2)_2$ [1 : 2 : 4], is said to form monoclinic crystals which melt at 36°, and also rhombic crystals which melt at 39°. Anthracene, $C_{14}H_{10}$, crystallises in monoclinic plates melting at 213° which are easily oxidised by the action of nitric acid to anthraquinone ($C_{14}H_8O_2$); when a solution, in benzene, of anthracene is exposed to sunlight small prismatic crystals separate, melting at 244°, having the composition $C_{14}H_{10}$, but not acted on by nitric acid, and not oxidised to anthraquinone by chromic acid[1]. A very remarkable instance of the phenomenon under consideration is presented by the derivative of diphenyl to which the formula $(C_6H_3BrNHCOC_6H_5)_2$ is assigned. This compound melts at 195°; if the melted substance is *cooled quickly* and again heated its melting point is now 99°; but if heating is continued the liquid again solidifies at 125—130°, and the solid thus obtained melts once more at 195°. Finally if the solid which melts at 195° is raised to that temperature and then *slowly cooled*, the product possesses the normal melting point[2], viz. 195. When a substance crystallises in more than one system, one crystalline form frequently approaches as nearly as possible to the other; one form may be said to imitate the other both crystallographically and optically[3]; thus arsenious oxide crystallises in regular octahedra and also in rhombic prisms, the latter exhibiting an angle identical with the angle of the regular octahedron.

O. Lehmann[4] has collected and discussed many instances of the exhibition of different physical properties by compounds possessing the same elementary composition[5]. The

[1] See Armstrong and Groves, *loc. cit.* p. 199.

[2] See E. Lellmann, *Ber.* **15**. 2835.

[3] Pasteur, *Ann. Chim. Phys.* [3] **23**. 267.

[4] *Zeitschr. fur Krystallog.* **1**. 97. See also, in connexion with the subject generally, the article 'Isomerie, physikalische' in *Neues Handwörterbuch der Chemie*, Bd. III. pp. 836—843.

[5] On this subject see also Laubenheimer, *Ber.* **9**. 760.

phenomenon, which may be called *physical isomerism*[1], presents analogies with allotropy (see *ante*, par. 67); in both, temperature is the most important condition affecting the change from one form to another, and this change is accompanied in both classes of phenomena by disappearance or production of heat.

Lehmann divides physically isomeric bodies into two classes: (1) those in which change from one form to another occurs at a definite temperature, the direction of the change being dependent on very small differences of temperature; (2) those which exhibit two forms, one more stable than the other, and in which change from one form to the other does not occur at a definite temperature, and is not reversible by heat alone.

Ammonium nitrate is an example of a substance belonging to the first class; the rhombic crystals of this salt, which separate at ordinary temperatures from an aqueous solution, melt at (about) 168°; as the molten mass cools crystals belonging to the regular system are formed, but at (about) 125° these change to rhombohedral forms; at (about) 87° the rhombohedral forms are converted into rhombic needles, from which, at 36° or so, the original rhombic crystals are produced. If the rhombic crystals are again slowly heated the rhombic needle-shaped crystals form at (about) 36°; the rhombohedral forms appear at (about) 87°; the regular crystals at (about) 125°; and finally the solid melts at 198°. Again, if a little sulphur is melted on a microscopic slide, under a cover, and the slide is arranged so that temperature can be easily regulated[2] monoclinic crystals are produced, but as temperature falls these change into rhombic forms; it is possible to regulate the temperature so that definite amounts of each form exist simultaneously, but on the slightest change of temperature the rhombic crystals grow at the expense of the monoclinic, or *vice versa*.

The behaviour of dibromopropionic acid when heated

[1] The term physical isomerism seems to have been first used by L. Carius, *Annalen*, **126.** 214 (see also *do.* **130.** 237).

[2] Lehmann describes an apparatus for this purpose (*loc. cit.* pp. 102–3).

illustrates the nature of the changes which characterise substances belonging to Lehmann's second class of physical isomerides. This substance crystallises in rhombic forms which melt at (about) 64°; if the molten mass is heated a few degrees above this point the same rhombic crystals are again produced on cooling; but if the molten substance is heated many degrees above 64° and is then allowed to cool, small flat nearly right-angled tables are obtained which melt at (about) 51°. If the less stable form melting at 51° is slowly heated growth of the other and more stable crystals is noticed under the microscope; the growth at first is rapid, then slower, but before the change has gone far the melting point of the less stable crystals is reached and the whole mass becomes liquid. If the more stable form is melted, heated some degrees above 64°, and is then brought into contact with crystals of both forms, growth of each modification proceeds until the crystals touch, after which the more stable (higher melting) crystals grow into the others until the latter are completely changed into the stabler forms.

Another instance of Lehmann's second class is furnished by paranitrophenol. This compound crystallises from hot aqueous solutions in monoclinic crystals, and from cold aqueous (or alcoholic) solutions in crystals belonging to the same system but differing in form and melting point from the others. By fusing either form and allowing the molten mass to cool, only the less stable (lower melting) crystals are produced; but if a little of the substance is melted on a microscopic slide, and a crystal of the second (stabler) form is placed in contact with the edge of the solidified mass, and heating is then again commenced, crystals of the stabler form begin to grow at the expense of the other crystals, at first rapidly and then more slowly, until both forms melt, the less stable at a lower temperature than the more stable.

Substances of which ammonium nitrate is the type appear to be less profoundly modified by the action of heat than substances belonging to the class represented by dibromopropionic acid. Substances belonging to the first of these classes shew analogies with many of the molecular com-

pounds discussed in the present section; compare e.g. the action of heat on hydrated cobalt salts, with the action of the same agent on dibromopropionic acid or on paranitrophenol. Moreover the course of the change brought about by the action of heat on these bodies shews some analogies with the processes of gaseous dissociation. For these reasons Lehmann has summarised the phenomena characteristic of bodies of this class under the term *physical polymerism*, and the phenomena characteristic of bodies of the other class under the term *physical metamerism*. The former term implies that the physically different forms exhibited by a substance belonging to this class are to be regarded as associated with the existence of physical molecules, each formed by the grouping together of a different number of chemical molecules (as defined in Chap. I. par. 13, p. 26). The term physical metamerism on the other hand implies that the physical molecule of each different form of a substance belonging to this class is composed of the same number of chemical molecules, but that the arrangement of these is different in each case.

Lehmann's classification is certainly based on no fanciful analogies. Polymerism and metamerism are well marked phenomena among gaseous molecules; and the hypothesis of the existence of groups of molecules characterised by definite properties, but each of which groups is readily decomposed by heat, appears to be as simple as any other molecular and atomic hypothesis that can be proposed to explain the observed facts. But the analogy between the reactions of gaseous molecules and the changes undergone by solid and liquid substances may be pushed too far; we ought to recognise how small and inexact our knowledge is of the molecular actions of the latter classes of bodies. Qualification of the terms molecule, polymerism, and metamerism, by the adjective physical, widens the meanings of these terms by making them applicable to a larger class of phenomena, but at the same time it makes the application less precise[1].

[1] Lehmann considers in considerable detail the phenomena attending the change of one form of a substance into another; he divides the changes into

The researches of Graham on colloidal and crystalloidal substances are of the utmost importance as regards the hypothesis we are considering; to understand the importance of Graham's work it is necessary carefully to study the whole series of papers on liquid diffusion which he communicated to the Royal Society[1]. Graham[2] found that certain substances when in solution pass very quickly through wet

groups, according as both forms are solid, or one solid and one liquid, &c. As the subject is important I give a brief resumé of some of Lehmann's results in this note, but the original paper ought to be studied by all who are interested in the subject.

A. Change of one, more complex, solid form of isomeride to another, less complex, solid form, attended with disappearance of heat; physical molecules of both kinds are present simultaneously, but at a certain temperature change will occur. If one modification is heated alone, the normal temperature of change may be largely exceeded without a complete change to the second modification, but at such a high temperature contact with the second modification may determine sudden and complete change.

B. Change of solid form to liquid form, occurring with disappearance of heat at a definite temperature dependent on the pressure; the change will not be complete, as molecules of both kinds will exist together. If the specific gravity of the solid form is greater than that of the liquid form, then on heating past the melting point there will be rapid expansion as the physical molecules of the solid form are separated into those of the liquid; this will be followed by a slower regular expansion. If the specific gravity of the solid is less than that of the liquid, expansion will be small, or even negative, until a point of maximum density is reached, after which expansion will proceed at the normal rate.

In some cases a solid form is changed, by the action of heat, into a liquid form, which, at a higher temperature, is again changed into a second solid form; e.g. when selenion is heated till it becomes viscous and is kept at this temperature for some time it changes into a crystalline form. So in the change of yellow to red phosphorus by the action of heat; in this case it is probable that the molecules which form the liquid phosphorus are kept apart for some time, by the energy added as heat acting against cohesion, and so are allowed to re-arrange themselves in loose groups.

C. Change of liquid to solid, modification is complex; a few crystals form and determine the crystallisation of the whole mass; in some cases the liquid, especially if viscous, may be cooled below the temperature at which crystallisation normally begins, and may then pass into an amorphous solid form.

[1] Happily Graham's papers have been collected and published by the late Drs Angus Smith and James Young.

[2] *Phil. Trans.* for 1861. 185.

animal or vegetable membranes, while others are scarcely, if at all, diffusible through the same septa. The more diffusible bodies Graham called *crystalloids*, the less diffusible he called *colloids*. Colloidal substances e.g. albumen, hydrated alumina or stannic oxide, &c. are very inert chemically considered, but at the same time they are affected by the smallest changes in their environment, e.g. slight alterations of temperature cause marked changes in their properties; they are easily permeated by diffusible crystalloidal substances, to which, says Graham, they give up water, 'molecule by molecule'; "their existence is a continual metastasis." Ice, which under ordinary conditions of formation is crystalloidal, when formed in contact with water at 0° possesses those properties which characterise colloids: "Can any facts," says Graham, "more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?"

The marked differences between the properties of colloids and crystalloids are associated, in the opinion of Graham, with differences of molecular structure. He regarded the reacting unit of a colloid as probably formed by the coalescence of a large number of molecules; hence the marked instability, and at the same time the chemical inertness, which characterise the class of colloidal substances.

Hittorf[1] has shewn that when a concentrated aqueous solution of cadmium iodide is electrolysed, more iodine is separated at the positive pole than could be the case were the composition of the body undergoing electrolysis represented by the formula CdI_2. Hittorf suggests that the solution in question contains molecular groups of the composition Cd_3I_6, and that these are separated by the electric current into Cd and Cd_2I_6.

Some interesting observations have been made by van Bemmelen[2] on the absorption of acids and salts by hydrated oxides. When the hydrated dioxide of tin, silicon, or manganese, is shaken with an aqueous solution of a mineral acid,

[1] *Pogg. Ann.* **106.** 337, 513.

[2] *J. für prakt. Chemie* [2] **23.** 324; see also **26.** 227.

or of a salt such as potassium sulphate or sodium chloride, a definite quantity of the acid or salt is absorbed by the oxide; the amount absorbed is dependent on the nature of the hydrated oxide and that of the acid or salt, on the relative masses of oxide, acid, or salt, and on the amount of water present. The substances which exhibit this absorptive action are characterised by the readiness with which the change from hydrated to dehydrated oxide and *vice versa* occurs; thus the hydrates $SnO_2.xH_2O$, $SiO_2.xH_2O$, and $MnO_2.xH_2O$, part with water when placed over sulphuric acid, and the oxides absorb water when placed in a moist atmosphere. The amount of water absorbed by any one of the dehydrated oxides depends in part on its physical state; if the oxide is strongly heated it absorbs less water than if dried over sulphuric acid *in vacuo*[1]; the 'looser' the aggregation of the particles, the greater the quantity of water absorbed by the oxide.

In some cases, e.g. the hydrate $SiO_2.4H_2O$, the amount of acid or salt withdrawn from an aqueous solution was found to be equivalent to the amount of water removed from the hydrated oxide by drying it over sulphuric acid *in vacuo*. In other cases, e.g. $SnO_2.3H_2O$, $3SnO_2.7H_2O$, $2SnO_2.3H_2O$, $2MnO_2.5H_2O$, $MnO_2.2H_2O$, the amount of acid or salt withdrawn by the hydrate from solution was greater than the quantity equivalent to the loosely-held water of the hydrate. As the amount of water which some of these oxides absorb from a moist atmosphere was found to vary with the physical aggregation of the oxide, so the amount of salt or acid absorbed by these hydrated oxides was found to shew analogous variations: this is specially worked out in detail by van Bemmelen for the action of metastannic acid on aqueous solutions of HCl, H_2SO_4, KCl, K_2SO_4, and KNO_3.

If these actions are to be classed as purely physical, we

[1] Graham [*Brit. Ass. Reports* for 1834. 579] called attention to the difference between strongly heated calcium sulphate and the same substance 'in a state for setting:' but, says Graham, "this is a department of corpuscular philosophy which stands much in want of further development."

should not expect to find a definite limit to the amount of salt or acid absorbed by each hydrated oxide: but van Bemmelen's researches shew that the process tends to the establishment of an equilibrium between acid (or salt), water, and hydrated oxide; that this condition is attained slowly; and that it is affected by the relative masses of the reacting substances in the original system. Thus less acid (or salt) is absorbed from a very dilute than from a more concentrated solution, but the amount of acid or salt absorbed increases much more slowly than the increase in the concentration of the solution of acid or salt. The final equilibrium is not disturbed by the addition of a solution of acid or salt of the same degree of concentration as that surrounding the hydrated dioxide, but if the added solution is relatively richer in acid or salt than the liquid surrounding the dioxide, then the equilibrium is overthrown and the absorption of acid or salt begins again and proceeds till a second condition of equilibrium is established.

Some hydrated oxides not only absorb, but also partially decompose, salts; for instance, when the hydrate $2MnO_2 . 5H_2O$ is shaken with an aqueous solution of K_2SO_4, it absorbs a definite amount of the latter and at the same time separates part of it into KOH and H_2SO_4. Again, one salt is sometimes absorbed in preference to another; thus if $MnO_2 . xH_2O$ is shaken in contact with H_2SO_4, washed, and again shaken in contact with an aqueous solution of K_2SO_4, a portion of the H_2SO_4 which had been absorbed by the hydrated oxide is replaced by K_2SO_4; again, if $SiO_2 . 4H_2O$ is allowed to absorb Al_2Cl_6, is then washed till the washings no longer contain chlorine, and is finally shaken with an aqueous solution of KCl, it is found that some of the KCl has been absorbed and some of the Al_2Cl_6 has passed into the surrounding liquid.

These substances investigated by van Bemmelen, whether they be called compounds or loose combinations of salt (or acid) and hydrated oxide, can scarcely be regarded as composed of molecules each built up of atoms of metal, oxygen, hydrogen, and the elements of acid or salt, but rather as

composed of molecular groups each constituted by the coalescence of molecules of acid (or salt), water, and metallic oxide, the number of such molecules in each group or reacting weight being variable within certain limits. The properties of many of the salts of the weaker acids—e.g. carbonic, boric, and sulphurous—are regarded by van Bemmelen as explicable in terms of the general hypothesis of molecular compounds; he would regard the reacting weights of these salts as molecular groups, more stable than those which compose the peculiar class of bodies just described, but less stable than the true chemical molecule.

102 In his second paper (*loc. cit.*) van Bemmelen has more particularly studied hydrated beryllium oxide $BeO \,.\, xH_2O$. He shews that two varieties of this oxide exist, viz. a gelatinous and a granular form; that the former alone exhibits the property of absorbing acids and salts from aqueous solutions; and also that the action of heat on the two hydrates is different. After heating to 220° the granular hydrate had lost 0·5 H_2O, and was now much altered in properties. This fact—and others analogous to this are known—seems to shew that by the application of energy from without the system the parts of a loose molecular group may be caused to react so as to bring about a marked change in the properties of the body composed of such groups. In other words, the comparative readiness with which definite chemical changes may be started among the constituents of a molecular group appears to shew that although these constituents are held together but loosely, nevertheless they are not merely mixed. Thus, $As(CH_3)_2Cl$ combines with Cl_2 to form $As(CH_3)_2Cl_3$; when this compound is heated it yields $As(CH_3)Cl_2 + CH_3Cl$; then $As(CH_3)Cl_2$ readily takes up Cl_2 to form $As(CH_3)Cl_4$, which on being heated separates into $AsCl_3 + CH_3Cl$. Now on account of their properties some of these compounds must be classed as molecular, yet under the influence of heat the parts of the molecular groups mutually act and react in a way analogous to, if not identical with, that characteristic of chemical change. But such phenomena as these are exactly what might be expected from the hypothesis of molecular

compounds; if these bodies are formed of groups of molecules we should expect that reactions between these groups would, in many cases, easily occur and result in the production of new, less complex, groups, or, it may be, new molecules. That a substance is found to behave in a definite manner under the influence of this or that reagent cannot be regarded as sufficient evidence for classing it among atomic rather than molecular compounds. Thus the observation recorded by R. W. Atkinson[1] regarding the identity of the salts produced by mixing (1) $SbCl_3$ and 3KBr, and (2) $SbBr_3$ and 3KCl, cannot be regarded as proving that the product of these actions is built up of molecules represented by the formula $n SbCl_3Br_3K_3$, the properties of which are conditioned only by the mutual interactions of the atoms Sb, Cl, Br, and K. Regarded however as a contribution towards solving the questions suggested by the term molecular compounds, the observations made by Atkinson are of interest, as shewing how possible it is to obtain substances which behave in some respects as molecular, and in other respects as atomic, compounds.

It cannot be too strongly insisted on that no hypothesis has been proposed regarding molecular compounds which furnishes us with a definition of the class 'molecular', or puts into our hands an instrument for determining whether a given compound belongs to this class or to the class of atomic compounds. What the hypothesis does is to negative the notion that the properties of all compounds are to be explained by the conception of actions and reactions between atoms which together constitute *a* molecule, and to open a path for future research by insisting on the complexity of chemical phenomena, and the folly of attempting to explain all in terms of a favourite theory.

103 But the consideration of molecular compounds leads to the discussion of questions which properly belong to chemical kinetics: we cannot separate these bodies from their environment; they are members of a system which is continually undergoing change and the comparative stability of which is

[1] *C. S. Journal*, **Trans.** for **1883.** 289.

the result of never ceasing action and reaction between its parts. Chemistry is not a collection of facts regarding the crystalline forms, melting points, boiling points, specific gravities, &c., &c., of elements or compounds; it is rather the orderly and regulated study of the changes which these kinds of matter undergo and which result in more or less profound modifications in the properties of the changing bodies.

A great advance has certainly been made by replacing the notion of a molecule as an undefined quantity of matter constructed of groups of atoms more or less loosely and vaguely arranged, by that conception which regards the molecule as a definite and definable quantity of matter, built up of atoms arranged in an orderly manner, and exhibiting functions dependent on the nature, arrangement, and mutual interactions, of these atoms. Among the functions of the molecule we must, I think, place the power of combining, under proper conditions, with other molecules to form more or less complex groups, less stable than the molecules of a gas, and not so sharply defined from other groups as the molecule of one compound is from that of another. Although the explanation of the properties of molecular compounds is not to be brought wholly within the scope of the hypothesis of valency, nevertheless if we regard the formation (or non-formation), and the relative stabilities, of such compounds, as functions of all the molecules concerned in their synthesis, we can see that the valencies of the elementary atoms must be important factors in determining the production of molecular compounds[1].

Although we can put our conception of the molecule into definite terms, yet the advance of knowledge regarding the properties of molecules warns us against attempting to define the molecule too rigidly. The molecular and atomic theory

[1] In connexion with this subject compare the presidential address to Section B of the British Association at Aberdeen [1885]. In this address Armstrong suggests that the "formation of so-called molecular compounds is mainly due to peculiarities inherent more especially in the negative elements—i.e. the non-metals and metalloids, and not in the positive elements—the metals." (See *Nature*, **32**. 470.)

presents the chemist with the conception of the gaseous molecule; by applying this to chemical facts he arrives at the conception of the atom, a conception much more definite than that of the molecule; he then rebuilds the molecule by putting together the atoms of which it is composed; but he does not always find the molecule thus re-constructed to be the same as the molecule he received from the physicist. The physical definition of the molecule applies in strictness only to perfect gases; but the chemist has to deal with imperfect gases, and also with liquids and solids.

Notwithstanding these difficulties fair progress has been made in the chemical investigation of the molecule. We have endeavoured to trace this progress, as it appears in the methods for finding the relative weights of atoms and molecules; in the distinction between the properties of atoms and the properties of molecules formed by the union of atoms; in the chemical conception of the molecule as a structure of atoms or groups of atoms, the functions of which structure are dependent on the nature, number, and arrangement, of its parts; in the development of this conception in the hypotheses of valency and isomerism; and in the recognition, forced on the chemist by the study of liquid and solid compounds, that although the properties of the molecule are conditioned by the properties of its parts, it has also an individual existence and is capable of interacting as a whole with other molecules.

CHAPTER III.

THE PERIODIC LAW.

IN the preceding Chapter we have endeavoured to trace the development of the conceptions of the atom and the molecule. The properties of compounds are regarded in chemistry as the properties of the molecules of these compounds, and these again as conditioned by the properties of the atoms which compose the molecules. Can we then trace a definite connexion between the properties of the atoms of the elements and the properties of the compounds formed by the union of these elements? A measurable property of the atoms is their relative masses. Is there any definite and definable relation between the atomic weights and the properties of the elements, and between the atomic weights of the elements and the properties of their compounds?

104 Attempts have been made from time to time throughout the preceding 50 or 60 years to trace connexions between the atomic weights and the general properties of groups of elements.

Soon after the appearance of Dalton's *New System of Chemical Philosophy*, an hypothesis was promulgated by Prout to the effect that the atomic weights of the elements are whole multiples of that of hydrogen; but the researches of Berzelius, Marignac, and Stas, shewed that this hypothesis was untenable. A modification of Prout's hypothesis was made by Dumas which appears to have a fair probability in its favour.

Gmelin, Dumas, Gladstone, Cooke, Kremers, Pettenkofer, Odling, and especially Newlands[1], who was among the earliest workers in this field, have drawn attention to points of connexion between the properties and the atomic weights of elements. In 1864 Newlands arranged a number of elements in order of their atomic weights, and shewed that these elements were divisible into groups of seven, and that the properties of one group were to some extent repeated in the next group. "The eighth element," said Newlands, "starting from a given element is a kind of repetition of the first, like the eighth note of an octave in music." In subsequent papers Newlands insisted on the general applicability of what he called the 'law of octaves.'

It is however especially to Mendelejeff[2] that we owe the systematic correlation of the atomic weights with the chemical and physical properties of the elements, and the properties of their compounds.

Lothar Meyer[3] has also made important contributions to the same subject, and in his *Modernen Theorien* he has gathered together the more important facts which have been established concerning the relation in question.

105 We may confidently say that a large probability has been established in favour of the hypothesis that the properties of the elements, and of the compounds of each element, are periodic functions of the atomic weights of the elements. Lothar Meyer puts the general statement of the "*Periodic Law*" in this form[4]: "*If the elements are arranged in order of increasing atomic weights, the properties of these elements vary from member to member of the series, but return more or less nearly to the same values at certain fixed points in the series.*"

Let the elements be arranged in the order of their atomic weights; let this list of elements be (broadly) divided into

[1] *Chem. News*, **7.** 70; and **10.** 59, 94; **12.** 83, 94; **13.** 113, &c. Newlands' contributions to this subject have been gathered together and published in a small volume entitled 'On the Discovery of the Periodic Law' [Spon, 1884].

[2] *Annalen*, Suppl. Bd. **8.** 133. See also *Chem. News*, Vols. **40** and **41.**

[3] *Annalen*, Suppl. Bd. **5.** 129, and **7.** 354 &c.

[4] *Die modernen Theorien*, 4th Ed. p. 136; English Ed. p. 117.

series of sevens; let the members of the second series be placed under those of the first, those of the third under those of the second, and so on: then the elements contained in a vertical column are said to form a *group*, while those in a horizontal column form a *series*.

In this arrangement of the elements each *group* corresponds, for the most part, with a natural family. This is more clearly shewn, and the relations between the atomic weights and the properties of the elements are more distinctly developed, if certain gaps are supposed to exist in the list of elements. The table[1] on p. 225 exhibits the arrangement of the elements in groups and series.

106 Before giving a detailed explanation of this table let us meanwhile gather together some of the best established generalisations concerning the periodic connexion of properties and atomic weights of the elements.

A phenomenon is said to be periodic when, if the conditioning circumstances vary continuously, it repeats itself at definite intervals. The variable under consideration is the atomic weight, the phenomenon to be examined is the nature of each chemical element and its compounds. Although it is not as yet possible to state quantitatively the nature of the periodic function which connects the atomic weights with the general properties of the elements, it may nevertheless be established that the function in question is periodic. For this purpose it will be necessary to break up the phenomenon 'nature of the chemical element and its compounds' and to endeavour to shew that the malleability, ductility, atomic volume, power of forming oxides (or chlorides) of definite composition, position in electrical series, &c, of the elements do vary periodically with variations in the atomic weights of these elements[2].

107 *Atomic volume.* The quotient obtained by dividing the

[1] Taken from a paper by B. Brauner in *C. S. Journal* **Trans.** for **1882.** 78: atomic weights are stated in round numbers.

[2] For greater details on this point see L. Meyer, *Die modernen Theorien*, 4th Ed. pp. 139—173 (English Ed. pp. 117—150), of which this and the few following pages must be regarded as an abstract.

GROUPS

	I	II	III	IV	V	VI	VII	VIII
Series	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	$[R_2O_8]$
1	H=1	—	—	—	—	—	—	
2	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	——
3	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5	
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Ni=58·6 Co=59 (Cu=63)
5	Cu=63	Zn=65	Ga=69	Ge=72	As=75	Se=79	Br=80	
6	Rb=85	Sr=87	Y=89	Zr=90	Nb=94	Mo=96	(? 100)	Rh=104 Ru=104·5 Pd=106 (Ag=108)
7	Ag=108	Cd=112	In=114	Sn=118	Sb=120	Te=125	I=127	
8	Cs=133	Ba=137	La=139	Ce=140	Di=144	? 149	? 150	? 152—156 4 Elements?
9	← ? 4 Elements 156 to 162? →				Er=166	? 167	? 169	
10	? 170	? 172	Yb=173	? 178	Ta=182	W=184	? 190	Ir=192·5 Os=193 (?) Pt=194 (Au=197)
11	Au=197	Hg=200	Tl=204	Pb=207	Bi=208	← ? 2 Elements 212 to 220? →		
12	← ? 3 Elements 220 to 230? →			Th=232	? 237	U=240	? 245	

atomic weight of an element by its specific gravity in the solid form is called the atomic volume of that element. This quotient expresses the volume, in cubic centimetres, occupied by an amount of the solid element, in grams, proportional to the atomic weight of that element.

Arranging the elements in order of increasing atomic weights it is found that the value for atomic volume reaches its first maximum at lithium, that it then diminishes through beryllium, boron, &c. and again increases through carbon, &c. reaching a second maximum at sodium; the other maxima occur at potassium, rubidium, and cæsium.

The periodic nature of the connexion between atomic volumes and atomic weights becomes very apparent when the magnitudes of those quantities are graphically represented as is done on the plate facing this page[1].

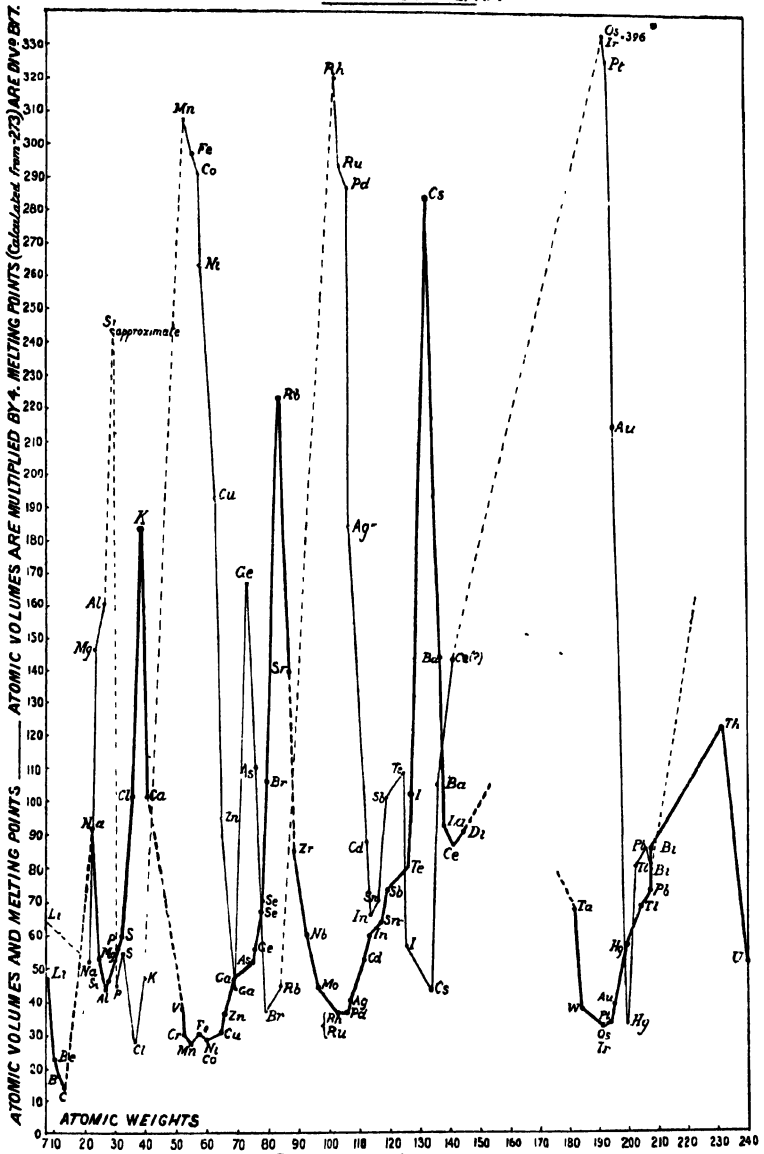
The maximum points on the curve are seen to be occupied by metals of low specific gravity, while the minimum points are occupied by heavy metals.

The position of an element on the curve, with reference to the preceding and succeeding elements, appears to be intimately connected with the properties of the element in question. Thus phosphorus and magnesium on the one hand, and calcium and chlorine on the other, have nearly equal atomic volumes; phosphorus and chlorine are followed by elements the atomic volumes of which are larger than their own (i.e. are situated on ascending portions of the curve), whereas magnesium and calcium are followed by elements having atomic volumes smaller than their own (i.e. are situated on descending portions of the curve).

The ductile metals are placed at or near to maximum and minimum points on the curve; those of low specific gravity occurring at, and immediately after, maximum points, and those of high specific gravity at, and immediately after, minimum points. The brittle heavy metals occur in sections 4, 5, and 7 immediately before the minimum points[2].

[1] Only those elements the specific gravities of which in the solid state have been directly determined are included in the curve; want of data is indicated by a broken line.

[2] A section of the curve means the part situated between two maxima; section



* THIS POINT SHOULD BE PLACED 66 DIVISIONS HIGHER

The elements on the descending parts of sections 2 and 3 of the atomic volume curve are electropositive and form basic hydroxides; those on the ascending portions of the same sections are electronegative and form acid hydroxides. Each of sections 4 and 5 contains four groups of elements arranged in accordance with their negative or positive character. Electropositive elements occur on the first portions of the descending curve in each of these sections (K, Ca; Rb, Sr); these are followed by a group of comparatively negative elements (V, Cr, Mn; Zr, Nb, Mo, Rh, Ru); these again by positive elements (Fe, Ni, Co, Cu, Zn, Ga; Pd, Ag, Cd, In); and after these comes a group of negative and acid-forming elements situated on the ascending part of the curve in each section (As, Se, Br; [Sn], Sb, Te, I). Sections 6 and 7 are too incomplete to allow of definite conclusions being drawn regarding the positive or negative character of the elements situated thereon.

108 *Fusibility.* The melting points of several elements have been determined by various observers[1]; of late especially by Carnelley[2], who has shewn that the fusibility of the elements varies periodically with their atomic weights. The thin line[3] curve on the plate on p. 227 graphically exhibits this connexion.

A connexion may be traced between the positions of an element on the curve of atomic volumes and on that of

1 includes hydrogen only, section 2 extends from lithium to sodium, section 3 from sodium to potassium, and so on. There are probably several unknown elements with atomic weights greater than that of didymium and smaller than that of tantalum; the curve, if complete, would probably be marked by a sixth maximum point between cæsium and thorium, this part of the curve is therefore said to comprise two sections (6 and 7).

[1] See *Constants of Nature*, Part I. and Supplement to do. Also L. Meyer, *loc. cit.* pp. 145, 6. (English Ed. pp. 129, 130.)

[2] *Phil. Mag.* [5] 8. 315 *et seq.*: this paper contains a good *resumé* of the *periodic law*. All well established data concerning melting points are collected in Carnelley's *Tables of melting and boiling points* (1885—87).

[3] The values of the melting points used in preparing this curve are taken for the most part from Carnelley's paper. The data are meagre, hence many gaps occur in the curve (indicated by the broken lines); many of the numbers, especially those for elements at and near to maximum points, must be regarded as only rough approximations to the true values.

fusibility; as a rule, only those elements which are situated on ascending portions of the former curve, are easily fusible. Generalisations have also been made concerning the connexions between the atomic weights of groups of elements and the melting points of these elements and some of their analogous compounds[1]. Thus the melting points of the haloid salts of the metals in Group II. (see table on p. 225) are considerably higher than those of the corresponding salts of the metals of Group III.:—

e.g.	$MgCl_2$	$MgBr_2$;	$CaCl_2$	$CaBr_2$	CaI_2;	$SrCl_2$	$SrBr_2$	SrI_2;
M.P.	708	695 ;	719	676	631 ;	825	630	507 ;
but	Al_2Cl_6	Al_2Br_6	Al_2I_6.					
M.P.	very low	90	185.					

Carnelley[2] found the melting point of beryllium chloride to lie between 585 and 617°, hence he concluded that beryllium belongs to Group II. and that the formula of its chloride is $BeCl_2$ (Be = 9·1), and not $BeCl_3$ or Be_2Cl_6 (Be = 13·15)[3]. The data, so far as obtained, concerning the boiling points, crystalline forms, and expansion by heat, of the elements, indicate that the connexion between these constants and the atomic weights of the elements is of a periodic character[4].

Hartley[5] has shewn that the ultra-violet spectra of elements **109** of the same group shew fairly marked analogies as regards general character; the spectra hitherto obtained do not permit him to affirm, or deny, the existence of numerical relations between the different groups of lines, sufficient to establish a definite periodic connexion between the atomic weights of the elements and the wave-lengths of the lines in the elementary spectra.

That there exists a well-marked connexion, of periodic character, between the atomic weights, and the heats of combination of the elements with chlorine, bromine, and iodine,

[1] See Williams and Carnelley, *C. S. Journal* **Trans.** for **1879.** 563: **1880.** 125.

[2] *Proc. R. S.* **29.** 190. See also *Ibid. Ber.* **17.** 1357.

[3] See forward, par. 111.

[4] For details see L. Meyer, *loc. cit.* pp. 150—152. (English Ed. pp. 130—152.)

[5] *C. S. Journal* **Trans.** for **1882.** 84: permanent photographs of the ultra-violet spectra of various elements are given in this paper. See also *ibid.* **Trans.** for **1883.** 390: and *Proc. R. S.* **36.** 462.

appears to have been first pointed out by Carnelley[1]. A little later Laurie[2] independently drew attention to this subject and exhibited the relation in question by means of a curve.

110 Having thus established the existence of a connexion, distinctly of a periodic character, between the atomic weights and the general nature of the elements, we may proceed to consider the more important applications of the periodic law. This consideration will also serve more fully to elucidate the meaning of the law.

The law has been applied to predict the properties of unknown elements. In the nomenclature of unknown elements Mendelejeff employs as prefixes the Sanskrit numerals *eka*, *dui*, *tri*, &c. Thus if no elements were known with atomic weights equal to about 48 and 90, two gaps would occur in Group IV. (see table, p. 225); from a general inspection of the table it would be seen that these gaps ought to be filled by elements bearing a more or less close analogy to carbon; the hypothetical elements would be called *eka-carbon* and *dui-carbon* respectively. At the time of Mendelejeff's earliest publication there was no element known which could be placed opposite the atomic weight 69 in Group III., nor any which could be placed opposite the atomic weight 44 in the same group. The former of these hypothetical elements Mendelejeff named *eka-aluminium*, the latter he called *eka-boron*. The properties of *eka-aluminium* were predicted by Mendelejeff from considering the position of the element in the same group as, and interposed between, aluminium and indium, and in the same series as, and following after, zinc. In 1875 a new metal was discovered by L. de Boisbaudran. The following table contains, in parallel columns, the leading properties of this metal, and those enumerated by Mendelejeff as characteristic of *eka-aluminium*: the hypothetical metal of Mendelejeff and the *gallium* of de Boisbaudran are one and the same element.

[1] *Proc. R. S.* **29**. 190.

[2] *Phil. Mag.* (5) **16**. 42. For data shewing that some of the physical properties of compounds, *e.g.* melting and boiling points, vary periodically with variations in the atomic weights of the constituent elements, see Carnelley, *Phil. Mag.* [5] **8**. 368—70.

Eka-aluminium.	*Gallium.*
Atomic weight about 69.	Atomic weight = 69.
Readily obtained by reduction.	Readily obtained by electrolysing alkaline solutions.
Melting point low. Sp. gr. = 5·9.	M.P. = 30·15°. Sp. gr. = 5·93.
Not acted on by air.	Non-volatile, and but superficially oxidised in air at bright red heat.
Will decompose water at a red heat.	Decomposes water at high temperatures. Soluble in hot hydrochloric acid, scarcely attacked by cold nitric acid; soluble in caustic potash.
Slowly attacked by acids or alkalis.	Forms a well-defined alum.
Will form a potassium alum more soluble, but less easily crystallisable, than the corresponding aluminium salt.	Oxide = Ga_2O_3. Chloride = Ga_2Cl_6.
Oxide = El_2O_3. Chloride = El_2Cl_6.	

Eka-boron belongs to Group III. the members of which group combine with oxygen to produce well-marked oxides having the composition R_2O_3. In its properties *eka-boron* ought to be related to aluminium as calcium is to magnesium, and as titanium is to silicon. The atomic weight of *eka-boron* must be about 43—46, inasmuch as it follows K (39) and Ca (40), and is followed by Ti (48) and V (51). Reasoning from these data, Mendelejeff[1] predicted certain properties as characteristic of *eka-boron* and its salts. Some of these are placed in parallel columns with a description of the properties of the metal *scandium*[2], discovered in 1879 by Nilson :—

Eka-boron.	*Scandium.*
Atomic weight about 44.	Atomic weight = 44.
Oxide Eb_2O_3 soluble in acids; sp. gr. about 3·5; analogous to but more basic than Al_2O_3; less basic than MgO; insoluble in alkalis.	Oxide Sc_2O_3; sp. gr. = 3·8; soluble in strong acids; analogous with but more decidedly basic than Al_2O_3; insoluble in alkalis.
Salts of Eb colourless, and yield gelatinous precipitates with KOH, K_2CO_3, Na_2HPO_4, &c.	Solutions of Sc salts colourless and yield gelatinous precipitates with KOH, K_2CO_3, and Na_2HPO_4.
Sulphate, $Eb_2.3SO_4$, will form a double salt with K_2SO_4, probably not isomorphous with the alums.	Sulphate, $Sc_2.3SO_4$, forms a double salt, not an alum, $Sc_23SO_4.3K_2SO_4$.
Chloride $EbCl_3$ or Eb_2Cl_6, sp. gr. about 2, less volatile than Al_2Cl_6.	

[1] See translation of Mendelejeff's paper in *Chem. News*, **41**. pp. 71—72.

[2] *Ber.* **14**. 1439. See also Cleve, *Ber.* **12**. 2264: and *Compt. rend.* **89**. 419, (abstract of latter paper in *C. S. Journal* for **1880**. 8, is useful).

There was a gap in Group IV. Series 5. *Eka-silicon* comes in the group which comprises Si, Sn, and Pb, and in the series including Ga and As. This hypothetical element ought also to shew analogies with other elements; thus,

Es : Ti :: Zn : Ca :: As : V.

From the position of *eka-silicon*[1] Mendelejeff concluded that it would be a grey metal, obtained by reducing the oxide by sodium, fusible with difficulty; it would decompose steam very slowly, would be scarcely acted on by acids, but easily by alkalis. The oxide, EsO_2, (sp. gr. about 4·7) would be obtainable by burning the metal in air, it would resemble TiO_2, but would be less basic than this oxide, although more basic than SiO_2; the hydroxide would be soluble in acids, but the solution would be easily decomposed yielding an insoluble metahydroxide. The oxide would yield a series of double fluorides M_2EsF_6 (M = alkali metal) isomorphous with the corresponding salts of Si, Ti, Zn, and Sn. The fluoride EsF_4 would not be gaseous; the chloride $EsCl_4$ would be a volatile liquid boiling at about 100°. *Eka-silicon* would form volatile organo-compounds.

The discovery and study of *germanium* by Winkler[2] have entirely confirmed Mendelejeff's prediction: *eka-silicon* and germanium are one and the same element.

111 The periodic law has also been successfully used as a guide in the comparative study of the properties of elements already known.

To which group of elements does beryllium belong? Is the formula of the oxide BeO or Be_2O_3, and of the chloride $BeCl_2$ or $BeCl_3$? Is the atomic weight of beryllium 9 or 13·5?

The arrangement of the elements in accordance with the periodic law seems to necessitate the placing of beryllium in Group II.; but Nilson and Pettersson, and also Humpidge, who had made a special study of this metal, were for some time strongly of opinion that beryllium should be classed with the

[1] See *Chem. News*, **41**. 83.

[2] *Ber.* **19**. 210; *J. für prakt. Chemie* [2], **34**. 177: *s.* also Krüss and Nilson, *Ber.* **20**. 1296: L. de Boisbaudran, *Compt. rend.* **102**. 1291; **103**. 452: Kobb, *Wied. Ann.* **29**. 670: also L. Meyer, *Ber.* **20**. 497.

elements which form oxides of the composition R_2O_3. The atomic weight of beryllium $= n \cdot 9{\cdot}1$: the data regarding the specific heat of this metal have been presented in Chapter I. par. 28, and it has there been shewn that, so far as specific heat data are concerned, the value of n is most probably 1.

Carnelley's determination of the melting-point of beryllium chloride (see *ante*, par. 108) points to the beginning of Group II. as the proper position for beryllium, and hence to the number 9·1 as the atomic weight of this metal.

The general chemical characters of beryllium salts are summed up in the three statements[1] (Be = 9·1);

(1) Li : Be = Be : B
(2) Li : Na = Be : Mg = B : Al
(3) Li : Mg = Be : Al = B : Si.

From these considerations we may conclude that there is a large probability in favour of the value 9·1 for the atomic weight of beryllium. This conclusion is supported by Hartley's observations on the spectrum of beryllium and his comparison of that spectrum with those of metals in Groups II. and III.[2]

Nilson and Pettersson[3] have succeeded in gasifying beryllium chloride; and Humpidge[4] has gasified beryllium chloride and bromide. The determinations of the vapour densities of these compounds shew that the formulæ $BeCl_2$ and $BeBr_2$ (Be = 9·1) really represent their molecular weights.

There can be no doubt that the atomic weight of beryllium is 9·1, and that this metal is to be placed in the same group as magnesium, calcium, zinc, strontium &c., all of which form oxides having the composition RO and chlorides having the composition RCl_2.

In the table on p. 225 tellurium and iodine are placed in Series 7. The atomic weight of iodine was for many years supposed to be less than that of tellurium; nor was this result contradicted by the work of Wills[5]. Nevertheless the

[1] See Brauner, *Ber.* **14.** 53.

[2] *C. S. Journal* **Trans.** for **1883.** 316, 390: also *Proc. R. S.* **36.** 462.

[3] *Ber.* **17.** 987.

[4] *Proc. R. S.* **38.** 188.

[5] *C. S. Journal* **Trans.** for **1879.** 704.

analogies between sulphur, selenion, and tellurium, on the one hand, and chlorine, bromine, and iodine, on the other, are so marked that it would be absurd to place tellurium in the same class as chlorine and bromine, and to classify iodine with sulphur and selenion. But if the grouping indicated by the periodic law is to be adhered to the atomic weight of tellurium must be less than that of iodine. Brauner[1] in 1883 made an experimental criticism of the method by which the atomic weight of tellurium had been determined by Berzelius and also by Wills; he shewed that this method almost necessarily gives results which are too high. By converting tellurium into the very stable basic sulphate $Te_2O_4SO_3$, and also by syntheses of copper telluride Cu_2Te, Brauner obtained a series of values for the atomic weight of tellurium varying from 124·94 to 125·4 with a mean value of 125. We are therefore justified in placing tellurium in Group VI. and iodine in Group VII.

Uranium is another element the comparative study of the properties of which has been much advanced by the application of the periodic law. The atomic weight of this element has been established as $= n.120$. If $n = 1$, the three oxides of uranium must be formulated UO, U_2O_3, and U_3O_4; but there is no place for an element with this atomic weight and forming these oxides in the periodic arrangement. If however $n = 2$, then (U = 240) the oxides become UO_2, UO_3, and U_3O_8, and uranium finds a place in VI—12. The preceding members of Group VI. which belong to even series, viz. Cr, Mo, and W, yield oxides of the form RO_3 which are acid-forming. But a comparative study of the relations between the properties of oxides and the atomic weights of the elements in these oxides shews, that as the atomic weight of the elements in a group increases the acidic character of the higher oxides formed by these elements becomes less marked (e.g. CrO_3 is more markedly an acidic oxide than MoO_3 or WO_3). Now the highest oxide of uranium is an acid-forming oxide, but its acidic functions are less marked than those of CrO_3, MoO_3, and WO_3; salts corresponding to

[1] See abstract in *Ber.* **16**. 3055 (original is in Russian).

K_2CrO_4 and $K_2Cr_2O_7$ in which Cr is replaced by U are known. Uranic chloride, UCl_4 if U = 240, resembles $MoCl_4$ in being volatile and decomposable by water.

The atomic volume $\left(\text{i.e. } \frac{\text{atomic weight}}{\text{spec. gravity}}\right)$ of the four metals, Cr, Mo, W, U, increases as atomic weight increases, the values being Cr = 7·6; Mo = 11; W = 11; U = 12·5.

Hence the comparative study of compounds of uranium, which is suggested by the periodic law, justifies the adoption of the number 240 as the atomic weight of this metal.

Determinations of the densities of gaseous uranium bromide and chloride, and of the specific heat of pure uranium, have fully confirmed this value. (See *ante*, Chap. I. pars. 19 and 25; also p. 59.)

The facts enumerated in the preceding pages undoubtedly 112
establish the periodic law on a firm basis, and justify the employment of this law as one of the main guides in a general scheme of chemical classification[1].

The following arrangement of the elements (the table is taken, with a few alterations, from a paper by Mendelejeff in *Ber.* **13.** 1804) is in the opinion of Mendelejeff himself the best for clearly setting forth the general teaching of the periodic law. (See next page.)

Each group—except Group VIII.—contains members belonging to odd and to even series; or it may be said that each vertical column, or large series, is subdivided into two parts having seven elements in each. The entire column, comprising an odd and an even series, forms a 'long period'; the seven members in the even or in the odd series form a 'short period.' The members of Group VIII. form 'transition 'periods' from series 4 to 5, 6 to 7, (probably 8 to 9), and 10 to 11. Including the 'transition periods,' each complete 'long period' should contain 17 elements.

Because of its peculiar properties, and also because of the

[1] The system of classification of elements and compounds adopted in *Elementary Chemistry* (Pattison Muir and Slater) is based entirely on the periodic law.

It is very unfortunate that Mendelejeff's *Treatise on Chemistry* should not have been translated into one of the languages of Western Europe.

			SERIES					
Groups	1		2	4	6	8	10	12
I		Typical Elements	Li= 7	K=39	Rb=85	Cs=133	—	—
II			Be= 9	Ca=40	Sr=87	Ba=137	—	—
III			B=11	Sc=44	Yt=89	La=139	Yb=173	—
IV			C=12	Ti=48	Zr=90	Ce=140	—	Th=232
V			N=14	V=51	Nb=94	Di=144	Ta=182	—
VI			O=16	Cr=52	Mo=96	—	W=184	U=240
VII			F=19	Mn=55	—	—	—	—
VIII				Fe=56 Ni=58·6 Co=59 Cu=63	Rh=104 Ru=104·5 Pd=106 Ag=108	— — —	Ir=192·5 Os=193 Pt=194 Au=197	— — —
I	H=1		Na=23	Cu=63	Ag=108	—	Au=197	—
II			Mg=24	Zn=65	Cd=112	—	Hg=200	—
III			Al=27	Ga=69	In=114	—	Tl=204	—
IV			Si=28	Ge=72	Sn=118	—	Pb=207	—
V			P=31	As=75	Sb=120	Er=166	Bi=208	—
VI			S=32	Se=79	Te=125	—	—	—
VII			Cl=35·5	Br=80	I=127	—	—	—
	1		3	5	7	9	11	13
			SERIES					

anomalous relations between the values of its atomic weight and those of succeeding elements, hydrogen is regarded as the sole representative of Series 1, Group I.

Comparing series, we find closer analogies between corresponding members of odd or of even series, than between those of odd and even series: thus, comparing Series 4 and 6, and 4 and 7, potassium and rubidium are seen to be more closely related than potassium and silver; calcium and strontium, than calcium and cadmium; vanadium and niobium, than vanadium and antimony. Again, comparing Series 5 and 7, and also 5 and 6, it is seen that the relations between zinc and cadmium, or between arsenic and antimony, are closer than those between zinc and strontium, or arsenic and niobium.

Omitting the 'typical' elements (see p. 238) it may be said that, as a rule, the most markedly nonmetallic elements are placed in odd series. Also, that the passage from an even to an odd series is accompanied by a gradual change, but that from an odd to an even series by a more sudden change, in the properties of the elements; thus chromium and manganese resemble copper and zinc much more than selenion and bromine resemble rubidium and strontium, or than tellurium and iodine resemble cæsium and barium. It may also be laid down as a general proposition that volatile organo-metallic compounds are formed only by metals which occur in odd series; should such compounds be hereafter formed containing metals which belong to even series, the properties of the compounds in question will probably differ much from those of the volatile organo-metallic compounds at present known. (Mendelejeff.)

The elements which form the 'transition periods' (Group VIII.) possess many characteristic properties. They are very infusible, have small atomic volumes, and occlude oxygen and other gases; oxides of the form RO_4 are met with in this group only; the highest oxides are basic or only slightly acidic; these metals form stable alkaline double cyanides K_4RCy_6, K_3RCy_6, or K_2RCy_4, and also stable ammoniacal compounds[1].

[1] See Mendelejeff, *Chem. News*, **40**. 267.

The elements in Series 2 (from lithium to fluorine), and perhaps the first member of Series 3, viz. sodium[1], are grouped together by Mendelejeff as 'typical' elements. There is no 'transition period' coming between the even Series 2 and the odd Series 3 as there is between Series 4 and 5, 6 and 7, and 10 and 11. The mean difference between the atomic weights of two elements in successive even series and in the same group (e.g. between potassium and rubidium, or between rubidium and cæsium) is 45; but the mean difference between the atomic weight of an element in Series 4 and the corresponding element (i.e. the element in the same group) in Series 2 is 35; hence we should expect to find the relations of Series 2 to other series different from the general mutual relations exhibited by these other series. As the lower members of an homologous series of carbon compounds are sometimes characterised by the possession of properties which do not belong to the higher members, so the elements with atomic weights ranging from 1 to 19 (? 23) are characterised by special properties which to some extent mark them off from the other elements.

As the atomic weight increases in each group, the basic character of the higher oxides formed by the members of the group becomes more marked, and at the same time these oxides become more easily reduced. It is also to be noted that the composition of the more stable haloid and oxyhaloid salts (and in some cases of the more stable salts as a whole) tends, as atomic weight increases, to correspond in form with an oxide containing less oxygen than the highest oxide. These statements hold good more especially for those members of a group which occupy the odd series. Group V. presents a good example. Sb_2O_5 is more basic than P_2O_5, and Bi_2O_5 is marked by an almost complete absence of acidic properties. The highest oxides of this group belong to the form RX_5 (see p. 240); the stable haloid and oxyhaloid salts of phosphorus, vanadium, niobium (PF_5, $VOCl_3$, $NbCl_5$), belong to the same form, but the bismuth haloid and oxyhaloid salts

[1] Some chemists class all the members of Series 2 and 3 (Li to Cl inclusive) as 'typical' elements.

are $BiCl_3$, $BiBr_3$, BiOCl, BiOBr, &c., which belong to the form RX_3 corresponding to that of the lower oxide Bi_2O_3.

The first and last members of a series, and more especially of a 'long period,' present marked differences in their general chemical behaviour; thus lithium, potassium, and rubidium, the first members of the long periods 1, 2, and 3, are strongly positive, whereas the last members of the same periods, viz. chlorine, bromine, and iodine, are typically negative elements.

Each group may be divided into two sub-groups, one comprising the elements belonging to even series, the other those belonging to odd series. Calling these sub-groups families, we may say that the family-character is more marked than the group-character in Groups I. and VII., but that in Groups III., IV., and V. the group-character preponderates, and that both the general group-character and the special family-character are well seen in Groups II. and VI.

The compositions of the highest oxides, and of some of **113**
the other salts, appear to be periodic functions of the atomic weights of the elements. In dealing with this question it will be well to use the term 'formula weight' rather than molecular weight, as the molecular weights of very few oxides have been determined.

If R be used to represent the mass of an element expressed by its atomic weight; and if X represent the masses of F, Cl, Br, I, expressed by the respective atomic weights of these elements, or the masses of the groups (OH), (NO_3), (ClO_3), &c., expressed by these formulæ, or the masses of the elements or groups of elements expressed by *halves* of the formulæ, O, S, (SO_4), (CrO_4), &c.; then we may say that the oxides

$$R_2O,\ RO,\ R_2O_3,\ RO_2,\ R_2O_5,$$

belong respectively to the forms

$$RX,\ RX_2,\ RX_3,\ RX_4,\ RX_5:$$

also that the salts

R_2SO_4; $R.2NO_3$; $R.3NO_3$, ROCl, $R_2.3SO_4$, $RO.NO_3$; $ROCl_3$,

belong respectively to the forms

$$RX;\ RX_2;\ RX_3,\ RX_4,\ RX_5;\ RX_6.$$

In this way it becomes possible to give general expressions for the forms of the highest stable oxides characteristic of each group; thus,—

Group	I	II	III	IV	V	VI	VII	VIII
	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	(R_2O_7)	(R_2O_8)
or	RX	RX_2	RX_3	RX_4	RX_5	RX_6	(RX_7)	(RX_8)

This statement may be put thus; the number of oxygen atoms in the general expression for the composition of the highest stable oxide characteristic of each member of a series increases as the atomic weights of the members of the series increase.

Most of the stable salts (haloid salts, oxyhaloid salts, nitrates, sulphates, chromates, phosphates, &c.) characteristic of the members of each group belong to the same general form (RX, RX_2, &c.) as the oxides. But in every group well-marked salts are known which belong to higher forms than the oxide form: thus, some of the members of Group I. form peroxides (K_2O_2, K_2O_4, &c.); some of the elements in Group II. form salts (such as K_2BeF_4, K_2ZnCl_4, &c.) of the form RX_6; salts, such as $BOCl_3$, KBF_4, $KAlBr_4$, &c., belonging to the form RX_5, are found in Group III. The forms of the highest salts belonging to each group, and also the oxide forms, are given by Brauner[1]; thus,—

Group	I	II	III	IV	V	VI	VII	VIII
Salt forms	RX_7	RX_6	RX_5	RX_4	RX_3	RX_2	RX	$\begin{pmatrix}R_2X\\R_2O_8\end{pmatrix}$
Oxide forms	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	(R_2O_7)	

or thus,—

Salt forms	RX_7	RX_6	RX_5	RX_4	RX_3	RX_2	RX	$\begin{pmatrix}R_2X\\RX_8\end{pmatrix}$
Oxide forms	RX	RX_2	RX_3	RX_4	RX_5	RX_6	(RX_7)	

The statements generalised in these expressions can be accepted only as rough approximations to general truths. Oxides of the forms given in the table are sometimes less stable than oxides of other forms; e.g. Cu_2O is less stable than CuO, PbO_2 than PbO, &c.: the form chosen for the highest oxides is sometimes represented by very few if any actually occurring compounds; thus the form R_2O_7, characteristic of Group VII., finds its only representative in I_2O_7,

[1] *Sitzberichte der K. Akad. zu Wien, (math-naturwiss. classe)* **84.** 1165.

and the existence of this oxide cannot be regarded as proved. Again, salts belonging to the general expressions given as representing the highest forms are sometimes fairly characteristic of the group, in other cases it is only by a dexterous manipulation of formulæ that the existence of such salts can be discovered; thus a great many well-marked salts of the members of Group V. undoubtedly belong to the form RX_3, but it is only by having recourse to such a substance as $NaOH \cdot 3H_2O$ [$Na(OH)(OH)_3H_3$] that a salt of the form RX_7 can be found belonging to Group I.

Relations can be traced between the general forms of hydrogen and hydroxyl compounds, especially in Groups IV., V., VI., and VII.; thus,—

Group	IV	V	VI	VII
Hydrogen compounds	RH_4	RH_3	RH_2	RH
e.g.	SiH_4	PH_3	SH_2	ClH
Hydroxyl compounds	RH_4O_4	RH_3O_4	RH_2O_4	RHO_4
e.g.	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClO_3(OH)$

Dalton, and after him Berzelius, sought to elucidate the laws of atomic synthesis; they strove to find forms capable of expressing the maximum number of atoms of this or that element which could combine to form salts. But much had to be done before these limiting forms could be found: a firm standing ground appears to be now gained in the periodic law; to build a structure worthy of the foundation must be the work of the future.

114 The valency of the elementary atoms probably varies periodically with the relative weights of these atoms. Thus taking Series 2, and assuming that the atom of lithium is monovalent, it is seen that in this series the valency of the elementary atoms increases from one to four, and again diminishes from four to one:—

	Li	Be	B	C	N	O	F
Valency	1	2	3	4	3	2	1.

If the evidence were sufficient to warrant the assumption that the valency varies in every series in the same way as in Series 2, we should have in the periodic law a most important aid towards determining the valencies of all the elementary

atoms. But the evidence at present available concerning valency does not permit us to make this assumption. A probable value for the valency of an elementary atom may be deduced from the position of the element in the periodic arrangement, but this value must not be considered as final. It has indeed been sought to fix the valencies of elementary atoms from considerations drawn from the positions of these elements in the periodic classification; but this has been done only by attaching to the term 'valency' a much looser meaning than that which I have attempted to shew must be given if an accurate working hypothesis is to be developed. In applying the periodic law to determine the valencies of elementary atoms, the formulæ of oxides and of solid salts generally have been employed as data from which conclusions might be drawn. But if we define the valency of an atom as the maximum number of other atoms with which the given atom can directly interact in any molecule, then, to deduce valencies from a study of solid salts, we must assume, (1) that the formula of a solid salt certainly represents at least the proportion between the numbers of atoms of each element in the molecule; (2) that the atom, the valency of which is to be determined, acts on, and is acted on by, certain other atoms in the molecule—in some cases it may be action is assumed between all the atoms, in other cases only between some of the atoms, in the molecule; and (3) we must assume a value for the valency of each atom, other than the given atom, in the molecule. Thus to take an extreme case, hydrated chloroplatinic acid $H_2PtCl_6 . 6H_2O$ has been represented in this way

$$\overset{\text{VIII}}{H_2}Pt(\overset{\text{III}}{-Cl}=\overset{\text{IV}}{O}=H_2)^{\text{vi}};$$

and the conclusion has been drawn that the platinum atom is octovalent.

I have already[1] discussed assumptions (2) and (3), and have, I hope, shewn how unsatisfactory any conception of valency must be which in the present state of knowledge is based on the study of other than gaseous compounds. A solid

[1] See chapter II, section 3, par. 63.

compound is prepared with definite properties; analysis serves to fix the composition; the atomic weights of the elements in the compound being known, a formula is found:—but to assume that this formula necessarily represents the ratio between the numbers of different elementary *atoms* in the *molecule* of this compound, is I think more than a fair inference from the facts. For is not this to assume that the 'chemical unit' of the solid compound is *a* molecule, whereas it may very probably be a group of molecules? The definition of 'molecule' is a physical definition, and is strictly applicable only to gaseous bodies. The properties of a solid may be the properties of a number of little definite parts, each of which decomposes into two or more simpler groups (molecules) when the solid is gasified; the ratio between the numbers of atoms in the true molecules may be different from the ratio between the numbers of atoms in those groups of molecules, which form the building-stones of the solid compound[1].

But it may be urged that a much wider meaning ought to be given to the term valency. Better, I would reply, employ another term or other terms. Let us make as much use of valency as we can; so far as it goes it is definite, without it the chemistry of carbon compounds especially could not have made the advances which it has made. But it is not all.

A suggestion, which seems fairly probable, has been made to the effect that the maximum valencies of the atoms increase from the members of Group I. to those of Group VII., but that the valency actually exhibited in the majority of gaseous compounds varies from a minimum in Group I. to a maximum in Group IV., and then decreases to a minimum in Group VII.

115 In applying the periodic law to the case of an individual element, it is necessary in the first place to consider the properties both of the group and the series to which the element belongs; then the position of the element in the group and series must be considered; the relations of other

[1] The experiments of Hittorf on the electrolysis of aqueous solutions of cadmium iodide are very suggestive (see *ante*, p. 215).

elements, situated similarly to the specified element, to the other members of their groups and series must also be considered, and these relations must be compared with those of the special element under consideration; and finally the relations of group to group and of series to series in the entire scheme must be looked to. The method is strictly comparative. It is necessary to study classes of elements and compounds, and to compare class with class and individual with individual, before just conclusions can be drawn[1].

The periodic law emphasises the existence of typical forms for the compounds of elements; it points to limiting values for the numbers of atoms which can be associated together in groups. It teaches the importance, in the chemistry of solid and liquid compounds, of the law of multiple proportions. It reminds us that at present we must study the properties of groups of compounds, that we must sum up these properties in the simplest possible formulæ, and that the whole chemical history of each compound must determine the form to be given to the symbol by which we express that history. It tells us that although we do not know whether such formulæ do or do not represent the relative weights of the molecules of the bodies formulated, nevertheless these formulæ can be classified under a few types; and that thus a certain amount of order can be introduced into the classification of solid and liquid compounds, general conclusions can be drawn, and predictions can be made which may be submitted to the test of experiment. And while doing this, the periodic law keeps before us the necessity of from time to time modifying our scheme of classification; it reminds us that a typical classification is of necessity temporary, but that just by reason of its elasticity it is suited to the present needs of the chemistry of solid and liquid substances[2].

[1] The student should work out some cases in detail; say lead in Group IV., antimony in Group V., and cadmium in Group II.

[2] It is interesting to observe in the applications of the periodic law the survival, in modified and more precise form, of the old conception of the element as an essence or principle, capable of impressing on all substances into which it entered properties sufficiently definite to mark off these substances from all others which did not contain this principle.

An interesting paper on the periodic law, especially as applied to the classification of elements and compounds, by T. Bayley, will be found in *Phil. Mag.* (5) **13.** 26. Other important papers on the same subject, by Carnelley, are published in *Phil. Mag.* (5). **18.** 1 *et seq.*: *do. do.* (5). **20.** 259. In these papers the periodic law is illustrated by considering the melting and boiling points, and to some extent also the heats of formation, of the halogen compounds of the elements, and also the compounds of elements with organic radicles, and also the occurrence in nature of the elements, and the relations between the colours of compounds and the atomic weights of their constituent elements; and the facts thus obtained are applied to determine the values to be assigned to the atomic weights of various elements, and also the positions of these elements in the general scheme of classification based on the law in question.

CHAPTER IV.

APPLICATIONS OF PHYSICAL METHODS TO QUESTIONS OF CHEMICAL STATICS.

116 CHEMISTRY being a more concrete science than physics must of necessity derive help in solving its problems from the use of physical methods of investigation; but while using such methods the chemist ought not to forget that his aim is to find answers to chemical, not to physical, questions.

Minute descriptions of physical processes and details of physical experiments are not demanded in a treatise on physical chemistry; much less is there required elaborate enunciations of the methods of calculation employed in physical researches. Such things give, it is true, an appearance of great accuracy and profound knowledge; but the apparently accurate knowledge and full discussion of physical details too frequently serves as an excuse for loose statements and superficial generalisations regarding those vital chemical questions for answering which so vast a collection of 'precautionary and vehiculatory gear' has been provided. In attempting to give an outline of the more important applications of physical methods to chemistry one is also liable to err in the other direction: vague statements to the effect that the boiling points of homologous hydrocarbons exhibit constant differences, or that the chemical constitution of carbon compounds is intimately connected with their optical activity, or that chemical actions which involve a degradation of energy in the reacting systems frequently occur,—statements such as these are utterly inadequate.

I cannot hope to avoid both dangers: but I may venture to believe that the contents of the present chapter will be of some assistance to those who attempt to gain clear conceptions of some of the important phenomena forming the subject-matter of physical chemistry.

Some of the physical methods employed by the chemist as aids in attempts to solve the questions of chemical statics have been considered in the foregoing chapters of this book; in addition to these I shall consider the following; (1) thermal methods, (2) optical methods, (3) methods which involve measurements of the volumes of reacting substances, (4) methods based on determinations of 'etherification-values', and (5) a few miscellaneous methods.

SECTION I. *Thermal Methods*[1].

117 The principle of the conservation of energy lies at the root of all thermo-chemical investigation. When two or more chemical substances react so as to produce a new system, or new systems, of substances, mechanical work may be done by expansion, electrical currents may be produced, heat may be generated, and energy may be lost to the system in the forms of sound or radiant heat. The sum of these various kinds of energy, together with the energy remaining in the final system, must be equal to the energy which was present in the original system. A very large part of the energy set free during chemical changes generally leaves the changing systems in the form of heat; hence, measurements of the quantities of heat produced during definite chemical processes afford valuable information with

[1] The principal text-books on the subject are NAUMANN'S *Lehr- und Handbuch der Thermochemie* (1882). THOMSEN'S *Thermochemische Untersuchungen*, containing in a systematic form the work of many years which has hitherto been scattered through various memoirs, 4 vols. (1882–86). BERTHELOT'S *Essai de Mécanique Chimique fondée sur la Thermochimie*, 2 vols (1879) with supplement. JAHN'S *Die Grundsätze der Thermochemie* (1882). PATTISON MUIR'S *The Elements of Thermal Chemistry* (1885).

The first book of the second volume of OSTWALD'S *Lehrbuch der Allgemeinen Chemie* is devoted to thermal chemistry (1887).

respect to the differences between the amounts of energy possessed by the systems in their original and final states. To measure such differences of energy is the primary aim of thermal chemistry.

We are accustomed to conceive of most chemical changes as divisible broadly into two parts, (1) separation of molecules into atoms, (2) re-arrangement of atoms to form new molecules. We picture to ourselves the final arrangement of the atoms as dependent on the nature of these atoms, and on their relative positions in the molecules which composed the original system, that is to say, we picture the progress of mutual actions and reactions among the separated atoms. We know little, or nothing, of the causes of this re-arrangement; but we are accustomed to say that the atoms interact because of their mutual affinities.

A consideration of the circumstances under which chemical changes proceed and of the connexions between these and the thermal changes which accompany them will, I think, make it evident that measurements of the quantities of heat produced during chemical occurrences do not represent measurements of the 'chemical affinities'[1] of the reacting atoms; but these measurements do enable us to draw conclusions as to the constitution of chemical substances, and the general laws of chemical change.

The bearing of thermochemical measurements on the subjects of affinity and chemical equilibrium in general will be considered in the second book: in the present section I propose to give a very brief sketch of the methods of thermal chemistry, and an outline of the more important results obtained relating to allotropy, isomerism, nascent state, and other phenomena of chemical statics, referring the student for more detailed information and discussion to my *Elements of Thermal Chemistry*.

118 The notation of thermal chemistry used by Thomsen is very simple: the formulæ of the reacting substances are enclosed in a square bracket, and each formula is separated from the other by a comma. The formulæ are always taken

[1] See *post*, Book II.

to represent so many grams of the substances. The unit of heat adopted is that quantity which raises the temperature of 1 gram of water at about 18° C. through 1° C. The signs + and − are used to express quantities of heat produced or which disappear. Thomsen writes the figure expressing the number of atoms of each element above the symbol of that element[1].

Thus, the formula $[H^2, Cl^2] = 44{,}000+$, means that a quantity of heat, sufficient to raise the temperature of 44,000 grams of water at about 18° through 1°, is produced during the chemical process represented in ordinary notation by $H_2 + Cl_2 = 2HCl$, the quantities of hydrogen and chlorine being taken in grams. The symbol Aq, separated by a comma from another symbol, means that a large excess of water is present and that its effect in the total thermal change is taken into account; thus, $[HCl, Aq] = 17{,}320+$, means that 17,320 gram-units of heat are produced during the solution of 36·5 grams of hydrochloric acid in a quantity of water so large that addition of more water would not affect the thermal value of the reaction. $[H^2, Cl^2, Aq] = 61{,}320+$, means that the combination of 2 grams of hydrogen with 71 grams of chlorine in the presence of an unlimited amount of water is attended with the production of 61,320 gram-units of heat. $[HClAq, KOHAq] = 13{,}750+$, means that when 36·5 grams of HCl dissolved in a large excess of water react with 56 grams of KOH, also dissolved in a large excess of water, 13,750 gram-units of heat are produced.

The symbol H_2O is used as in ordinary notation to represent 18 grams of water; thus

(1) $[Mn, O^2, SO^2, 4H^2O] = 190{,}810+$;
(2) $[MnSO^4 4H^2O, Aq] = 1770+$;

mean, (1) that in the formation of the amount, in grams, of crystallised manganous sulphate expressed by the formula $MnSO_4 4H_2O$, from the amounts, in grams, of manganese,

[1] Thomsen appears to be the only chemist who systematically writes the indices above the symbols of elements in the formulæ of thermal chemistry. Thomsen also sometimes uses the colon in place of the comma to express chemical reaction between the substances whose formulæ are separated by this symbol.

oxygen, sulphur dioxide, and water, expressed by the respective formulæ Mn, O_2, SO_2, and $4H_2O$, 190,810 gram-units of heat are produced: (2) that 1770 gram-units of heat are produced in the solution of the foregoing number of grams of crystallised manganous sulphate in an unlimited quantity of water.

Generally then[1], let r = the thermal value of a chemical change: let the change be the formation of a definite amount of a compound[2] viz. $(X_a Y_b Z_c)$, consisting of a parts by weight of the element X, b parts by weight of the element Y, and c parts by weight of the element Z; then

$$r=[X^a,\ Y^b,\ Z^c] \quad \text{.....} \quad \text{.....} (1).$$

Let the compound $X_a Y_b Z_c$ be produced as before, but in presence of a large excess of water which holds it in solution; then

$$r=[X^a,\ Y^b,\ Z^c,\ \text{Aq}] \quad \text{.....} (2).$$

Let the substance $X_a Y_b Z_c$ already existing be dissolved in an unlimited amount of water; then

$$r=[X^a Y^b Z^c,\ \text{Aq}] \quad \text{.....} (3).$$

Let the compound XY be decomposed by the element Z with formation of XZ and Y; we get the expression

$$r=[XY,\ Z]=[X,\ Z]-[X,\ Y] \quad \text{.....} (4),$$

that is, the total thermal change consists of two parts, (a) the heat used in separating XY into $X+Y$, and (b) the heat produced in the union of X and Z to form XZ.

Finally let the compound XY react with the compound VZ to produce XZ and VY; the value of r is found by the formula

$$r=[X,\ Z]+[V,\ Y]-[X,\ Y]-[V,\ Z] \quad \text{.....} (5).$$

Equations (1) to (3) have already been illustrated. As an example of the use of (4) we may take the reaction of zinc with hydrochloric acid whereby zinc chloride and hydrogen are produced;

$$[\text{Zn},\ 2\text{HClAq}]=[\text{Zn},\ \text{Cl}^2\text{Aq}]-2[\text{H},\ \text{ClAq}];$$

[1] Thomsen, *Thermochemische Untersuchungen*, **1.** 5 *et seq.*

[2] In many cases we may use the term 'molecule' in place of 'definite amount', and 'atom' in place of 'parts by weight': but as we shall frequently deal with solids and liquids it is better at present not to speak of atoms and molecules.

or that of iron with a solution of copper sulphate to produce ferrous sulphate and copper;

$$[CuSO^4Aq, Fe]=[Fe, SO^4Aq]-[Cu, SO^4Aq].$$

As an illustration of (5) the decomposition of PbO by H_2S resulting in the production of PbS and H_2O, may be used;

$$[PbO, H^2S]=[Pb, S]+[H^2, O]-[Pb, O]-[H^2, S].$$

Ostwald (*Lehrbuch*) uses a system of notation which expresses more facts about each reaction than that employed by Thomsen. The latter does not indicate the products of the chemical change the thermal value of which is stated. Ostwald employs the ordinary notation, but supplements each equation by a statement of the quantity of heat which is produced or disappears in the reaction: he also uses three kinds of type to express the state of aggregation of the various bodies. A symbol printed in thick type indicates a solid, ordinary type indicates a liquid, and italics shew a gas. The following examples illustrate Ostwald's system.

(1) $H_2+Cl_2=2HCl+44{,}000.$
(2) $2H_2S+2\mathbf{I}_2=4HI+2\mathbf{S}-34{,}000.$
(3) $2H_2SAq+2I_2Aq=4HIAq+2\mathbf{S}+34{,}000.$

These equations tell (1) that the sum of the internal energies of 2 grams of gaseous hydrogen and 71 grams of gaseous chlorine exceeds the internal energy of 73 grams of gaseous hydrochloric acid by a quantity equal to 44,000 gram-units of heat, and (2) and (3) that the sum of the internal energies of 68 grams of gaseous sulphuretted hydrogen and 508 grams of solid iodine is equal to that of 512 grams of gaseous hydriodic acid and 64 grams of solid sulphur diminished by 34,400 gram-units of heat, but that the sum of the energies of the same masses of hydrogen sulphide and iodine in dilute aqueous solution exceeds the sum of the energies of the same mass as before of hydriodic acid in dilute aqueous solution and the same mass as before of solid sulphur by 34,400 gram-units of heat. If it is required to indicate a particular temperature at which one or other of the reacting bodies is caused to take part in

the reaction, this is done by Ostwald by putting the number indicating the temperature in small figures in a bracket below the symbol of the body; thus $\mathbf{S}_{(20)}$ means 32 grams of solid sulphur at 20°; $2S_{(600)}$ means 64 grams of gaseous sulphur at 600°. The value of the thermal change accompanying a change of state, or a change of the same body from one temperature to another, may be very easily indicated by using Ostwald's system of notation. Thus $H_2O_{(0)} = \mathbf{H_2O}_{(0)} + 1440$, or what is the same thing $H_2O_{(0)} - \mathbf{H_2O}_{(0)} = 1440$, tells that the change from 18 grams of liquid water at 0° to the same mass of solid water at the same temperature is accompanied by the production of 1440 gram-units of heat. Again $\mathbf{Cu}_{(100)} = \mathbf{Cu}_{(0)} + 600$ tells that 63·5 grams of solid copper at 100° contain energy equal to 600 gram-units of heat more than 63·5 grams of solid copper at 0°.

Both Thomsen's and Ostwald's system of notation will be used in this book; the latter especially when it is desired to indicate, shortly and clearly, differences in the states of aggregation of the reacting bodies.

119 A distinction has been drawn between so-called *exothermic* and *endothermic* changes; the former are accompanied by production, the latter by disappearance, of heat.

Let (P^aQ^b) represent the energy in a compound formed of a parts of element P and b parts of element Q: let (P^a) and (Q^b) represent the energy in a parts of P, and in b parts of Q, respectively; then, inasmuch as the energy in any system resulting from a definite chemical change is equal to the difference between the energy in the original system from which it was produced and that lost to the system during the process, it follows that

$$(P^aQ^b) = (P^a) + (Q^b) - (P^a, Q^b),$$

assuming that the heat produced in the formation of P^aQ^b measures the total loss of energy;

and therefore $$(P^a) + (Q^b) > (P^aQ^b).$$

This equation represents an exothermic change.

But in some cases a chemical change occurs only when heat is added to the changing system from without; in such a case

$$(P^a Q^b) = (P^a) + (Q^b) + (P^a, Q^b),$$

and therefore

$$(P^a) + (Q^b) < (P^a Q^b).$$

This equation represents an endothermic change.

In some cases, a chemical reaction which seems to be accompanied by disappearance of heat is found, on more careful study, to form one member of a series of changes the thermal sum of which is represented by a positive quantity. Indeed any chemical reaction is a most complex phenomenon when regarded from the thermal point of view; physical changes (expansion or contraction, passage from solid to liquid or gas, or *vice versa*, &c., &c.) form part of the total change the thermal value of which is set down in a lump sum. The purely chemical part of the change may be accompanied by disappearance of heat, while the complete occurrence may involve the production of heat.

The following example will serve to illustrate the use of the terms endothermic and exothermic.

Naumann[1] shewed that no action occurs when dry sulphuretted hydrogen is passed into a solution of iodine in dry carbon disulphide, but that as soon as water is added, hydriodic acid and sulphur are produced. The reaction

$$\underset{\text{(gaseous)}}{2H_2S} + \underset{\text{(solid)}}{2I_2} = \underset{\text{(gaseous)}}{4HI} + \underset{\text{(solid)}}{S_2}$$

would be thermally represented as

$$\begin{aligned}[2H^2S, 2\mathbf{I}^2] &= 4[H, I] - 2[H^2, \mathbf{S}] \\ &= -24800 - 9200 \\ &= -34{,}000.\end{aligned}$$

When water is present, the reaction

$$\underset{\text{(in solution)}}{2H_2S} + \underset{\text{(in solution)}}{2I_2} = \underset{\text{(in solution)}}{4HI} + \underset{\text{(solid)}}{S_2}$$

would be thermally represented as[2]

$$\begin{aligned}[2H^2SAq, 2I^2Aq] &= 4[H, \mathbf{I}, Aq] - 2[H^2, \mathbf{S}, Aq] \\ &= 52{,}800 - 18400 \\ &= 34{,}400+.\end{aligned}$$

The reaction of dry sulphuretted hydrogen with dry iodine would be markedly endothermic; but when this change is made

[1] *Ber.* **2.** 177; and *Annalen* **151.** 145.

[2] No notice is taken in these thermal expressions of the change, if any, which accompanies the decomposition of $2I_2$ and the production of S_2. See *post*, pars. 122, 132.

one of a series the thermal value of which, taken as a whole, is positive, then the complete cycle of change proceeds rapidly.

But the more concentrated an aqueous solution of hydriodic acid becomes the less heat is there produced on each addition of the acid, until the specific gravity of the liquid is 1·56, after which no more heat is produced[1]; the liquid is saturated. If therefore the hydriodic acid formed in the foregoing reaction is allowed to accumulate in the liquid, no more water being added, a point will be reached at which the sum of the thermal changes is equal to zero; at this point the chemical change stops, but proceeds again on the addition of a little water. It is possible to obtain an aqueous solution of hydriodic acid of specific gravity 1·67; if sulphur is shaken with this liquid a little sulphuretted hydrogen and iodine are produced, i.e. the change

$$\underset{\text{(solid)}}{S_2} + 4HI = \underset{\text{(concentrated) (solution)}}{2H_2S} + \underset{\text{(solution)}}{I_2}$$

proceeds until the hydriodic acid becomes reduced to specific gravity 1·56, when equilibrium is again established.

Portions of this cycle of change are exothermic, other portions are endothermic. Variation of the mass of one of the members of the changing system determines whether the thermal value of the complete change shall be positive or negative, and also determines the direction in which the change shall proceed. This reaction may be taken as typical of most if not all chemical processes Such processes consist of portions having positive thermal values and portions having negative values; small variations in the conditions may determine whether the process as a whole shall belong to the class of exothermic or to that of endothermic changes.

Too much stress has been laid by one school of chemists on the differences between exothermic and endothermic changes.

120 Direct measurements of the thermal changes which accompany chemical changes can only be made in a few simple cases; it is generally necessary to have recourse to indirect methods.

[1] This liquid contains about 25 per cent. of HI.

All the calculations rest on the following deduction from the theory of energy.

The total change of energy which accompanies the passage of a chemical system from a definite initial to a definite final state is independent of the intermediate states.

The total change of energy is of course measured by the heat which is produced or disappears, and the work done by, or on, the system in its passage from one state to the other. But for our purpose the energy given out in forms other than that of heat may be overlooked, and we may put the statement in this form; the total thermal change during a chemical process is dependent only on the initial and final states of the chemical system[1].

In applying this statement, it is necessary to arrange series of reactions each beginning with the same materials in the same conditions and ending with the same products under the same conditions; all the processes which form one of the cycles of change must be capable of calorimetrical measurement, and all the processes in the other cycle, except that one the thermal value of which is to be determined, must also be capable of measurement by the calorimeter: if this be done, it follows from the principle just stated that the difference between the total thermal values of the two cycles of changes represents the thermal value of that special portion of one of the cycles which it is wished to determine. Each cycle may however consist of various parts, so that it is sometimes a little difficult to unravel all the changes, and to find that portion of one cycle the thermal value of which has to be determined by calculation.

I shall now give some examples to shew how the thermal values of various chemical changes are deduced from the results of experiments.

A. It is required to determine the thermal value of the synthesis of CH_2O_2 from C, H_2, and O_2.

We start with 12 grams of carbon, 2 of hydrogen, and 48 of oxygen; these combine to form 18 grams of water,

[1] The truth of this generalisation was first proved experimentally by Hess in 1840 (*Pogg.* **50**. 385).

and 44 grams of carbon dioxide ($C + H_2 + O_3 = CO_2 + H_2O$). But the same quantities of carbon, hydrogen, and oxygen might be (theoretically) combined to form 46 grams of formic acid and 16 grams of oxygen, and the formic acid could then be oxidised, by the oxygen, to form 18 grams of water and 44 grams of carbon dioxide. Stated in formulæ these changes are

(1) $C+H_2+O_2=CH_2O_2$; (2) $CH_2O_2+O=CO_2+H_2O$.

The following are the thermal values of the different portions of these changes:

$$[C, O^2]=96{,}960+ : [H^2, O]=68{,}360+ : [CH^2O^2, O]= 65{,}900+$$

but $$[C, O^2]+[H^2, O]=[C, H^2, O^2]+[CH^2O^2, O]=165{,}320+$$

$$\therefore [C, H^2, O^2]=[C, O^2]+[H^2, O]-[CH^2O^2, O]= 99{,}420+.$$

B. A rather more complicated example is furnished by the determination of the thermal values of the actions (1) $[H, Br]$, (2) $[H, I]$; i.e. of the reactions whereby HBr and HI are conceived to be formed from their elements.

(1) $[H, Br]$. The data are

$$[H, Cl, \text{Aq}]=39{,}300; [HBr, \text{Aq}]=19{,}900^1:$$

therefore assuming that

$$[H, Br, \text{Aq}]=[H, Cl, \text{Aq}]$$

it follows that

$$[H, Br]=39{,}300-19{,}900=19{,}400.$$

But is the formation of an aqueous solution of HBr from H, Br, and water, attended with the same thermal change as accompanies the formation of an aqueous solution of HCl from H, Cl, and water? Or, if this assumption is not justified by facts, what is the difference between the thermal values of the two changes?

Now, in the first place, the thermal values of the formation of KCl and KBr in aqueous solution are equal, i.e.

$$[\text{KOHAq, HClAq}]=[\text{KOHAq, HBrAq}].$$

[1] When no + or − sign is given it is to be understood that heat is evolved.

But the replacement of Br by Cl is attended with production of a considerable quantity of heat; the data here are

$$[\mathrm{KBrAq}, Cl] = 11{,}500.$$

Now if we analyse this change we find that the thermal expression when expanded becomes

$$[\mathbf{K}, Cl, \mathrm{Aq}] + [Br, \mathrm{Aq}] - [\mathbf{K}, Br, \mathrm{Aq}] = 11{,}500:$$

but

$$[Br, \mathrm{Aq}] = 500:$$

$$\therefore [\mathbf{K}, Cl, \mathrm{Aq}] - [\mathbf{K}, Br, \mathrm{Aq}] = 11{,}500 - 500 = 11{,}000.$$

That is to say, the replacement of Br by Cl in aqueous solution is represented by the thermal value 11,000 units, and as the heat of neutralisation. in aqueous solution, of KOH by HCl is equal to that of KOH by HBr, it follows that

$$[H, Br, \mathrm{Aq}] = [H, Cl, \mathrm{Aq}] - 11{,}000 = 28{,}300:$$

and as $[HBr, \mathrm{Aq}] = 19{,}900$, it follows that $[H, Br] = 8{,}400$.

(2) $[H, \mathbf{I}]$. The data are

$$[H, Cl, \mathrm{Aq}] = 39{,}300; \quad [HI, \mathrm{Aq}] = 19{,}200.$$

Now

$$[\mathrm{KOHAq}, \mathrm{HIAq}] = [\mathrm{KOHAq}, \mathrm{HClAq}] - 70:$$

also

$$[\mathrm{KIAq}, Cl] = 26{,}200 \text{ (iodine separating as solid)}:$$

$\therefore$ replacement of I by Cl is accompanied by production of $26{,}200 - 70 = 26{,}130$ units:

$$\therefore [H, \mathbf{I}, \mathrm{Aq}] = [H, Cl, \mathrm{Aq}] - 26{,}130 = 13{,}170:$$

and as

$$[HI, \mathrm{Aq}] = 19{,}200$$

it follows that

$$[H, \mathbf{I}] = 13{,}170 - 19{,}200$$
$$= -6030.$$

The calculations of the *heats of formation* of compounds are all based on the principle we are now discussing.

C. Thus, required the heat of formation of methane (CH_4). We start with the two systems (1) $\mathbf{C} + 4H$, (2) CH_4. Each is completely oxidised to the same final products, viz. $CO_2 + 2H_2O$; the difference between the quantities of heat produced in these two changes is called the heat of formation of CH_4. Thus,

$$[\mathbf{C}, O^2] = 96{,}900: \quad 2[H^2, O] = 136{,}800: \text{ sum} = 233{,}700$$
$$\text{but } [CH^4, O^4] = 213{,}500$$
$$\therefore [\mathbf{C}, H^4] = 20{,}200.$$

As it is important that a definite meaning should be attached to the expression 'heat of formation,' a few more examples are given.

D. Required the thermal value of the reaction $[H, \mathbf{C}, N]$, that is, of the reaction whereby HCN may be conceived to be formed from its elements.

Data; $[\mathbf{C}, O^2]=96{,}900$: $\frac{1}{2}[H^2, O]=34{,}200$: sum $=131{,}100$ (N is incombustible)
but $[CNH, \frac{5}{2}O]=159{,}500$
$\therefore [\mathbf{C}, N, H]^1=-28{,}400.$

E. Required the thermal value of the reaction $[N^2, O]$.

Data; the reaction
$\mathbf{C}+2N_2O=2N_2+CO_2$ when expanded thermally is
$[\mathbf{C}, 2N^2O]=[\mathbf{C}, O^2]-2[N^2, O]=133{,}900$:
but $\mathbf{C}+2N_2+O_2=CO_2+2N_2$
i.e. $[\mathbf{C}, 2N^2, O^2]=[\mathbf{C}, O^2]=96{,}900$:
$\therefore\ 2[N^2, O]=-37{,}000$
$\therefore\ [N^2, O]=-18{,}500.$

F. Required the thermal value of the reaction $[N, O]$.

Data; $CN+2NO=CO_2+3N$, or in thermal notation
$[CN, 2NO]=[C, O^2]-[C, N]-2[N, O]=174{,}600$:
but $CN+O_2=CO_2+N$, or in thermal notation
$[CN, O^2]=[C, O^2]-[C, N]=130{,}900$
$\therefore\ 2[N, O]=-43{,}700$:
$\therefore\ [N, O]=-21{,}850.$

The heat of formation of a substance will of course vary according as the substance is formed in the gaseous, liquid, or solid, state, and also according to the temperature of formation. The following examples will illustrate this.

G. Required the thermal value of the formation of aldehyde from its elements, i.e. of the reaction $[\mathbf{C}^2, H^4, O]$, when the aldehyde is (*a*) liquid, (*b*) gaseous.

(*a*) *Liquid: data,*
$C_2H_4O+5O=2CO_2+2H_2O$;
i.e. $[C^2H^4O, O^5]=2[\mathbf{C}, O^2]+2[H^2, O]-[\mathbf{C}^2, H^4, O]=275{,}500$[2]
but $2[\mathbf{C}, O^2]+2[H^2, O]=330{,}600$
$\therefore [\mathbf{C}^2+H^4+O=C^2H^4O]=55{,}100$

[1] The transference of N from the molecule N_2 to the molecule HCN is assumed to be accompanied by no thermal change. See *post* par. 132.

[2] The CO_2 produced is gaseous; the heat of formation of liquid CO_2 is unknown.

(*b*) *Gaseous: data,*

$$[C^2H^4O, O^5] = 266{,}000; \text{ and } 2[H^2, O] = 117{,}400:$$
$$\therefore [C^2 + H^4 + O = C^2H^4O] = 45{,}200.$$

H. If the products of a reaction are gaseous and are maintained at a high temperature, it becomes necessary to introduce corrections for the specific heats, and heats of vaporisation, of these products, into the calculation of the thermal value of the reaction.

Thus, required the thermal value of the reaction $[C^2H^2, O^5]$ at 150°.

Data, $C_2H_2 + 5O = 2CO_2 + H_2O$

at ordinary temperatures (20°)

$$[C^2H^2, O^5] = 2[C, O^2] + [H^2, O] - [C^2, H^2] = 310{,}600:$$

but thermal capacity of 2 gram-molecules of CO_2 for temperature-interval 20°—150° ... ... = 2482 units.

thermal capacity of 1 gram-molecule of H_2O:

(*a*) 1 mol. liquid H_2O 20°—100° = 18 × 80 = 1440 „

(*b*) heat of vaporisation of do. at 100° = 18 × 536·5 = 9657 „

(*c*) thermal capacity of 1 mol. steam 100°—150° = 18 × 50 × 0·4805 = 432 „

total = 14011 units.

$\therefore [C^2H^2, O^5]$ at 150° = 310,600 − 14,011 = 296,589 (*say* 296,600) gram-units[1].

121 From these examples we may provisionally conclude that a chemical change which is accompanied by a considerable loss of energy to the changing system, as indicated by the production of a considerable quantity of heat, will generally occur unless prevented by actions outside the system.

The following processes may be taken as illustrative of this somewhat vague generalisation.

The acids of the acetic series readily yield chloro- or bromo-derivatives by the direct action on them of chlorine or bromine, iodine however does not react under similar conditions to form iodo-acids. The thermal values of the reactions of the three halogens with acetic acid are as follows;—

[1] For further examples of calculations of the thermal values of chemical changes, see *The Elements of Thermal Chemistry*, par. 60.

$$C_2H_4O_2+X_2=C_2H_3XO_2+HX \begin{cases} X=Cl= & 30{,}000 \text{ units.} \\ X=Br= & 4{,}800 \quad \text{,,} \\ X=\mathbf{I} & =-18{,}000 \quad \text{,,} \end{cases}$$

The reverse action in the case of iodine, viz.

$$C_2H_3IO_2+HI=C_2H_4O_2+\mathbf{I}_2$$

is represented thermally thus,

$$[C^2H^3IO^2, HI]=18{,}000.$$

This action occurs provided a concentrated aqueous solution of hydriodic acid is employed.

Now
$$2HI=H_2+\mathbf{I}_2,$$
$$=-2[H, I]$$
$$=12{,}400.$$

But
$$[2HI, \text{Aq}]=38{,}000:$$

hence it follows that in the decomposition of $2HI$ into $H_2+\mathbf{I}_2$ in dilute solution $38{,}000-12{,}400=25{,}600$ units of heat would disappear.

These thermal numbers shew that the process which is accompanied by a large loss of energy occurs, whereas that which would involve gain of energy to the system does not occur.

But why does a concentrated aqueous solution of hydriodic acid act as an energetic reducing agent? We have already learned (p. 254) that little or no heat is produced during the absorption and solution of gaseous hydriodic acid by a solution of that gas containing about 20—25 per cent. of HI; hence a concentrated solution of this compound contains a considerable quantity of HI, as distinguished from HIAq. But the numbers given above shew that HI contains much more energy than HIAq; hence a concentrated aqueous solution of hydriodic acid is much more energetic than a dilute solution of the same compound[1].

The following tables[2] contain thermal data for discussing the action of sulphuretted hydrogen as a reagent for precipitating certain metals from acid solutions, and other metals only from neutral or alkaline solutions.

[1] See Naumann, *Thermochemie*, 495 and 501.

[2] See Naumann, *loc. cit.* 505—510.

TABLE I.

Reaction		*Base* CdO	PbO	CuO	HgO	Tl_2O	Cu_2O	Ag_2O
[Base 2HClAq, H^2SAq]	(1)	27,300	29,200	31,700	45,300	38,500	38,500	58,500
[Base Aq, 2HClAq]	(2)	20,300	15,400	15,300	19,000	27,500	14,700	42,600
(1) − (2) =		+ 7,000	13,800	16,400	26,300	11,000	23,800	15,900

TABLE II.

Reaction		*Base* CdO	PbO	CuO	HgO	Tl_2O	Cu_2O	Ag_2O
[**Base**, H^2S]	(1)	32,100	34,000	36,500	50,000	43,300	43,300	63,300
[**Base**, 2*HCl*]	(2)	55,000	50,000	50,000	53,500	62,200	49,300	77,200
(1) − (2) =		− 22,900	16,000	13,500	3,500	18,900	6,000	13,900

TABLE III.

Reaction		*Base* MnO.H_2O	FeO.H_2O	NiO.H_2O	CoO.H_2O	ZnO.H_2O
[Base 2HClAq, H^2SAq]	(1)	10,700	14,600	18,600	17,400	18,600
[Base Aq, 2HClAq]	(2)	23,000	21,400	22,600	21,100	20,300
(1) − (2) =		− 12,300	6,800	4,000	3,700	1,700

To illustrate the application of these data, take the case of cadmium.

(1) [CdO2HClAq, H^2SAq] = 27,300:

i.e. the thermal change which occurs when aqueous H_2S reacts on a dilute solution of CdO in HCl is represented by the production of 27,300 units.

(2) [CdOAq, 2HClAq] = 20,300:

i.e. the thermal change which would occur if CdO in aqueous solution were neutralised by a dilute solution of HCl would be represented by the production of 20,300 units. The former number exceeds the latter by 7,000, ∴ the action of H_2S, in solution, on CdO, in dilute HCl solution, is accompanied by the production of 7,000 units of heat; this action readily occurs. But

[**CdO**, H^2S] = 32,100; and [**CdO**, 2*HCl*] = 55,000:

i.e. the formation of CdS, by the action of gaseous H_2S on solid CdO, is accompanied by the production of 22,900 units of

heat less than attends the action of gaseous HCl on CdO; now solid CdS is decomposed by gaseous HCl with formation of $CdCl_2$.

Moreover the numbers

$$[2HCl, \text{Aq}] = 34{,}600; \text{ whereas } [H^2S, \text{Aq}] = 4{,}800$$

shew, that gaseous hydrochloric acid possesses an excess of energy measured by about 34,000 thermal units above what it possesses when in dilute solution, whereas the excess of energy of an equivalent mass of gaseous H_2S above that possessed by H_2SAq is measured by about 5000 thermal units. But the more concentrated an aqueous solution of hydrochloric acid, the less is the quantity of heat produced by adding hydrochloric acid gas to that solution; in other words, a concentrated aqueous solution of this acid is nearly as energetic a reagent, provided it is used in sufficient quantity, as gaseous hydrochloric acid. Hence we should conclude, and our conclusion is verified by experiment, that cadmium sulphide will be decomposed by concentrated aqueous hydrochloric acid.

The case of antimony is especially interesting.

Antimony sulphide is decomposed by aqueous hydrochloric acid of greater concentration than $HCl.6H_2O$; but if more water than this is present, antimony chloride is decomposed by sulphuretted hydrogen. Hence the two reactions

$$\left.\begin{matrix} Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S \\ 2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl \end{matrix}\right\} \textit{water being present}$$

may occur until a state of equilibrium is established, which is conditioned by the relative energies of the components, and this again is conditioned by the relative masses of these components, temperature being constant throughout.

122 We have been accustomed to regard most processes of chemical change as consisting of two parts, (1) decomposition of the molecules forming the initial system, (2) rearrangement of the atoms thus produced to form the new molecules which compose the final system. The first part of a change, as thus regarded, must be accompanied by gain of energy to the entire system, and the latter part by loss of energy. The gain may exceed the loss, or *vice versa;* the process as a

whole may be endothermic or exothermic. In the preceding paragraphs of this section no attempt has been made to separate the thermal values of these two parts of any change; the numbers given in these paragraphs represent the algebraic sums of two or more quantities. In some cases the chemical changes are represented in formulæ which are undoubtedly molecular, but in most cases we have dealt with solid or liquid substances, and the thermal values assigned to the various changes must therefore generally be regarded as only measuring the quantities of heat produced or used during the reactions, as defined in the equations, between those masses of the various chemical substances which are expressed by their formulæ when read in grams.

But if relative measurements of the gains of energy which accompany the formation of atomic, from molecular, systems, could be obtained, much light would certainly be thrown on many questions which have been discussed or alluded to in preceding chapters.

123 Thomsen[1] has attempted to calculate the quantity of heat required to separate the molecule of carbon, assumed to be diatomic, into atoms; his results and methods cannot be accepted as conclusive[2]. The 'heat of dissociation' of a carbon atom is supposed by Thomsen to be equal to about 37,000 gram-units.

E. Wiedemann[3] has measured the heat required to change the 'band spectrum' of hydrogen into the 'line spectrum'; and, on the assumption that the 'line spectrum' is associated with vibrations of atoms and the 'band spectrum' with vibrations of molecules, he has calculated that about 128,000 gram-units of heat are required in order to separate 1 gram-molecule of hydrogen into its constituent atoms; and that a greater quantity of heat than this is required in the case of the molecule of nitrogen.

Thomsen and Wiedemann have shewn that more energy is almost certainly associated with a mass of hydrogen,

[1] *Ber.* **13.** 1321 and 1388. *Do.* **15.** 328. See also *Thermochemische Untersuchungen*, **2.** 101 *et seq.*

[2] See *The Elements of Thermal Chemistry*, pars. 73—75: see also *post* par. 134.

[3] *Wied. Ann.* **5.** 500, and do. **18.** 509.

nitrogen, or gaseous carbon, when the greater part of the matter is in the state of atoms than when in the state of molecules; in other words, their investigations furnish physical evidence in favour of the generally adopted explanation of nascent actions.

124 Some of the reactions of metals with acids were considered in Chap. II pars. 42 to 44. Thermal measurements help to elucidate these actions.

If the heats of formation in aqueous solution of the sulphates of silver, thallium, copper, cadmium, mercury, nickel, cobalt, iron, manganese, and zinc, are compared with the heat of formation of sulphuric acid in aqueous solution, it is found that the former values are greater than the latter except in the cases of copper and silver: i.e. for the heavy metals

$$[\mathbf{M}(\text{or } \mathbf{M}^2), O^2, SO^2, \text{Aq}] > [H^2, O^2, SO^2, \text{Aq}],$$

except when $M = Cu$ or $M_2 = Ag_2$; hence we might expect the heavy metals, except copper and silver, to decompose dilute sulphuric acid with evolution of hydrogen.

When $M_2 = Tl_2$ the positive value of the difference in question is not large (1,900 units); the action between this metal and dilute sulphuric acid does not proceed rapidly. But when the acid is concentrated action is more energetic; now inasmuch as the heat of solution of H_2SO_4 is large

$$[H^2SO^4, \text{Aq}] = 17{,}000$$

it follows that a given mass of concentrated sulphuric acid contains considerably more energy than the same mass of dilute acid, and hence the concentrated acid will probably be less chemically stable than the dilute. The reaction of thallium with the concentrated acid results in the production of some sulphur dioxide. Now the change $H_2SO_4 + H_2 = SO_2 + 2H_2O$ (assuming that this expresses the origin of the sulphur dioxide) is accompanied by the production of 14,900 units of heat. This change is represented thermally thus,

$$[H^2SO^4, H^4] = [\mathbf{S}, O^2] + 2[H^2, O] - [\mathbf{S}, O^2, O^2, H^2]$$
$$= 2[H^2, O] - [SO^2, O^2, H^2].$$

If the temperature is raised the acid becomes more concentrated, and at a certain stage sulphuretted hydrogen is

evolved. This action is thermally probable, because

$$\tfrac{1}{4}H_2SO_4 + H_2 = \tfrac{1}{4}H_2S + H_2O$$

when expanded thermally, is

$$\begin{aligned}[\tfrac{1}{4}H^2SO^4, H^2] &= [H^2, O] + \tfrac{1}{4}[H^2, \mathbf{S}] - \tfrac{1}{4}[H^2, \mathbf{S}, O^4] \\ &= [H^2, O] - \tfrac{1}{4}[H^2S, O^4] \\ &= 23{,}700 \text{ units.}\end{aligned}$$

A similar treatment of the action of copper on sulphuric acid shews that this metal would probably not decompose the acid when dilute, but that the metal might be expected to react slowly with concentrated acid, provided one of the products were sulphur dioxide; because

$$Cu + nH_2SO_4 = CuSO_4 + SO_2 + 2H_2O + (n-2)H_2SO_4$$

when expanded thermally, is

$$\begin{aligned}[\mathbf{Cu}, 2H^2SO^4] &= [\mathbf{Cu}, SO^2, O^2] + 2[H^2, O] - 2[H^2, O^2, SO^2] \\ &= 4{,}500 \text{ units.}\end{aligned}$$

The quantity of heat set free in this action will in reality considerably exceed 5000 units, because heat will be produced by the action between the sulphuric acid and the water formed in the change; the amount of heat thus liberated may amount to as much as 8,000 or 9,000 units per gram-molecule of water.

The fact that the mutual action of sulphuric acid and water is accompanied by the production of much heat complicates such calculations as those given above. The relations between the masses of H_2SO_4 and H_2O employed will certainly condition the direction and progress of the change. Starting with the system $H_2SO_4 + xH_2O + xH_2$, for a certain concentration of acid the final configuration will be SO_2 and H_2O, for another concentration of acid it will rather be H_2S and H_2O, or SO_2, H_2S, and H_2O. The action will also of course be conditioned by temperature.

If the foregoing considerations are correct, it follows that any metal which reacts with dilute sulphuric acid with evolution of hydrogen, might fairly be expected to react with the same acid to produce sulphuretted hydrogen or sulphur dioxide under certain conditions of temperature and concentration; zinc and tin certainly do produce both of these gases by their action on hot concentrated sulphuric acid[1].

[1] See p. 103. The subject of the reactions of metals with acids is treated from the thermal standpoint in pars. 120—122 of *The Elements of Thermal Chemistry*.

125 From what we have learned regarding atomic and molecular systems, and from a consideration of the preceding paragraphs of this section, it follows almost necessarily that the change from one allotropic modification of an element to another must be attended by production or disappearance of heat. A few thermal measurements are given here to shew that this conclusion is fully justified by facts.

A. $[\mathbf{P}^2, O^5] = 369{,}100$ units when P_2 is 62 grams of ordinary phosphorus (P_α);

$[\mathbf{P}^2, O^5] = 326{,}800$ units when P_2 is 62 grams of amorphous phosphorus (P_β);

$\therefore$ the change of P_α to $P_\beta = 21{,}150$ units of heat.

In the oxidation of 31 grams P_α to H_3PO_4 in aqueous solution by hypochlorous acid, 209,500 thermal units are produced;

in the oxidation of 31 grams P_β to H_3PO_4 in aqueous solution by hypochlorous acid, 181,200 thermal units are produced;

$\therefore$ the change of P_α to $P_\beta = 28{,}300$ units of heat.

Hence mean value of this change $= 24{,}725$ gram-units.

B. $[2O_3 = 3O^2] = 59{,}200$ units of heat; that is to say

the separation of 2 gram-molecules of ozone (O_3) into 3 gram-molecules of oxygen (O_2) is attended by the production of 59,200 units of heat.

The comparative thermal instability of the molecule O_3 helps us to understand why ozone is so much more active as an oxidising agent than ordinary oxygen[1].

126 Too little has as yet been done to allow of the application of thermal measurements to the classification of the elements in any but a very general way.

The relations existing between the members of a group of elements are sometimes summarised in the thermal values of comparable reactions undergone by these elements. Thus, (see table p. 225) taking Mendelejeff's Group II. we have,

			Series.				
4	6	8	3	5	7	9	11
Ca	Sr	Ba	Mg	Zn	Cd	–	Hg
atomic weights 40	87	137	24	65	112		200

[1] According to van der Meulen (*Ber.* **16.** 1853) the thermal value of the change in question, $2O_3 = 3O_2$, is about 68,000 units.

The heats of formation in aqueous solution of the haloid salts of these metals are arranged in the following table (data from Naumann's book):

	[M, Cl^2, Aq]	[M, Br^2, Aq]	[M, I^2, Aq]
Ca	187,600	165,800	135,300
Sr	195,700	173,800	143,400
Ba	196,300	174,400	144,000
—			
Mg	186,900	165,000	134,600
Zn	112,800	90,900	60,500
Cd	96,300	74,400	44,000
—			
Hg	59,900	?	?

Hence we conclude that in each case the value for Ba > Sr > Ca > Mg, and for Mg > Zn > Cd > Hg. In other words, the thermal value of the change [M, X^2, Aq] increases as the atomic weight of M increases, when M is a member of an even series belonging to Group II. but decreases as the atomic weight of M increases, when M is a member of an odd series of the same group. The difference between the values of [M, X^2, Aq] for each pair of elements is nearly constant. Thus

	X=Cl	X=Br	X=I
Ba − Sr =	600	600	600
Sr − Ca =	8,100	8,000	8,100
Ca − Mg =	700	800	700
—		—	—
Mg − Zn =	74,100	74,100	74,100
Zn − Cd =	16,500	16,500	16,500
Cd − Hg =	36,400	?	?

The close relationship of magnesium to calcium, and also its relations to barium and strontium, and the comparatively feebly marked relations existing between magnesium, zinc, cadmium, and mercury, are brought into forcible relief by these numbers[1].

127 The comparative study of classes of compounds, no less than that of classes of elements, has already been considerably

[1] Attention has already been drawn to the fact that there exists a well-marked connexion of a periodic character between the atomic weights of the elements and their heats of combination with chlorine, bromine, and iodine. (See *ante*, par. 109.)

advanced by the application of thermal methods. Thus, a study of some of the thermal relations of the hydracids and oxyacids of the halogens helps towards a classification of the latter group of acids.

The close thermal analogy between the hydracids in question is exhibited by these, among other, numbers;

[*HX*, Aq]	[HXAq, NaOHAq]
X=*Cl* =17,400	X=Cl =13,700
X=*Br*= 19,900	X=Br= 13,700
X=I =19,200	X=I =13,700.

When we compare the heats of formation of these acids in aqueous solution, we find that the value of this constant for each acid decreases as the atomic weight of the halogen increases: thus

[*H*, *X*, Aq]
X=*Cl* =39,300
X=*Br*=28,400
X=I =13,200.

The three oxyacids which correspond in composition to the three hydracids are $HClO_3$, $HBrO_3$, and HIO_3. The following numbers shew that, in some respects at any rate, the thermal relations between $HClO_3$ and $HBrO_3$ are analogous to those between HCl and HBr:—

[*H*, *X*, O^3, Aq]
X=*Cl* =23,900
X=*Br*=12,400

hence the difference, [*H*, *Cl*, Aq] − [*H*, *Br*, Aq] is approximately equal to the difference [*H*, *Cl*, O^3, Aq] − [*H*, *Br*, O^3, Aq.]

We might provisionally conclude from these data that the difference between the heats of formation, in aqueous solutions, of chloric and iodic acids, would probably be nearly the same as the difference between the heats of formation, under the same conditions, of hydrochloric and hydriodic acids. The value of the second difference is 26,100; hence, on this supposition, the first difference should be about 26,000. Now,

[*H*, *Cl*, O^3, Aq]=23,900;
∴[*H*, I, O^3, Aq]= −2,100.

But experiment shews that

[*H*, I, O^3, Aq]= +55,700.

Hence it is evident that iodic acid differs in the most marked manner from bromic and chloric acids. This difference is accentuated in the numbers expressing the heats of formation of these three acids from the three hydracids: thus,

$$[HXAq, O^3]$$
$$X=Cl = -15{,}400.$$
$$X=Br = -15{,}900.$$
$$X=I = +42{,}600.$$

But it is to be remembered that gaseous chlorine and bromine and solid iodine are employed in the calculations[1].

128 A comparison of the mutual thermal actions of acids and bases throws considerable light on the classification of the substances which are included under these terms. The first volume of Thomsen's *Untersuchungen* is devoted to a consideration of this subject.

'Heat of neutralisation of an acid by a base' is defined as, the quantity of heat produced on mixing equivalent quantities, in grams, of the acid and base, in dilute aqueous solutions, the products of the action being also soluble in water.

Thomsen employs a solution of 2NaOH in about 200 H_2O (grams), and adds the acid solution diluted to a similar degree, temperature being 18°—19°; in other words he determines the thermal value of the change

[2NaOHAq, 2HXAq]	in the case of a	monobasic	acid,
[2NaOHAq, H^2XAq]	„	dibasic	„
[2NaOHAq, $\frac{2}{3}H^3XAq$]	„	tribasic	„
[2NaOHAq, $\frac{1}{2}H^4XAq$]	„	tetrabasic	„

(X=acid radicle)

Most of the general conclusions drawn by Thomsen, and others, belong more to chemical kinetics than to statics, but some of the generalisations may fitly be introduced here[2].

The commoner acids may be broadly divided into four groups according to the values of their heats of neutralisation, as thus defined.

[1] The application of thermal data to the classification of elements and compounds is considered more fully in section 4 of Chap. III. of *The Elements of Thermal Chemistry*.

[2] See especially for more details Thomsen, *loc. cit.* 1. 293—309, and 422—449.

I. Those acids which have a heat of neutralisation approximately equal to 20,000 gram-units:—

HNO_2, $HClO$, $H_2B_2O_4$, H_2CO_3 &c.

II. Those acids which have a heat of neutralisation approximately equal to 25,000 gram-units:—

H_2CrO_4, $C_2H_4(CO_2H)_2$, $CH_2CHOH(CO_2H)_2$ &c.

III. Acids the heat of neutralisation of which is equal to about 27,000 gram-units:—

HCl, HBr, HI, $HClO_3$, $HBrO_3$, HIO_3, HNO_3, $H_2S_2O_3$, H_2SiF_6, $H.CO_2H$, $CH_3.CO_2H$ &c.

Most of the acids belong to this class.

IV. Acids having a heat of neutralisation greater than 27,000 units, and varying from 28,000 to 32,500 units;—

$CH_2Cl.CO_2H$, $CHCl_2.CO_2H$, $CCl_3.CO_2H$, $H_2C_2O_4$, H_3PO_3, H_2SO_3, H_2SO_4, H_2SeO_4, HF, HPO_3 &c.

A few acids have heats of neutralisation less than 20,000 units.

The basicity of an acid may be determined by thermal methods. One gram-molecule of the acid in dilute aqueous solution is mixed with $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, 1, 2, &c. gram-molecules of caustic soda also in dilute solution, and the heat produced in the reactions is measured. (The ordinary formulæ NaOH, H_2SO_4, &c. are here assumed, for the sake of convenience of nomenclature, to be molecular.) Comparing in this way HCl, H_2SO_4, and $C_6H_8O_7$ (citric acid), we have this result;—

[HClAq, $\frac{1}{2}$NaOHAq] = about 6,000	[H^2SO^4Aq, $\frac{1}{2}$NaOHAq] = about 7,000
[HClAq, NaOHAq] = „ 13,500	[H^2SO^4Aq, NaOHAq] = „ 14,500
[HClAq, 2NaOHAq] = „ 13,500	[H^2SO^4Aq, 2NaOHAq] = „ 31,000
	[H^2SO^4Aq, 3NaOHAq] = „ 31,000

[$C^6H^8O^7$Aq, NaOHAq] = 12,400
[$C^6H^8O^7$Aq, 2NaOHAq] = 24,800
[$C^6H^8O^7$Aq, 3NaOHAq] = 38,000
[$C^6H^8O^7$Aq, 4NaOHAq] = 38,000.

Hence we conclude that HCl is a monobasic, H_2SO_4 a dibasic, and $C_6H_8O_7$ a tribasic, acid.

The polybasic acids may also be classified in accordance with the thermal value of the action of each gram-molecule

of soda with one gram-molecule of acid. Thus, comparing oxalic with sulphurous acid, we find the difference between the quantities of heat produced during the action of the first and second molecules of soda, in the case of oxalic acid to be 600, and in that of sulphurous acid to be 2750: the data are,

Difference.

$[H^2C^2O^4Aq, NaOHAq] = 13{,}840$ / $[HNaC^2O^4Aq, NaOHAq] = 14{,}440$ } 600; 2750 { $[H^2SO^3Aq, NaOHAq] = 15{,}85$ / $[HNaSO^3Aq, NaOHAq] = 13{,}10$

Thomsen[1] divides the dibasic acids which he has examined into three groups:—

I. Those in the neutralisation of which each molecule of soda has the same thermal value: this group is at present represented by H_2SiF_6, and H_2PtCl_6[2].

II. Those in the neutralisation of which the first molecule of soda has a smaller thermal value than the second, the difference between the two values varying from 450 to 1900 units: this group contains the acids H_2SO_4, H_2SeO_4, $H_2C_2O_4$, and $H_2.C_4H_4O_6$.

III. Those in the neutralisation of which the first molecule of soda has a larger thermal value than the second, the difference between the two values varying from 1850 to 2750 units: the acids in this group are H_2SO_3, H_2SeO_3, H_2CO_3, and $H_2B_2O_4$; H_2CrO_4, H_2PHO_3, and $C_2H_4(CO_2H)_2$ also probably belong to this group, although the differences between the thermal values of the first and second molecule of soda are smaller in the case of these acids than of those already mentioned.

Thomsen suggests (I. pp. 304-5) that the foregoing classification of dibasic and tribasic acids may be summarised in these typical formulæ:—

Dibasic Acids.

Acid of Group I.	Typical formula	RH_2	e.g. $SiF_6.H_2$;
„ II.	„	$R(OH)_2$	e.g. $SO_2(OH)_2$;
„ III.	„	$R(OH)H$	e.g. $SO_2(OH)H$.

[1] *loc. cit.* 1. 302—306.

[2] But it seems doubtful whether the numbers obtained by Thomsen really represent the neutralisation of this acid. See *Thermochemische Untersuchungen*, I. 229.

Tribasic Acids.

Acid of Group II. Typical formula $R(OH)_3$ e.g. $C_4H_5O_4(OH)_3$;
„ III. „ $HR(OH)H$ e.g. $HPO_3(OH)H$.

The 'heat of neutralisation of a base' is defined by Thomsen[1] to be the thermal value of the change which occurs when equivalent quantities of base and acid react in dilute aqueous solution, the products of the action being also soluble in water. A dilute solution of one gram-molecule of sulphuric acid (i.e. the amount of acid, in grams, expressed by the formula H_2SO_4) is employed; temperature being 18°—19°.

In other words, Thomsen measures the thermal values of the following reactions:—

$[H^2SO^4Aq, 2MOHAq$ or $2NX^3Aq]$ in the case of a mono-acid base,
$[H^2SO^4Aq, M(OH)^2Aq$ or $N^2X^6Aq]$ „ di-acid „
$[H^2SO^4Aq, \frac{2}{3}M(OH)^3Aq$ or $\frac{2}{3}N^3X^9Aq]$ „ tri-acid „
$[H^2SO^4Aq, \frac{1}{2}M(OH)^4Aq$ or $\frac{1}{2}N^4X^{12}Aq]$ „ tetracid „
($X = H$, or a radicle C_nH_{2n+1})

The bases which are soluble in water may be divided into two thermal groups:—

I. The group of the hydrates or hydroxides, represented by NaOH and KOH.

II. The group of the anhydrous bases, represented by NH_3.

The first group comprises LiOH, NaOH, KOH, and TlOH; $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$; $N(CH_3)_4OH$, $(C_2H_5)_3S.OH$, and $Pt(NH_3)_4(OH)_2$: the mean value of the change $[H^2SO^4Aq, 2MOHAq$ (or $M(OH)^2Aq)]$ is equal to 31,350 units, when M(OH) or $M(OH)_2$ is one of the bases of this group.

The second group comprises NH_3 and the amines of the form $NH_2(C_nH_{2n+1})$ and $NH(C_nH_{2n+1})_2$: the mean value of the change $[H^2SO^4Aq, 2NX^3Aq]$ is equal to 28,200, when NX^3 is one of the bases of this group.

Substitution of negative radicles for H in NH_3 causes a considerable decrease in the heat of neutralisation of the base; thus,

$[2NH^2(C^6H^5)Aq, H^2SO^4Aq] = 15{,}500$,
$[2NH^2(C^7H^7)Aq, H^2SO^4Aq] = 15{,}200$;
$[2NH^2OHAq, H^2SO^4Aq] = 21{,}600$.

[1] See especially *loc. cit.* 1. 422—449.

When CO is substituted for H_2 in $2NH_3$, the heat of neutralisation of the product $[(NH_2)_2CO]$ is almost nil.

Measurements of the quantities of heat produced during the reactions of acids with those bases which are insoluble in water shew great irregularities. The true heats of neutralisation of these bases cannot be determined. But from the analogies between the hydrates of barium, strontium, and calcium, and those of magnesium, zinc, and manganese[1], Thomsen concludes that the heats of neutralisation of the bases of the magnesian class are equal to those of the bases of the akaline earth metals; but as the heats of neutralisation of the latter and of the alkalis are equal, Thomsen argues that the mean value of the heat of neutralisation of $M(OH)_2$, when M = Mg, Mn, Ni, Co, Fe, Cd, Zn, or Cu, is 31,350 units.

From what has been said regarding the classification of acids in accordance with their heats of neutralisation[2], it will be apparent that if 2HClAq is substituted for H_2SO_4Aq in the preceding reactions, the mean heats of neutralisation of the two groups of bases will be represented by numbers smaller than 31,350 and 28,200 respectively.

The identity of the numbers expressing the heats of neutralisation of bases of such different composition as KOH and $Pt(NH_3)_4(OH)_2$ points to the possibility of connecting similar changes of energy with similarity of chemical type, maintained through series of more or less unlike individuals. The heats of neutralisation of the bases MX_3 also point to the existence of a relation between change of energy and composition; but the influence of the structure of the individual substance is shewn in the small values obtained for $NH_2(C_6H_5)$ and $NH_2(C_7H_7)$, in which, although the chemical type is maintained, the typical thermal value is widely departed from.

The quantity of heat produced in the reaction [2MOHAq, HXAq] when M = K, Na, &c. is nearly constant, whether X = Cl, Br, or I; but the value of the reaction $[PbO.H_2O$, HXAq], or $[Tl_2O.H_2O$, HXAq] &c. differs very considerably

[1] See Thomsen, *loc. cit.* 1. 435—440.

[2] See *ante*, p. 270.

according as X = Cl, Br, or I. In the reaction with $PbO.H_2O$, the thermal value is greatest for HIAq, and least for HClAq. Now in the reactions just mentioned, haloid salts are produced which are only slightly soluble: if the heats of solution of these salts are added to the values of the apparent heats of neutralisation of the bases, it is found that the true heats of neutralisation of $PbO.H_2O$, $Tl_2O.H_2O$ &c. are represented by the same number, whether HClAq, HBrAq, or HIAq is the acid employed. If it is granted that the true heats of neutralisation of these acids are the same for other bases which form insoluble haloid salts, it becomes possible to calculate the heats of solution of these salts. Thomsen has done this for $PbCl_2$, $PbBr_2$, PbI_2, AgCl, &c., and, carrying out the same method, he has even given a value for the heat of solution of barium sulphate.

Thomsen's investigation of the heats of neutralisation of acids and bases serves to shew the complexity of many of the reactions to which thermal values are assigned, and also the necessity of making all the conditions of the changes we wish to study as exactly comparable as possible. At the same time it illustrates one of the dangers which beset the employment of thermal methods in chemistry, the danger namely of theorising regarding chemical changes which do not occur, and of speculating about chemical compounds which have no existence[1].

129 The primary aim of thermal chemistry was stated in par. 117 to be the measurement of the differences between the quantities of energy possessed by chemical systems when in certain definite initial and final states; the basis of these measurements being the deduction from the general theory of energy which states, that the total loss of energy during the passage of a chemical system from a definite initial to a definite final state is independent of the intermediate states.

The application of this generalisation was illustrated in par. 120; but we may now examine a little more closely the

[1] Section 2, of Chap. III. of *The Elements of Thermal Chemistry* is devoted to the consideration of neutralisation-phenomena.

connexion between thermal and material changes occurring in the same chemical system.

130 When heat is imparted to a gaseous system of chemical substances, a portion may be employed in increasing the kinetic energy of the molecules, i.e. in raising the temperature of the system; another portion may be employed in doing work against external forces, e.g. in causing expansion of the system; and another portion may do work against molecular and atomic forces, and so produce a rearrangement of molecules, or atoms, i.e. may cause chemical changes to proceed within the system. The exact manner of the distribution of the energy imparted in the form of heat will vary in each case. If the purely chemical part were separated from the other parts of the complete change, it is evident that the thermal value of this part would be a constant quantity only under constant physical conditions. Thus the difference between the energy of the system $2H_2 + O_2$ and that of the system $2H_2O$ (both in grams) at ordinary temperatures, say at 15°, is measured by 136,800 thermal units; but if the initial system is at 200° and the final system is at 15° the difference will be only 116,500 units[1]; assuming that the total loss of energy to the system during the change is measured in each case by the quantity of heat produced. Indeed in some cases change of temperature may reverse a process both chemically and thermally without altering the nature or the masses of the reacting substances; thus

at ordinary temperatures $2H_2O + 2Cl_2 = 4HCl + O_2$ .....(1)

but at about 200° $4HCl + O_2 = 2H_2O + 2Cl_2$ .....(2);

if reaction (1) is expanded thermally it becomes

$$[2H^2OAq, 2Cl^2Aq] = 4[H, Cl, Aq] - 2[H^2, O, Aq] = 20{,}400 \text{ units}:$$

if reaction (2) is treated in the same way we have

$$[4HCl, O^2] = 2[H^2, O] - 4[H, Cl] = 28{,}500 \text{ units (at 200°)}.$$

If the reaction occurs between bodies in solution, the quantity of heat which is produced or disappears will be dependent on the temperature, and in determining the thermal value of the chemical change it will be necessary to determine

[1] For the method of calculation, see *The Elements of Thermal Chemistry*, par. 57.

the specific heat of a solution of each of the reacting bodies and of each of the products of the reaction[1]. Heat may also be produced or disappear in changes of volume, or changes in the states of aggregation, of the reacting bodies; thus any comparisons or contrasts instituted between hydrochloric, hydrobromic, and hydriodic, acid from a consideration of these numbers,

$$[H, Cl]=22{,}000;\ [H, \mathrm{Br}]=8{,}440;\ [H, \mathrm{I}]=-6{,}050$$

must be accepted with great reserve, because at ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid; the reactions formulated are not, therefore, strictly comparable.

131 There is another point to be noticed in analysing the thermal changes which accompany chemical processes, viz., that the ordinary notation usually represents a chemical change as a much simpler phenomenon than it really is. Most chemical reactions are accomplished only by employing 'an excess,' sometimes a large excess, of one or more of the reacting substances: thus the equation

$$\mathrm{AgCl}+\mathrm{HI}\ (\text{grams})=\mathrm{AgI}+\mathrm{HCl}$$

would more nearly express the distribution of the masses of the reacting bodies if it were written

$$x\,\mathrm{AgCl}+x'\mathrm{HI}=x''\,\mathrm{AgI}+x''\mathrm{HCl}+(x-x'')\,\mathrm{AgCl}+(x'-x'')\,\mathrm{HI}.$$

Potilitzin has investigated this subject of the relations between the thermal value of a change and the masses of the changing substances[2]. The heat of formation of a metallic chloride is greater as a rule than that of the corresponding bromide,

$$[\mathbf{MBr}, Cl]=[\mathbf{M}, Cl]-[\mathbf{M}, Br]>0.$$

Again it is generally true that

$$[\mathbf{MBr}, HCl]=[\mathbf{M}, Cl]+[H, Br]-[\mathbf{M}, Br]-[H, Cl]<0;$$

e.g. $[\mathbf{AgBr}, HCl]=-6{,}900$: $[\mathbf{KBr}, HCl]=-3{,}250$; $[\mathbf{NaBr}, HCl]=-1{,}600$. Therefore, it would appear probable that chlorine should decompose metallic bromides, but that hydrochloric acid should not react with these salts.

But Potilitzin's experiments shew that the reaction

$$x\mathrm{MCl}+x'\mathrm{Br}=x''\mathrm{MBr}+x''\mathrm{Cl}+(x-x'')\,\mathrm{MCl}+(x'-x'')\,\mathrm{Br}$$

[1] See *The Elements of Thermal Chemistry*, par. 55.

[2] See abstract in *Ber.* **14.** 2044; and **15.** 918; also **16.** 3051.

proceeds at 275—300° when MCl and Br are employed in equivalent quantities, (M = K, Na, or Ag), and also that when MBr and Cl react in equivalent quantities the whole of the bromine is not replaced by the chlorine.

By increasing the amount of bromine, relatively to MCl, in the reaction above formulated, more MBr is produced until a limit is reached whereat equilibrium is established. This equilibrium is not overthrown even by increasing the mass of bromine, raising the temperature, and prolonging the time of action.

132 I think the position has now been clearly established that the thermal value of a chemical change, even of a simple reaction between gaseous substances, really represents the sum of various changes some of which have a positive and others a negative value. Assuming that in any case it is possible to separate the gain or loss of energy, measured thermally, during a definite chemical reaction, into a portion representing physical changes and another portion representing purely chemical changes, it is nevertheless generally the case that the latter portion of the total energy-change must itself be analysed before an accurate and precise application of the thermal value can be made; that is if the application is to proceed on the lines of the molecular and atomic theory. For, assuming that we have made due allowance for the influence of the masses of the reacting substances and for the possible formation and decomposition of molecular groups during the reaction, there yet remains the important consideration that heat is produced or disappears not only in the formation or the decomposition of compounds, but also in reactions of decomposition or formation of elements, which take part in the chemical process.

Let us analyse a comparatively simple reaction;

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

When this is expanded thermally we have

$$[2H^2O, 2Cl^2] = 4[H, Cl] + [O, O] - 2[H^2, O] - 2[Cl, Cl].$$

That is to say, heat is used in separating each chlorine molecule into atoms, and heat is produced in the union of each pair of oxygen atoms to form a molecule.

Let us take an apparently more simple instance

$$[H^2, Cl^2] = 44{,}000 \text{ units.}$$

Remembering the fundamental distinction between atoms and molecules, and moreover bearing in mind the fact that the molecules of hydrogen and chlorine are both diatomic, we may expand this equation thus

$$[H^2, Cl^2] = 2[H, Cl] - [H, H] - [Cl, Cl] = 44{,}000.$$

But we do not know the true thermal value of any one of the three parts of this reaction; when therefore we write $[H^2, Cl^2] = 44{,}000$, we use a short way of expressing the fact that when 2 grams of gaseous hydrogen combine with 71 grams of gaseous chlorine to produce 73 grams of gaseous hydrochloric acid, at ordinary temperatures, 44,000 gram-units of heat are produced.

As long as thermal measurements are regarded in this way they convey precise and important information. But we want something more than this; we desire to have some light thrown on the rationale of chemical changes. Now our most far-reaching conceptions in chemistry are based on the distinction implied in the terms atom and molecule; until then this distinction is practically recognised in thermal chemistry, we cannot expect great advances to be made in applying the mass of data already accumulated to questions of the mechanism of chemical change.

133 In the Introduction to volume I. of his *Essai de mécanique chimique*, Berthelot lays down three fundamental principles of thermal chemistry [p. xxviii—xxix].

(1) The quantity of heat produced in a reaction measures the sum of the physical and chemical changes which occur in that reaction.

(2) The total thermal value of a reaction is dependent only on the initial and final states of the changing system.

(3) Every chemical change accomplished without addition of energy from without tends to the formation of that body or system of bodies the production of which is accompanied by the development of the maximum quantity of heat.

The first and second principles have already been illustrated and discussed. The third, under the name of the "law

of maximum work" forms the basis of all Berthelot's thermochemical generalisations. It is stated in an even more rigid form as the *theorem of the necessity of reactions*[1], "Every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system necessarily occurs if it is accompanied by disengagement of heat."

This so-called *law of maximum work* may be shewn theoretically to be untrue[2]; but even supposing it were true, I think that if the fundamental distinction between atom and molecule is clearly grasped it will be seen that Berthelot's statement is too general to throw much light on chemical changes.

Berthelot's law is simply a crude application of the principle of the degradation of energy; the principle, namely, that energy always tends to run down from a more available to a less available form. Inasmuch as the formation of a chemical compound, with production of heat, is an instance of such running down of energy, from the form of chemical affinity to that of heat, it follows that the reversal of this process will require the expenditure of work. But the *law of maximum work* does not attempt to analyse the expression *chemical affinity*. Under this term Berthelot includes actions and reactions of different kinds. This is at once apparent from the statement in the *Essai*[3] that the first fundamental principle of thermal chemistry, viz.—"the quantity of heat produced in a reaction measures the sum of the physical and chemical changes which occur in that reaction"—furnishes the measure of chemical affinities[4].

Berthelot's work is saturated with the conceptions of the molecular theory: but, by some fatal perverseness, he refuses to apply this theory to chemical phenomena. While recognising the existence of molecules and building his generalisations on a molecular foundation, he refuses to accept the

[1] *loc. cit.*; Introduction, p. xxix., also 2. 422.
[2] See Book II. Chap. II. par. 191.
[3] Introduction, p. xxviii.
[4] '*Ce principe fournit la mesure des affinités chimiques.*'

conception of atom, or rather he hopelessly confuses it with that of equivalent. The molecule is for him a definite and definable portion of matter, the parts of the molecule are only numbers.

If by chemical affinity is meant an action and reaction between atoms, then the principle already quoted certainly does not afford a measure of this affinity.

Berthelot's law, then,—assuming its truth—appears to be a definite statement applicable to chemical reactions; but more precise investigation shews that the application is only possible when 'chemical' is used in a vague way as including much that is usually called 'physical.'

The principle of the degradation of energy is a highly generalised statement applicable to certain cycles of change; Berthelot attempts to apply it to parts of such cycles, forgetting that what is true of the whole is not necessarily true of the parts.

Thirty years ago Thomsen[1] generalised the relations between chemical action and thermal change in the statement, "Every simple or complex reaction of a purely chemical kind is accompanied by production of heat."

If by a reaction 'of a purely chemical kind' is meant the combination of atoms to form molecules, no objection can be made to this statement; we recognise its importance and universality, as we recognise the same qualities in such statements as 'all men are mortal,' or 'no white men are black.' But we may doubt its utility. Thomsen explains[2] that 'reactions of a purely chemical kind' are those which proceed without addition of energy from sources external to the system, and consist only of the strivings of atoms towards more stable equilibrium[3]. On the other hand a chemical system may be raised to a temperature such that its constituents are no longer stable, and reactions may then occur with expenditure of external energy; but these changes

[1] See *Thermochemische Untersuchungen*, 1. 12—16.

[2] *loc. cit.* 1. 16.

[3] "Der chemische Process ist rein chemischer Natur, wenn er ohne Aufwand fremder Energie verlauft, und nur durch das Streben der Atome nach mehr stabilen Gleichgewichtslagen zu Stande kommt."

do not depend solely on mutual atomic attractions. But actions 'of a purely chemical kind' never occur except as parts of cycles of reactions which include changes that do not consist 'solely of the strivings of atoms towards more stable equilibrium.' Hydrogen and oxygen do not combine to form water, neither do chlorine and hydrogen combine to form hydrochloric acid, without the addition of energy from external sources.

If the statements quoted from Thomsen or Berthelot are ever true, they are true only when an arbitrary separation is made of chemical changes into two parts, and one of these parts is alone called chemical. Every chemical change, however simple, consists of at least two parts, the first of which is the necessary antecedent of the second; the *law of maximum work* ignores this duality, or, it might be more accurate to say, the law assumes that the second part of a chemical process can occur without the first. Every process of chemical change may be compared to the flight of a stone from, and its return to, the surface of the earth. During the first part of this process there is a continual transference of kinetic energy from the moving stone to the surrounding medium, and during the second part there is a continual transference from the medium to the stone, until the stone comes to rest when its energy becomes a part of the total energy of the system, earth + stone. If the final resting-place of the stone is nearer the centre of the earth than the spot from which it was projected on its upward flight, then the stone contains less energy, relatively to surrounding systems, at the close of the transaction than at the beginning. On the other hand, if the starting-point is nearer the earth's centre than the final point of rest, then the transaction has resulted in gain of energy to the stone. In both cases the second part of the transaction, that which occurs between the turning-point and the final resting-point of the stone, is attended with loss of energy to the stone; but this second part does not represent the complete transaction. The *law of maximum work* if applicable at all is applicable only to the second part. And moreover this law ignores the fact that the stone (or chemical system)

does not leave its initial point of rest of its own accord; the law assumes that no work need be done, no energy expended, in the passage of the stone (or system) from its original position to that at which the energy-relations between it and surrounding systems come within the cognisance of the law.

134 An attempt has been made by Thomsen to measure the thermal values of the first parts, i.e. separation of molecules into atoms, of certain changes which result in the production of hydrocarbons. Attention has been already[1] drawn to this investigation. An account of Thomsen's argument by which he arrives at a certain thermal value for each of the four 'bonds' of the atom of carbon is given in *The Elements of Thermal Chemistry* (pars. 73—75). I will not reproduce that account here, but rather give a brief statement of another and later argument by which Thomsen has arrived at certain conclusions regarding the thermal values of the 'bonds' of the atom of carbon.

Thomsen[2] assumes (1) that the four 'bonds' or 'affinities' of an atom of carbon are of equal value, at least as regards combination with atoms of hydrogen, (2) that all the hydrogen atoms in the molecule of a hydrocarbon are bound to the carbon atom with equal vigour, and (3) that carbon atoms may be united together in three different ways, viz. by single, double, or treble, linkings.

The heat of combustion of a gaseous hydrocarbon molecule is theoretically divisible into two parts, (1) the heat used in separating the molecule into atoms of carbon and hydrogen, and (2) the heat produced in the combination of these atoms with oxygen to form carbon dioxide and water.

The formula C_aH_{2b} expresses the composition of paraffins. As each atom of carbon has four bonds, a atoms of carbon have $4a$ bonds; as each atom of hydrogen has one bond $2b$ atoms have $2b$ bonds; but every carbon atom must be united to another carbon atom by at least one bond, hence the total number of single linkings between the carbon atoms in a

[1] See *ante*, chapter II. section IV. par. 85.

[2] *Zeitschr. fur physikal. Chemie*, I. 369.

paraffin molecule C_aH_{2b} is

$$\frac{4a-2b}{2}=2a-b \quad \text{....(1).}$$

Let v be the work required to tear asunder two singly linked carbon atoms, then the work required to tear asunder all the singly linked carbon atoms in a paraffin molecule C_aH_{2b} is

$$(2a-b)v \quad \text{....(2).}$$

Let r be the work required to tear asunder an atom of hydrogen from an atom of carbon to which it is linked in the molecule C_aH_{2b}, then the work required to tear asunder all the hydrogen atoms in the molecule is

$$2br \quad \text{....(3).}$$

Hence the work required to isolate all the atoms composing the molecule C_aH_{2b} is

$$(2a-b)v+2br \quad \text{....(4).}$$

Let fc be the heat of combustion of an isolated gaseous carbon atom, and let fh_2 be the heat of combustion of two isolated gaseous hydrogen atoms, then the heat of combustion of the isolated atoms obtained by tearing asunder the molecule C_aH_{2b} will be

$$afc+bfh_2 \quad \text{....(5).}$$

And the difference between (4) and (5) will express the heat of combustion at constant volume of the gaseous molecule C_aH_{2b};

$$f.C_aH_{2b}=a(fc-2v)+b(fh_2-2r+v) \quad \text{....(6).}$$

The heat of combustion of the gaseous molecule C_aH_{2b} at constant pressure is found by taking into account the thermal change accompanying the change of volume from C_aH_{2b} to aCO_2+bH_2O; the expression is

$$f.C_aH_{2b}\text{ (const. press.)}=a(fc-2v)+b(fh_2-2r+v+290)+580 \quad \text{...(7).}$$

As this equation holds good for all paraffins, and as the expressions in brackets are the same for all, $fc-2v$ may be put as $=x$, and $fh_2-2r+v+290$ as $=y$; thus we get the simpler form

$$f.C_aH_{2b}\text{ (const. press.)}=ax+by+580 \quad \text{....(8).}$$

Thomsen then finds probable values for x and y from the following heats of combustion at constant pressure of five paraffins:—

$CH_4 = 211{,}930$ $C_2H_6 = 370{,}440$ $C_3H_8 = 529{,}210$
$CH(CH_3)_3 [= C_4H_{10}] = 687{,}190$ $C(CH_3)_4 [= C_5H_{12}] = 847{,}110.$

From these data, ten values for x and y are found, and from these the following most probable values are deduced by the method of least squares:—

$$x = 106{,}170 \qquad y = 52{,}530.$$

The heats of combustion of the five paraffins given above calculated with these values of x and y closely agree with the observed values; the largest difference is 720 units in the case of C_4H_{10}.

But when the observed heats of combustion of four olefines (C_aH_{2b} where $a = b$) are compared with the values calculated by the use of the above values for x and y, it is found that the observed are always much greater than the calculated numbers. The following data give the differences in question:—

$C_2H_4 \ldots 15{,}370$ $C_4H_8 \ldots 15{,}240$ $C_6H_{12} \ldots 32{,}570.$
$C_3H_6 \ldots 16{,}060$ $C_5H_{10} \ldots 15{,}550.$

In the molecule C_6H_{12} there are two double linkings between carbon atoms, and in each of the other molecules there is one double linking; therefore the mean increase of the observed over the calculated heat of combustion is 15,465 units for each double linking.

Thomsen then develops a formula for calculating the heat of combustion of a gaseous olefine in a way similar to that already sketched, but taking account of the existence of 'double linkings' in the olefine molecules: applying this formula he arrives at the conclusion that

$$2v - u_2 = 15{,}465 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9),$$

where v means, as before, the work required to tear asunder two singly linked gaseous carbon atoms, and u = the work required to tear asunder two doubly linked carbon atoms.

Thomsen then turns to the acetylenes (C_aH_{2b} where $b = a - 1$), and by similar reasoning to that applied to the

paraffins and olefines he concludes that

$$3v - w_3 = 43{,}922 \quad \text{.....(10)},$$

where v has the same meaning as before, and w represents the work required to tear asunder two trebly linked carbon atoms.

These results may be stated in various ways. If we regard a double link between carbon atoms as two several linkings, and a treble as three several linkings, then

$$u + 7732 = v, \text{ and } w + 14640 = v.$$

Thomsen's results are thus equivalent to asserting that the quantity of heat produced in forming the hypothetical group $\equiv C - C \equiv$ from gaseous isolated carbon atoms is 7732 units greater than half the quantity of heat produced in forming the hypothetical group $= C = C =$ from carbon atoms, and is 14640 units greater than one-third of the quantity of heat produced in forming the hypothetical group $- C \equiv C -$ from atoms of carbon. Or, let the heat produced in forming $= C = C =$ from $-\overset{|}{C}-$ and $-\overset{|}{C}-$ be x units, then the heat produced in forming $\equiv C - C \equiv$ from the same carbon atoms is $\frac{x}{2} + 7732$ units; and let the heat produced in forming $- C \equiv C -$ from $-\overset{|}{C}-$ and $-\overset{|}{C}-$ be y units, then the heat produced in forming $= C - C =$ from the same materials is $\frac{y}{3} + 14640$ units.

Thomsen's values represent differences; in this paper he does not attempt to find the actual thermal value of either a single, a double, or a treble, linking between carbon atoms.

If the combination of a pair of carbon atoms by a double link is regarded as occurring in two parts each bond having its own thermal value, then Thomsen's numbers assert that each half of this process is accompanied by the production of rather less heat than half of that produced when two carbon atoms combine by a single bond.

If we admit the justness of Thomsen's conclusions we shall be forced to acknowledge that the bonds of the carbon atom are of unequal value; but one of the assumptions on which

Thomsen has based his argument is that the bonds in question are equal in value. In one case however *value* here means chemical value and in the other it means thermal value. Both terms, value and bond, are misleading. Instead of the frequently used expression, 'in the molecule CH_4 all the bonds of the carbon atom are of equal value,' it would be much better to say, 'in the molecule CH_4 each hydrogen atom is related to the carbon atom and to the rest of the molecule in the same way as every other hydrogen atom.'

It should be noted that the conclusions arrived at by Thomsen are applicable only to hydrocarbons, and that they are based on but scanty data.

If, as Thomsen's results assert, the thermal value of a carbon bond depends on whether that bond is satisfied by the bond of another carbon atom or by that of a hydrogen atom, it is almost certain that the thermal value of the carbon bond will vary according as it is satisfied by the bond of an oxygen, a sulphur, or a chlorine, &c. atom; and if this is so, then in all probability the thermal value of each bond of the atom of oxygen, sulphur, &c., will vary with the nature of the other atoms with which the atom of oxygen or sulphur is combined. The affinity of atoms for atoms cannot be measured by the thermal values of the atomic bonds. Indeed these bonds are wholly imaginary existences; they are protean and for ever escape one's grasp; whether the conception we try to form of them be purely chemical or partly chemical and partly thermal, it is at the best but a blurred and wavering image which comes between us and reality.

135 A few generalisations have been established regarding the connexion between the structure and the boiling points of carbon compounds. Thus the difference between the boiling points of two consecutive members of an homologous series of carbon compounds is frequently about 19°: but the numbers actually obtained shew that variations in the boiling points are connected with variations other than those of molecular weight. Goldstein[1] attempts to shew that the proportion

[1] *Ber.* **12.** 689: also abstract of paper in Russian, *C. S. Journal* **Abstracts for 1882,** 374.

between the numbers of hydrogen and carbon atoms, besides the total number of these atoms, influences the boiling points of the members of an homologous series. Hydrocarbons of analogous constitution must be compared, i.e. normal hydrocarbons must be compared with normal,

e.g. $CH_3-CH_2-CH_2-CH_3$ with $CH_3-CH_2-CH_2-CH_2-CH_3$;

or iso-hydrocarbons must be compared with iso-, e.g.

$CH(CH_3)_2-CH_2-CH_3$ with $CH(CH_3)_2-CH_2-CH_2-CH_3$;

nor can the differences between the boiling points of normal hydrocarbons be compared with the differences between the boiling points of iso-compounds.

Goldstein investigates the change of boiling point in the series of normal paraffins, i.e. hydrocarbons of the form $CH_3-(CH_2)_x-CH_3$ [or $CH_3-CHR'-CH_3$]. He gives the formula

$$\text{B. P.} = \text{b. p.} + \left(19 + \frac{380}{n(n+1)}\right),$$

where B. P. = boiling point required, b. p. = boiling point of the paraffin containing CH_2 less than that whose B.P. is required, and n = number of atoms of carbon in the molecule of the paraffin whose b. p. is known. Thus, the boiling point of C_5H_{12} (i.e. $CH_3(CH_2)_3CH_3$) is 39°·0; required the boiling point of C_6H_{14} (i.e. $CH_3(CH_2)_4CH_3$).

$$\begin{aligned}\text{B.P. required} &= 39+\left(19+\frac{380}{n(n+1)}\right)\\ &= 39+19+\frac{380}{30}\\ &= 39+19+12{\cdot}66\\ &= 70°{\cdot}66 \qquad\qquad \text{B.P. observed} = 70°{\cdot}6.\end{aligned}$$

Goldstein calculated the B.P. of normal heptane (C_7H_{16}) to be 98°·65; shortly after this, the paraffin was obtained in quantity by Thorpe, and the boiling point was found to be 98°·5.

The same formula appears to hold good for determining the difference between the boiling points of any two consecutive iso-paraffins belonging to the form $CH(CH_3)_2-(CH_2)_x-CH_3$.

Thus,

		B.P.	*Difference*	
(*a*)	$CH(CH_3)_2-CH_2-CH_3$	30°·5	31°·5	...calculated difference = 31°·66.
(*b*)	$CH(CH_3)_2-(CH_2)_2-CH_3$	62°·0		

If this is so, it follows that the difference between the boiling point of a normal paraffin and its corresponding iso-paraffin (of this form) must be the same whatever be the molecular weight of the two isomerides. Experiment, so far as it has gone, seems to confirm this result; thus,

Formula.	Difference between B P of normal and iso-paraffin.
C_5H_{12}	8°·5
C_6H_{14}	8°·6
C_7H_{16}	8°·5

We have very little precise knowledge regarding the boiling points of isomeric hydrocarbons. From the data accumulated it has been concluded, that, of two or more isomeric hydrocarbons, that one has the lowest boiling point the molecule of which is characterised by containing the greatest number of 'side chains'[1]. Thus

		B.P.
	Pentane (C_5H_{12}).	
(*a*)	normal :—$CH_3(CH_2)_3-CH_3$	39°
(*b*)	isopropyl-methylmethane :—$CH_2-CH(CH_3)_2-CH_3$	30°·5
(*c*)	tetramethylmethane :—$C(CH_3)_4$	9°·5
	Hexane (C_6H_{14}).	
(*a*)	normal :—$CH_3(CH_2)_4CH_3$	70°·5
(*b*)	isopropyl-ethylmethane :—$CH_2-CH(CH_3)_2-C_2H_5$	62°
(*c*)	di-isopropyl :—$CH(CH_3)_2-CH(CH_3)_2$	58°
(*d*)	trimethyl-ethylmethane :—$C(CH_3)_3(C_2H_5)$	43°—48°

The replacement of one or more atoms in a molecule by another atom or other atoms is attended with a change of boiling point. The data accumulated point to the existence of definite relations between the boiling points of the compounds and the nature and relative positions in the molecules of the substituted and substituting atoms. Thus the change from a hydrocarbon to an alcohol by substitution of OH for H is accompanied in many cases by a rise of about 100° in the boiling point; the change from a monohydric to a dihydric

[1] For data see Naumann, *loc. cit.* pp. 168—172.

alcohol is also attended by a rise of B. P. amounting to about 100°; the substitution of a bromine atom for an atom of chlorine in chloroderivatives of hydrocarbons is accompanied by a rise of B. P. equal to about 23°, and the value of the increase is nearly constant in very many cases[1].

136 In this section I have tried to trace some of the connexions between the results of thermal measurements of chemical phenomena and certain statical aspects of these phenomena. We have found that every chemical phenomenon is a complex occurrence, and that it is almost impossible fully to distinguish those portions which would more appropriately be called physical from those which are undoubtedly chemical. We have also found that thermal measurements, being essentially measurements of changes of energy, are intimately connected with problems belonging to chemical kinetics, and that until we know something of chemical affinity we are not in a position fully to discuss the data of thermal chemistry.

SECTION II. *Optical Methods.*

137 In this section I wish to give some account of the attempts which have been made to elucidate the relations existing between the composition of chemical compounds and (1) the refractive powers, (2) the power of rotating a ray of polarised light, and (3) the absorption-spectra, of these compounds. The subject is more limited than that considered in the first section of the present chapter; it belongs more completely than thermal chemistry to the domain of chemical statics, although like other questions in chemical science it presents aspects which are essentially kinetical.

138 Let a ray of light pass from air into a liquid medium denser than air; let the angle of incidence $= i$, and the angle of refraction $= r$; then $\frac{\sin i}{\sin r} = \mu =$ *refractive index* of the medium.

[1] An account of the present state of knowledge regarding the connexions between the B.P. and constitution of carbon compounds will be found in a pamphlet by W. Marckwald, *Über die Beziehungen zwischen dem Siedepunkte und der Zusammensetzung chemischer Verbindungen* (Friedlander, Berlin, 1888).

Let the light employed consist only of light of one wave-length, and let the liquid medium consist of a single definite chemical compound, then the quantity $\left(\frac{\mu-1}{d}\right)$ was called by Gladstone and Dale[1] the *specific refractive energy* of the liquid examined (d = spec. grav. of the liquid referred to water as unity). Landolt[2] called the product obtained by multiplying $\left(\frac{\mu-1}{d}\right)$ into the molecular weight of the liquid, i.e. $\left(\frac{\mu-1}{d}\right) M$, the *refraction-equivalent* of the liquid compound in question.

The quantity $\left(\frac{\mu-1}{d}\right)$ was said by Gladstone and Dale to be independent of temperature[3].

Objection has been taken to the use of this purely empirical formula in attempts to trace connexions between the constitution and refractive powers of compounds[4]. The formula $\left(\frac{\mu^2-1}{\mu^2+2}\right).\frac{M}{d}$ for finding the refraction-equivalent of a compound was deduced from the general principles of Clerk Maxwell's electro-magnetic theory of light by A. Lorenz, and also independently by H. Lorenz[5]. The formula $\left(\frac{A^2\mu-1}{A^2\mu+2}\right).\frac{M}{d}$, where $A\mu$ = refractive index of the theoretical ray of infinite wave-length, was deduced by the use of a method given by Cauchy, and was supposed to give results practically independent of dispersion. Other formulæ have been proposed by different physicists. Brühl[6] has recently examined all the formulæ hitherto proposed for calculating the refraction-equivalents of compounds; he concludes that no formula gives the true laws of dispersion, and that none of them enables us to determine whether a limiting value independent

[1] *Proc. R. S.* **12.** 448, and *Phil. Trans.* **153.** 317.

[2] *Pogg. Ann.* **122.** 545; and **123.** 595.

[3] See *Proc. R. S.* **18.** 49; and also *Phil. Trans.* **160.** 9.

[4] See especially Wiedemann, *Ber.* **16.** 467.

[5] *Wied. Ann.* **9.** 641; **11.** 70.

[6] *Ber.* **19.** 2821 (references are here given to many other memoirs).

of dispersion does or does not exist for the quotient $\frac{\mu-1}{d}$.

Brühl states that the influence of the dispersion of different bodies on their refractive powers has not been satisfactorily deduced from any optical theory; and that in investigations into the connexions between the refractive powers and the chemical constitution of compounds the influence of dispersion must be neglected if it cannot be eliminated by purely empirical methods.

Of the different formulæ proposed, Brühl prefers

$$\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{M}{d},$$

because it gives results which are more consistent and less influenced by changes of temperature than those obtained by any of the other formulæ.

139 In 1863 Gladstone and Dale[1] concluded that 'every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, modified by the manner of combination.' Many and lengthy memoirs have been published on this subject since 1863; the general result has been to confirm the statement of Gladstone and Dale, and at the same time to trace a more precise connexion between the refraction-equivalent of a compound and the manner in which the elements of that compound are combined. One of the fullest and most important memoirs is that published in 1887 by Bruhl[2]. As this investigation includes many of the results formerly obtained I propose to confine myself in the main to giving an account of this work. Investigations have been confined hitherto chiefly to liquid compounds of carbon.

140 Let us follow Bruhl in calling the product of the specific refractive energy and the molecular weight of a compound the *molecular refraction* (R), and the product of the specific refractive energy and the atomic weight of an element

[1] See *Phil. Trans.* **160.** 9.

[2] *Annalen*, **235.** 1; or *Ber.* **19.** 2746; or *Zeitschr. fur physikal. Chemie*, **1.** 307.

the *atomic refraction* (r). And, as Brühl does, let us use the following formulæ for determining these constants:—

$$\left(\frac{\mu^2-1}{\mu^2+2}\right)\cdot\frac{M}{d} \text{ and } \left(\frac{\mu^2-1}{\mu^2+2}\right)\cdot\frac{A}{d},$$

where M = molecular weight, and A = atomic weight[1].

Assuming that the molecular refraction of a compound is the sum of the atomic refractions of its constituent elements, and that the refraction of each atom has a constant value in all its compounds, we may express the molecular refraction (R) of a compound of carbon hydrogen and oxygen, $C_nH_{2m}O_p$, as

$$(R)=n(r)C+2m(r)H+p(r)O$$

where (r)C, (r)H, and (r)O represent the atomic refractions of carbon, hydrogen, and oxygen, respectively.

By determining the differences between the molecular refractions of members of an homologous series of carbon compounds, values are obtained for what may be called the molecular refraction of the group CH_2; by determining the differences between the molecular refractions of a series of compounds, differing by 2H, values are obtained for the atomic refraction of hydrogen; and by deducting the value for 2H from that for CH_2, a number is obtained which is taken as the atomic refraction of carbon. By similar methods a value can be found for the atomic refraction of oxygen. The molecular refraction of any compound of carbon hydrogen and oxygen can then be calculated, on the assumption that the value is equal to the sum of the atomic refractions of the constituent elements, and compared with the observed value.

141 The calculated values for (R) do not agree in every case with the observed values. Hence the molecular refraction of a compound is probably connected with the arrangement, as well as with the nature and number, of the atoms which compose the molecule of the compound. What then is the nature of the connexion between the arrangement of the atoms forming a molecule and the refraction of that molecule?

Brühl thinks that the present data warrant general con-

[1] Brühl uses light with the wave-length of the ray C; many observers determine μ for the red hydrogen line H_α.

clusions only regarding compounds of carbon, hydrogen, and oxygen.

The paragraphs devoted to isomerism (par. 69 *et seq.*) contain data which shew that isomerism may be connected either with changes in the actual valencies of the atoms forming a molecule, or with changes in the distribution of the interatomic reactions. Thus, the formula C_3H_6O expresses the composition of (1) propylic aldehyde, (2) acetone, and (3) allylic alcohol; assuming the correctness of the structural formulæ of these three compounds, viz.

(1) $H_3C-CH_2-C\begin{smallmatrix}O\\H\end{smallmatrix}$, (2) $H_3C-\underset{\underset{O}{|}}{C}-CH_3$, (3) $H_2C-CH-CH_2OH$,

(1) and (2) contain each a trivalent carbon atom and a monovalent oxygen atom in direct union, and also a pair of tetravalent carbon atoms, and (3) contains two trivalent carbon atoms neither of which is in direct union with oxygen, and also a tetravalent carbon atom in direct union with an atom of oxygen which is divalent. The actual valencies of the atoms are the same in (1) as in (2), but are not the same in (3) as in (1) or (2); the distribution of some of the interatomic reactions varies in (1), (2) and (3). In none of these cases is the molecule saturated, i.e. in no case does each polyvalent atom directly interact with its maximum number of monovalent atoms (see *ante*, par. 70). These examples shew that isomerism occurring in unsaturated molecules may be connected either with changes in the actual valencies of some of the atoms or with changes in the distribution of the interatomic reactions. But when isomerism occurs in saturated molecules it must be connected with changes in the distribution of the interatomic reactions and not with changes in the actual valencies of the atoms, because saturated molecules are, by definition, those in which each polyvalent atom directly interacts with its maximum number of monovalent atoms. The following structural formulæ for different propylic alcohols (C_4H_9OH) illustrate this kind of isomerism:—

$$H_3C-CH_2-CH_2-CH_2OH, \quad \begin{smallmatrix}CH_3\\ \diagup\\ CH-CH_2OH\\ \diagdown\\ CH_3\end{smallmatrix}, \quad \begin{smallmatrix}CH_3\\ \diagup\\ HO-C-CH_3\\ \diagdown\\ CH_3\end{smallmatrix}.$$

That kind of isomerism which is exhibited only by unsaturated molecules and is connected with changes in the actual valencies of the atoms is called by Bruhl *saturation-isomerism*, while that kind of isomerism which is exhibited both by saturated and unsaturated molecules and is connected with changes in the distribution of the interatomic reactions unaccompanied by changes of valencies is called by Brühl *position-isomerism*.

Bruhl's data shew that different *saturation-isomerides* of the general form $C_xH_yO_z$ have different molecular refractions, but that the molecular refraction of a series of *position-isomerides* of the general form $C_xH_yO_z$ is nearly a constant quantity.

In order to find the exact influence on the molecular refraction of a compound $C_xH_yO_z$ of changes in the valencies of the carbon and oxygen atoms, Brühl first finds values for the atomic refraction of the tetravalent carbon atom and the divalent oxygen atom in saturated molecules. The difference between (R) for each pair in the homologous series C_nH_{2n+2} gives a value for (R) CH_2; as the formula C_nH_{2n+2} can be expressed as nCH_2+H_2, the same data allow a value for (R)H_2 to be found; the difference between (R)CH_2 and (R)H_2 gives (r)C. By similar methods (r) O is found.

Taking C^{IV} and O^{II} to represent a tetravalent atom of carbon and a divalent atom of oxygen, respectively, then Brühl's data lead to the values[1]

(r) $C^{IV}=2{\cdot}48$; (r) $O^{II}=1{\cdot}58$; (r) $H=1{\cdot}04$.

Values of (R) are then calculated for unsaturated compounds containing a pair of directly interacting trivalent carbon atoms, using the above values for (r) C &c., and the calculated values are compared with those obtained by experiment.

The influence on (R) of the change from a pair of directly interacting tetravalent carbon atoms to a pair of directly interacting trivalent carbon atoms is then determined; Brühl's data, given for about 20 compounds of the general form C_xH_y, $C_xH_yO_z$,

[1] The formula $\left(\frac{\mu^2-1}{\mu^2+2}\right).\frac{M}{d}$ is used, and μ is determined for the line *C*.

and $C_vH_yCl_wO_z$, shew that this change is accompanied by an increase in (R) amounting to about[1] 1·85. Determinations of (R) for seven compounds[2] each containing two pairs of directly interacting trivalent carbon atoms, shew a mean increase in (R) of $2 \times 1{\cdot}75$.

Brühl states these results by saying that the mean partial value of an *ethylene grouping of a pair of carbon atoms* in the molecular refraction of a compound of the form $C_xH_yO_z$ is 1·75. The phrase *ethylene grouping of two carbon atoms* is used because ethylene, H_2C-CH_2, is the simplest compound containing a pair of directly interacting trivalent carbon atoms.

Brühl then determines (R) for various ketones, aldehydes, and other compounds $C_nH_{2n}O$ containing a monovalent oxygen atom in direct union with an atom of carbon, or it may be said containing a carbonyl group, $C-O$, and by subtracting (R) C_nH_{2n} ($=nCH_2$), he obtains the mean partial value of a *carbonyl grouping of an oxygen and a carbon atom* in the molecular refraction of a compound $C_xH_yO_z$; this value is found to be ·76.

These conclusions may be stated thus:—

$$(R)\ C_xH_yO_z = x\ (r)\ C + y\ (r)\ H + z\ (r)\ O,$$

where (r) C = 2·48, (r) O = 1·58, and (r) H = 1·04, with 1·75 added for each pair of carbon atoms grouped as in ethylene, $\rangle C - C \langle$, and ·76 added for each carbonyl grouping, $\rangle C - O.$

142 Let us now consider one or two of the applications which Brühl makes of these conclusions.

Acetic aldehyde CH_3CHO is easily polymerised to paraldehyde $C_6H_{12}O_3$. The change is probably represented by the equation

$$3H_3C-CHO = H_3C.HC(-O-CH.CH_3)(-O-C(-O)-HCH_3).$$

[1] The maximum is 2·29, and the minimum 1·59; difference = ·7.

[2] Two compounds C_nH_{2n-2} and five diallyl compounds.

If this is correct, we have three carbonyl groupings in $3CH_3.CHO$, and no carbonyl groupings in $C_6H_{12}O_3$; therefore $(R)C_6H_{12}O_3$ ought to be equal to three times $(R)CH_3.CHO$ diminished by $3 \times 76 = 2{\cdot}28$. The observed value of $(R)CH_3.CHO$ is 11·5, and $(11{\cdot}5 \times 3) - 2{\cdot}28 = 32{\cdot}22$; the observed value of $(R)C_6H_{12}O_3$ is 32·4.

Amylene C_5H_{10} is easily polymerised to diamylene $C_{10}H_{20}$; the molecules of both compounds probably contain one pair of directly interacting trivalent carbon atoms, or one ethylene grouping; if this is so, the molecular refraction of diamylene ought to be equal to twice that of amylene diminished by the value for one ethylene grouping, which is 1·75. The observed values of (R) are these; $C_5H_{10} = 24{\cdot}64$, $C_{10}H_{20} = 47{\cdot}12$; now $24{\cdot}64 \times 2 = 49{\cdot}28$, and $49{\cdot}28 - 47{\cdot}12 = 2{\cdot}16$ which is slightly greater than 1·75 Two isomerides of diamylene are known, tetrahydroterpene obtained by the reaction of phosphonium iodide with turpentine, and cymhydrene obtained from camphor by reaction with iodine. The observed molecular refractions of the three isomerides ($C_{10}H_{20}$) are these :—

diamylene	47·12	
tetrahydroterpene	46·02	...diff. = 1·1
cymhydrene	45·80	...diff. = ·22.

The calculated value of $(R)C_{10}H_{20}$ is 45·6, if (r)C = 2·48 and (r)H = 1 04; as (R) observed is nearly equal to (R) calculated in the cases of tetrahydroterpene and cymhydrene, and is greater by 1·52 than (R) calculated for diamylene, we should conclude that diamylene contains one ethylene grouping, and that the other isomerides contain only tetravalent carbon atoms. The study of the three hydrocarbons so far as it has gone confirms this conclusion.

Both the isomerides pentene and isoprene, C_5H_8, probably contain a pair of ethylene groupings; pinene, $C_{10}H_{16}$, probably contains one ethylene grouping, and each of its isomerides diisoprene and limonene probably contains a pair of ethylene groupings. Assuming these statements to be correct, and comparing the observed with the calculated values of (R) for these five hydrocarbons, we have these results :—

		(R) calcd	(R) observd.	diff
C_5H_8	pentene, two ethylene groupings	24·22	24·60	+·38
	isoprene, two	24·22	24·62	+·40
$C_{10}H_{16}$	pinene, one.....	43·19	43·66	+·47
	diisoprene, two.....	44·94	45·04	+·10
	limonene, two.....	44·94	45·06	+·12

The structural formulæ of the different hydrocarbons C_5H_{10}, $C_{10}H_{20}$, C_5H_8, and $C_{10}H_{16}$, are not yet fully ascertained, but it is very probable that the statements made by Brühl concerning the number of ethylene groupings in each are correct; some of these hydrocarbons belong to the class of open chain compounds and others to the closed ring group; hence, if we may judge from these data, the closing of a chain of carbon atoms, or the opening of a ring of the same atoms, does not affect the molecular refraction provided there is no change in the saturation-isomerism of the molecules. In confirmation of the conclusion that molecular refraction is not directly connected with the existence of closed rings, Brühl tabulates the molecular refractions of 24 benzene compounds, belonging to many different classes but each containing a single benzene nucleus, and shews that the mean difference between the observed and the calculated values of (R) is $+ 3 \times 1{\cdot}81$ (max. diff. $= 3 \times 2{\cdot}17$, min. diff. $= 3 \times 1{\cdot}58$), the calculated values being arrived at by using (r)C = 2·48, (r)O = 1·58, (r)H = 1·04. Hence it appears that the six-carbon benzene nucleus contains three ethylene groupings[1].

A considerable amount of evidence is certainly brought forward by Brühl in support of the statement that "position-isomerides have nearly identical molecular refractions, but saturation-isomerides have different molecular refractions... the increase in molecular refraction being *nearly* proportional to the number of ethylene, acetylene[2], and carbonyl, groupings, and this proportionality being more exact the smaller is the dispersion of the compounds."

[1] For an example of the application of Bruhl's method to the terpenes, see *Ber.* **21**. 145.

[2] A pair of directly interacting divalent carbon atoms is called by Bruhl an *acetylene grouping* of two carbon atoms; acetylene (HC – CH) being the simplest compound in which such a grouping occurs.

Brühl then formulates the fundamental refraction-law as follows:—

"The atomic refraction of carbon and oxygen is not invariable, but depends upon the [actual valencies of those atoms in different molecules][1]. The atomic refraction of these elements is however *nearly* constant provided saturation is unchanged, and in such cases is only very slightly dependent on the configurations of the atoms. The monovalent elements exhibit nearly invariable atomic refractions."

In support of the last part of this statement Brühl shews that the atomic refractions of hydrogen and chlorine calculated from direct observations very closely agree with the values calculated from observations made on compounds of these elements; that (R) HCl gas = (r) H + (r) Cl (from direct observations of (r) H and (r) Cl); and lastly that (r) H and (r) Cl deduced from observations on liquid carbon compounds are the same as (r) H and (r) Cl deduced from observations on gaseous carbon compounds.

Nasini[2] has made determinations of (R) for various carbon compounds containing sulphur, and has deduced two values for the atomic refraction of sulphur according as the atom directly interacts with two other atoms or with only one. Wiedemann[3] has arrived at similar results. The atomic refraction of sulphur appears to vary largely in compounds containing both oxygen and sulphur.

143 It should be noticed that the conclusions arrived at by Brühl can be applied at present only to such compounds of the forms $C_x H_y$ and $C_x H_y O_z$ as do not exhibit large dispersion. Nasini's observations[4] on naphthalene derivatives and other compounds with large dispersive power, and some of the experiments of Gladstone[5] on compounds containing relatively very much carbon, shew that the nature of the connexion between the refractive powers and the compositions of compounds has not yet been fully elucidated[6].

[1] Brühl uses the expression 'satisfaction of the affinity' (*Befriedigung der Affinität*). [2] *Ber.* **15.** 2878. [3] *Wied. Ann.* **17.** 577.

[4] *Gaz.* **14.** 150; **15.** 59; **17.** 72.

[5] *C. S. Journal Trans.* for 1884, 241.

[6] Kanonnikow (original paper in Russian; see abstract in *Ber.* **16.** 3047) has

144 If a ray of plane polarised light is passed through a plate of quartz cut at right angles to its optical axis, the position of the plane of polarisation of the emergent ray does not coincide with that of the incident ray; the plane has been rotated through a certain angle, called the angle of rotation. If the rotation takes place in the same direction as that in which the hands of a watch appear to move as we look at the face, the quartz is said to exhibit dextrorotatory power; this is expressed by prefixing + to the value of the angle of rotation. If the rotation takes place in the direction opposite to that in which the hands of a watch appear to move as we look at the face, the quartz is said to exhibit lævorotatory power; this is expressed by prefixing − to the value of the angle of rotation.

Optically active transparent media are those which rotate the plane of polarisation of a ray of light passed through them; they are divided into dextrorotatory substances, e.g. some specimens of quartz, sugar in aqueous solution, &c., and lævorotatory substances, e.g. other specimens of quartz, turpentine, quinine in alcoholic solution[1], &c.

To determine the amount of rotation caused by any substance, it is necessary to have an instrument wherein a ray of light may be polarised, and the position of the plane deter-

found the molecular refractions of a number of solid carbon compounds, by dissolving them in chemically inactive solvents and measuring the refractive indices of the solutions, the values of the indices of the solvent being known. Kanonnikow concludes that neither the degree of concentration of the solution, nor the physical condition of the solid, exerts any marked effect on the refractive power of the dissolved substance. Conclusions are drawn as to the structural formulæ of various carbon compounds; Bruhl's generalisations, on the whole, are confirmed.

The same chemist (see abstract in *Ber.* **17. ref.** 157; the abstracts, *referate*, in the *Berichte* beginning with vol. 17 are paged separately from the original papers) has attempted to determine (r) for various metals, by finding (R) for various salts of carbon acids and deducting (R) for the acids. His numbers point to the conclusion that in a 'group' of metals (as 'group' is used in the classification based on the periodic law) (r) increases as the atomic weights of the metals increase. Kanonnikow also tries to deduce values for (R) for the groups NO_3, SO_4, &c., and so to find the distribution of the interatomic actions in sulphates, nitrates, &c. (See also *Bull. Soc. Chim.* **41.** 548.)

[1] For details concerning polarised light, and circular polarisation considered from the physical stand-point, see Glazebrook's *Physical Optics*, chaps. XI. and XIV.

mined; the polarised ray may be passed through a known quantity of the medium under examination; and finally the position of the plane of the emergent ray may be determined. Such instruments, known as *polarimeters* or *polaristrobometers*, are described in detail in various text-books[1].

Let us consider a liquid carbon compound, say $C_{10}H_{16}$. The angle of rotation, α, depends on (1) the thickness of the layer of liquid through which the light passes, (2) the wave-length of the ray of light employed, and in most cases (3) the temperature at which the observation is made. The first of these conditions will be determined if we know the length of the column of liquid employed, and the second is rendered definite by making use of monochromatic light.

Let l = length of column of liquid in decimetres, d = spec. grav. of liquid referred to water at 4°, and α = angle of rotation of plane of polarisation of light of given wave-length[2]; then

$[\alpha]$ = *specific rotatory power* of the liquid, for the given ray, $= \frac{\alpha}{l.d}$.

That is to say, the specific rotatory power of an optically active substance is the angle through which the plane of polarisation of a given ray is rotated by passing through a column 1 decimetre long of a liquid containing 1 gram of the substance in 1 cubic centimetre.

For chemical purposes it is sometimes better to adopt the definition of *molecular rotatory power* $[m]$ suggested by Krecke[3], viz.

$$\frac{m}{100}\cdot\frac{\alpha}{l.d},$$

where m = molecular weight: m is divided by 100 to obviate the use of inconveniently large numbers.

We have then

$$[\alpha]=\frac{\alpha}{l.d}$$

and

$$[m]=\frac{m}{100}\cdot\frac{\alpha}{l.d}.$$

[1] See especially Armstrong and Groves, *Organic Chemistry*, 569 *et seq.*; and also Watts's *Dictionary*, **3rd Supplt.** 1198—1207.

[2] It is customary to indicate the light employed by placing a letter below the bracket; thus $[\alpha]_D$ means spec. rotatory power for light of wave-length *D*.

[3] *J. fur prakt. Chemie* (2). **5.** 12.

If the substance to be examined is a solid, it must be dissolved in an optically inactive menstruum. In such a case, l = length in decimetres of column of solution employed, p = grams of optically active substance in 100 grams of solution (i.e. gram-percentage composition), and d = spec. grav. of solution referred to water at 4°; then $p.d = c$ = concentration, i.e. grams of active substance in 100 c.c. of solution; and, assuming that the solvent has no influence on the rotatory power of the dissolved substance,

$$[\alpha] = \frac{100\,\alpha}{l.p.d} = \frac{100\,\alpha}{l.c}.$$

As the value of $[\alpha]$ generally rises as temperature rises[1], thermometric observations must be made. The value of $[\alpha]$ also varies with variations in (1) the nature, and (2) the quantity, of the inactive solvent employed; the preceding formula therefore gives only the apparent specific rotatory power of the solid substance.

That $[\alpha]$ varies according to the nature of the solvent is shewn by Hesse's observations on turpentine oil[2];

	pure turpentine ($C_{10}H_{16}$)	oil + alcohol (amount of solvent varied in each case from 10 per cent to 90 per cent.)	oil + benzene	oil + acetic acid
$[\alpha]_D$	37°·01 ;	37°·035 to 38°·486 ;	37°·194 to 39°·449 ;	37° 148 to 40°·222.

The following numbers[3] illustrate the dependence of $[\alpha]$ on the amount of solvent employed;

	Value of $[\alpha]_D$		
Aqueous solution of	maximum	minimum.	Difference.
Tartaric acid	+ 14°·18	+ 3°·20	10°·98
Codeine	− 137°·75	− 111°·50	26°·25
Quinine	− 169°·25	− 116°·0	53°·25

Landolt (*loc. cit.*) has shewn that the true value of $[\alpha]$ for a solid or liquid may be found in many cases from a number of observations made with solutions of varying concentration; the more concentrated the solution the more nearly

[1] For numbers illustrative of this in the case of aqueous solutions of tartaric acid see *Dict.* **3rd Supplt.** 1209.

[2] Hesse, *Annalen* **176.** 89 and 189: see also Landolt's *Handbook of the Polariscope* (English translation), 54—94. This book presents a view of the whole subject of circular polarisation, chemically considered. See also Landolt, *Ber.* **21.** 191.

[3] Landolt, *loc. cit.*

does the value found for $[\alpha]$ approach the true value, i.e. the more nearly does the observed, agree with the true, specific rotatory power. It is better to use several solvents and make a series of observations with each; the value deduced for $[\alpha]$ is generally the same for each solvent.

The nature and extent of the variations in $[\alpha]$ caused by varying the quantity of solvent appear to differ for each optically active solid substance[1]; in some cases the relation is very complicated, in others it may be expressed by a comparatively simple formula[2].

That the observed and calculated values of $[\alpha]$ agree closely, provided a sufficient number of observations is made, is evident from these results (Landolt):—

Active substance	$[\alpha]_D$ observed	$[\alpha]_D$ calculated from observations on mixtures with (1) C_2H_5OH	(2) CH_3OH	(3) H_2O	(4) C_6H_6	(5) CH_3CO_2H	max. diff
Dextrorotatory ethyl tartrate	8°·31	8°·27	8°·42	8°·09	—	—	−·22
Dextrorotatory turpentine	14°·15	14°·87	—	—	—	—	+·72
Lævorotatory turpentine	37°·01	36°·97	—	—	36°·97	36°·89	−·12
Lævorotatory nicotine	161°·55	160°·83	—	161°·29	—	—	−·72

The true specific rotatory powers of camphor, cane sugar,

[1] The following numbers illustrate this statement (Landolt, *loc. cit.* 82):

Active substance	Solvent.	$[\alpha]_D$ for pure substance.	$[\alpha]_D$ for maximum dilution	Difference.
lævorotatory turpentine	alcohol	36°·97	38°·79	+ 1°·82
dextrorotatory ,,	,,	14°·17	15°·35	+ 1°·18
lævorotatory nicotine	alcohol	160°·83	138°·59	−22°·24
	water	161°·29	74°·13	−87°·16
dextrorotatory ethyl tartrate	alcohol	8°·27	10°·19	+ 1°·92
	water	8°·09	28°·12	+20°·03

[2] Thus, for solutions of turpentine in alcohol, Landolt gets the formula

$$[\alpha]_D = 36°·974 + ·0048164q + ·0001331q^2$$

where q = percentage of inactive solvent. (For more details see Landolt, *loc. cit.* 81—94.) For dry inverted sugar Grubbe (*Ber.* **18.** 2207) finds the following formula when $t°$ varies from 0° to 30°;—

$$[\alpha]_D^t = -23°·305 + ·30406\,(t-20) + ·001654\,(t-20)^2.$$

For a fuller treatment of the methods employed for finding the true value of $[\alpha]$ from observations on solutions, see *Dict.* **3rd Supplt.** 1212—1213; also Landolt, *Ber.* **21.** 191.

and dextroglucose, have been determined by Landolt, Tollens, and Schmitz[1]. But I think it should be noted that the observations on which is based the method for determining [α] were necessarily made with solutions of liquid compounds in inactive solvents, whereas in the cases of camphor and sugar we have to deal with solutions of solid substances; it is possible that the value of [α] for liquid camphor may be different from that for solid camphor[2]. It should also be observed that any deductions concerning the relations between specific rotatory power and molecular structure, drawn from a study of liquid compounds, could not be applied in a precise manner to solid compounds, assuming the true value of [α] for these compounds to be known.

145 In attempting to trace relations between the specific rotatory power and the composition of compounds, we must distinguish relationships between [α] and the composition of molecules whose empirical formulæ at least are known, from those between the same constant and such mixtures of molecules in varying proportions as are presented by solutions of varying concentration.

For although in the latter cases no precise conclusions can be drawn regarding the relative arrangements of the atoms in the molecules, yet the study of specific rotatory power may help to throw light on such general questions as the action of solvents, the distinction between chemical and physical change, and so forth.

Pribram[3] has determined [α] for aqueous solutions of cane sugar, tartaric acid, and nicotine, with the result that [α] does not become constant even in very dilute solutions[4]. Pribram thinks that this result is more in keeping with the hypothesis

[1] See Landolt, *loc. cit.* 84—92: Tollens, and Schmitz in *Ber.* **9.** 1531: **10.** 1403: and *do.* 1414.

[2] Biot states that fused liquid tartaric acid is markedly dextrorotatory, but the solidified acid is feebly lævorotary (*Dict.* **3rd Supplt.** 1209). Landolt's value of [α] for solid camphor is 55°·6 (see *Dict., loc. cit.* 374): while Gernez obtained the value 70°·33 for fused camphor (*do. do.* p. 1209).

[3] *Ber.* **20.** 1840.

[4] The most dilute solutions used were, ·222 p.ct. for cane sugar, ·3471 p.ct. for tartaric acid, and ·8826 p.ct. for nicotine.

that the solvent brings about some gradual change in the configuration of the atoms forming the molecule of the dissolved compound, than with either of the other hypotheses[1] that have been suggested, one of which asserts that the molecules of the solid consist of aggregates of true molecules, and that these are separated by the solvent, and the other supposes that the solvent forms a series of compounds with the dissolved substance, which compounds are of different rotatory powers and vary in quantity with variations in the relative amounts of the solvent and the dissolved substance.

146 All known compounds which possess the power of rotating the plane of polarisation of a ray of light when in the liquid state or in solution are compounds of carbon: van't Hoff[2], following in the steps of Le Bel[3], has endeavoured to trace a precise connexion between the molecular structure of these compounds and their rotatory power. The hypothesis of Le Bel and van't Hoff connects optical activity with the presence of one or more *asymmetric* carbon atoms in the molecule of the optically active body. The definition of an asymmetric carbon atom implies the conception of the arrangement of atoms in three dimensions in space. An atom of carbon is supposed to be situated at the centre of a regular tetrahedron, and to be in direct union with four atoms or radicles situated at the four summits of the tetrahedron; when these four atoms or radicles are all different, two geometrically different forms of the configuration may

Fig. 46.

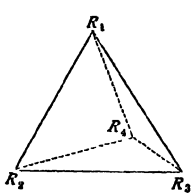
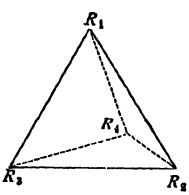


Fig. 47.



[1] References to memoirs in which these hypotheses are discussed will be found in Pribram's paper.

[2] *La Chimie dans l'Espace;* and more particularly in a pamphlet published in 1887, entitled *Dix Années dans l'histoire d'une Théorie.*

[3] *Bull. Soc. Chim.* **22.** 337; **23.** 295.

exist. These two forms bear to each other the relation of an object to its image; neither is superposable on the other (s. figs. 46 and 47). An atom of carbon related in this way to four different radicles is said to be *asymmetric*, because there is no symmetry in the configuration, while at the same time a plane of symmetry arises so soon as two of the four radicles are the same.

Any compound containing an asymmetric carbon atom may exhibit geometrical isomerism: each isomeride will differ from the other in rotatory power, and if the isomerides are crystallisable they will assume *enantiomorphous* (non-superposable) forms. Ammonium malate, for instance, crystallises in two enantiomorphous forms, as represented in figs. 48 and 49; these crystals differ exactly in the same way as the

Fig. 48.

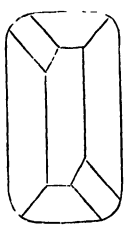
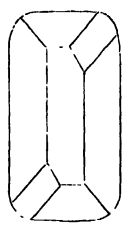


Fig. 49.



molecules of the two isomerides are supposed to differ. Many other optically active compounds shew differences in rotatory power accompanied by the power of crystallising in enantiomorphous forms[1].

We should expect then to find all those compounds optically active the molecules of which contain one or more asymmetric carbon atoms, and also to find that all optically active compounds contain asymmetric carbon atoms.

So far as investigation has gone, the molecule of every compound which exhibits rotatory power contains at least one carbon atom in direct union with four different radicles[2]. The following formulæ, in which the asymmetric carbon

[1] Van't Hoff's *Dix Années*... p. 30.

[2] For details of individual compounds *s.* van't Hoff, *l. c.* pp. 31—48.

atoms are indicated by italics, shew the composition of some commonly occurring optically active compounds;—

Tartaric acid..... $CO_2H-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CO_2H$;

Lactic acid ..... $CH_3-\overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CO_2H$;

Secondary amylic iodide $CH_3-\overset{H}{\underset{I}{\overset{|}{\underset{|}{C}}}}-C_3H_7$.

Investigation has also shewn that those derivatives of optically active compounds which do not themselves contain asymmetric carbon atoms do not possess rotatory power; in other words, a change of structure resulting in the removal of the asymmetric atoms is always accompanied by loss of optical activity. But compounds do exist which certainly contain asymmetric carbon atoms and yet do not rotate the plane of polarisation of a ray of light. Some of these may be resolved into two isomerides of equal and opposite rotatory powers, e.g. racemic acid; others cannot be resolved into active isomerides, e.g. mesotartaric acid.

Consider the formulæ

$$(R_1R_2R_1)C.C(R_1R_2R_3) \text{ and } (R_6R_5R_4)C.C(R_1R_2R_3),$$

where R_1R_2 &c. represent different radicles; the first formula shews each of the two asymmetric carbon atoms in direct combination with the same radicles [R_1, R_2, R_3, and $(CR_1R_2R_3)$], the second formula shews one asymmetric carbon atom directly combined with the radicles R_1, R_2, R_3, and $(CR_4R_5R_6)$, and the other asymmetric carbon atom in direct union with the radicles R_4, R_5, R_6 and $(CR_1R_2R_3)$. The first formula represents a *symmetrical* molecule, the second an *unsymmetrical* molecule.

Let us now advance a step farther and compare the structures represented by the formulæ

$$(R_3R_2R_1)C.C(R_1R_2R_1) \text{ and } (R_2R_3R_1)C.C(R_1R_3R_2).$$

Both formulæ are symmetrical, but the structure represented by one is the reflection or image of that represented by the other. The isomeride represented by one of these formulæ ought to rotate the plane of polarisation to the right, and the other isomeride ought to rotate the plane an equal amount to the left. A mixture or compound of these isomerides in equal molecular proportions would be optically inactive, because every dextrorotatory molecule would be opposed by a lævorotatory molecule. But such a mixture or compound would be resolvable into a dextrorotatory and a lævorotatory isomeride.

Unsymmetrical compounds containing asymmetric carbon atoms must be active, or if inactive they must be resolvable each into two isomerides of opposite rotatory powers.

Inactive compounds which are resolvable into two isomerides of equal and opposite activities are said in the language of van't Hoff's hypothesis to be *inactive by external compensation.*

Now let the structure represented by the formula

$$(R_2R_3R_1)\ C\,.\,C\ (R_1R_2R_3)$$

be considered[1]. Each half of this molecule is the complement or reflected image of the other; one half will neutralise the optical activity of the other half; the whole will be *inactive by internal compensation.*

A compound which is inactive by internal compensation must contain at least two asymmetric carbon atoms, and the formula must be symmetrical. The hypothesis asserts the existence of such inactive compounds, and declares that they cannot be resolved into active isomerides because their inactivity is the result of the atomic configuration of their molecules, and is not produced by the opposition of molecules of dextrorotatory power to an equal number of isomeric molecules of lævorotatory power.

The hypothesis of van't Hoff divides compounds containing asymmetric carbon atoms into three classes:—

(1) Those which are optically active: such compounds are produced in pairs consisting of a dextrorotatory

[1] Models of the different structures made in pasteboard are helpful.

and a lævorotatory isomeride; they are either symmetrical or unsymmetrical.

(2) Those which are inactive but may be resolved into two isomerides of equal and opposite rotatory powers; they are inactive by external compensation.

(3) Those which are inactive and non-resolvable; they are inactive by internal compensation.

Van't Hoff (*l.c.* pp. 54—55) shews that an unsymmetrical compound containing n asymmetric carbon atoms may exist in 2^n optically different modifications, and that a symmetrical compound containing n asymmetric carbon atoms may have $\frac{1}{2}2^n$ active isomerides, and $\frac{1}{2}2^{\frac{n}{2}}$ inactive non-resolvable isomerides[1].

There are three general methods for separating inactive resolvable bodies into their dextrorotatory and lævorotatory isomerides.

In the first method advantage is taken of the differences between the actions of some minute organisms on the two active isomerides. For instance, when *penicillium* is allowed to act on a dilute solution of ammonium racemate, lævorotatory tartrate of ammonium is found in the liquid after a time, the isomeric dextrorotatory tartrate being destroyed by the action of the organism.

The second method proceeds by treating the inactive compound with an active body with which one of the isomeric constituents of the inactive compound combines more readily than the other. For instance, crystals of lævorotatory tartrate of cinchonine, and a solution of dextrorotatory tartaric acid, may be obtained by adding the proper quantity of active cinchonine to a solution of racemic acid, and crystallising.

The third method consists in separating the inactive body into two active isomerides by crystallisation at a definite temperature. For instance, when a solution of racemic acid is neutralised by soda and another equal quantity by ammonia, and the solutions are mixed and evaporated at a temperature a little below 28°, crystals both of dextrorotatory and lævoro-

[1] Many applications are given in pp. 55—62 of van't Hoff's *Dix Années*, &c.

tatory sodium-ammonium tartrate are obtained[1]. Van't Hoff[2] has shewn that the change from sodium-ammonium racemate to the two tartrates is accomplished by heating the dry salt with water in the ratio $NaNH_4.H_4C_4O_6.H_2O$: $3H_2O$ to a little under 27°; and that the change from the two tartrates to the racemate (and water) is effected by heating the dry mixture to a little above 27°. The changes may be represented thus (the racemate crystallises with H_2O and the tartrates with $4H_2O$):

$$2(NaNH_4.H_4C_4O_6.4H_2O) \rightleftarrows 2(NaNH_4.H_4C_4O_6.H_2O)+6H_2O.$$

Slight variations of temperature above or below 27° determine the direction in which the change occurs. Some other racemates appear to undergo change to tartrates at a definite temperature[2].

The change of inactive racemates to the active tartrates and *vice versa* is closely analogous to some changes which occur among inorganic compounds; for instance, when a mixture of the sulphates of magnesium and sodium in molecular proportion is heated a little above 21° it is changed to a double sulphate and water, and at a little under 21° the double sulphate is resolved into the two single sulphates:—

$$MgSO_4.7H_2O+Na_2SO_4.10H_2O \rightleftarrows MgNa_2(SO_4)_2.4H_2O+13H_2O.$$

The process of resolution by heat of the inactive racemate is also very analogous to the physical process of fusion; and as one speaks of the *fusion-point*, so van't Hoff uses the expression *transition-point* to indicate the temperature at which the chemico-physical change in question occurs[3].

147 The hypothesis of van't Hoff and Le Bel connects the power of rotating the plane of polarisation of a ray of light primarily with the configuration of the parts of molecules, but it points to the formation of molecular aggregates without change of molecular structure as a cause of the removal, or rather disappearance, of optical activity. Optical activity appears to be independent of the nature and number of the

[1] For examples of the application of the three methods, see van't Hoff, *l. c.* pp. 64—69.

[2] See van't Hoff, *l. c.* p. 69.

[3] For details, see van't Hoff, *Journal fur physikal. Chemie*, **1**. 165, 227.

atoms which form the molecule of a carbon compound, and to be connected only with the configuration of these atoms. We cannot assign a definite part of the total rotatory power of a compound molecule to each of the atoms or even groups of atoms which form the molecule; nor can we connect the rotatory power with changes of valency or with changes in the distribution of the atomic interactions, except in so far as these are concerned in changes from a configuration containing asymmetric carbon atoms to another configuration which does not contain such atoms.

The specific rotatory powers of many compounds readily undergo change when small changes occur in certain physical conditions. Some active bodies become inactive by heating, and at another temperature the change is sometimes reversed. The value of $[\alpha]$ of a solution of an active body in an inactive solvent is dependent on the nature and the quantity of the solvent. The addition of one inactive solvent to the solution of an active body in another solvent is sometimes accompanied by a great change in the rotatory power of the liquid; thus about one half of the alcohol in an alcoholic solution of cinchonine may be replaced by chloroform without much change of rotatory power, but if as much as $\frac{1}{300}$th of the chloroform in a solution of the same alkaloid in this solvent is replaced by alcohol a marked change in rotatory power occurs[1]. Again, the rotatory power of a body in solution sometimes changes on keeping until a constant value is attained; thus the value of $[\alpha]$ for a freshly prepared aqueous solution of milk sugar or certain glucoses decreases on keeping, and the final value is more quickly attained by boiling the liquid[2].

This readiness to change shewn by the rotatory powers of carbon compounds finds some explanation in van't Hoff's hypothesis, especially in the development of it made by Wislicenus. For Wislicenus shews[3] that besides those configurations which are conditioned by the affinities of the

[1] Watts's *Dict.* **3rd Supplt.** 1210.

[2] Landolt's *Handbook of the Polariscope*, p. 62.

[3] See *ante*, par. 94.

atoms of a molecule containing asymmetric carbon atoms, other configurations will probably exist which will be relatively unstable, and that the existence and number of these will be conditioned by the action of heat and by collisions with molecules of other kinds; as these unstable forms are only geometrically different from the stable configurations they will be optically active, but their rotatory power will not probably be the same as that of the stable form.

Krecke[1] has endeavoured to generalise the relations between the *molecular rotatory powers*[2] $[m]$ of certain compounds and of their active derivatives; but the data are insufficient.

148 A large number of measurements of the rotatory power of compounds when under magnetic influence has been made by Perkin[3]. The liquid compound to be examined was placed in a glass tube the ends of which were let into the poles of a large electromagnet; the tube formed part of a polariscope. Sodium light was employed.

A great many compounds exhibit optical activity under these conditions.

Perkin measures the rotations of liquid compounds and refers the results to lengths of liquids related to each other in the same proportion as the molecular weights of the gases obtained by vapourising these liquids.

The molecular rotation of water is taken as unity. Let r = observed rotation of a specified compound and r' = rotation of water; let Mw = molecular weight of the compound and Mw' = molecular weight of water; and let d = spec. grav. of the compound and d' = spec. grav. of water [= 1]; then molecular rotatory power (Mol. R) $= \frac{r.Mw}{d} \div \frac{r'.Mw'}{d'}$

$$= \frac{r.Mw.d'}{r'.Mw'.d}$$

$$= \frac{r.Mw}{r'.Mw'.d}.$$

[1] *J. für prakt. Chemie*, (2). 5. 6. See also Flavitsky, *Ber.* 15. 5; Th. Thomsen, *Ber.* 13. 2168, 2264, 2269; 14. 29, 134, 203, 807, 1647; and against him, Landolt, *Ber.* 14. 296, 1048.

[2] See *ante*, p. 300.

[3] *C. S. Journal*, Trans. 1884. 421; 1886. 777; 1887. 808.

About 150 compounds were examined, the observation of r being repeated five to ten times for each compound, and the spec. grav. of each being carefully determined.

In strictly homologous normal carbon compounds each increment of CH_2 produces a constant increment (1·023) in molecular rotatory power. But when the addition of CH_2 is accompanied by a change in the distribution of the atomic interactions the change of Mol. R. is not constant; for instance, the change from a normal paraffin $CH_3.nCH_2.CH_3$ to the next higher isoparaffin $CH(CH_3)_2.nCH_2.CH_3$ produces an increase in Mol. R. equal to 1·023 + ·105; in the change from a normal acid to the next higher iso-acid of the same series, CH_2 has a different value; and so on. When chlorine is substituted for hydrogen in a hydrocarbon the molecular rotatory power is increased, but each chlorine atom has a different value from the others.

These results indicate that the molecular rotatory power of a compound is not the sum of certain constant values assignable to each atom or atomic group, but that it depends on the arrangement of the atoms which form the molecule. This result is confirmed by the outcome of attempts to assign values to the atomic rotatory powers of oxygen and carbon. The atomic rotatory power of hydrogen may be deduced thus:—

(1) Mol. R. of C_nH_{2n+2} = Mol. R. of $nCH_2 + H_2$;

but Mol. R. of $nCH_2 = n$ 1·023.

The value thus deduced for At. R. of H is ·254.

(2) $\frac{\text{Mol. R. of } C_nH_{2n+2}}{2} = \text{Mol. R. of } C_mH_{2m+1}$;

then Mol. R. of C_nH_{2n+2} − Mol. R. of C_mH_{2m+1} = At. R. of H, if n = m;

[e.g. $\frac{\text{Mol. R. of } C_6H_{14}}{2} = 3{\cdot}323 = \text{Mol. R. of } C_3H_7$;

but Mol. R. of $C_3H_8 = 3{\cdot}577$, ∴ At. R. of H = ·254].

The value thus deduced for At. R. of H is ·254.

The difference between ·508 (At. R. of H = ·254) and 1·023 (Mol. R for CH_2 in normal homologous series) gives the num-

ber ·515 as the atomic rotatory power of carbon in normal homologous series. Similar methods are applied to the data for oxygen compounds, and the results are these;—

Oxygen in alcoholic OH ..... At. R. = ·194,
Oxygen in carboxylic OH ..... „ = ·137,
Oxygen in carboxylic CO ..... „ = ·261.

When these values are applied to calculate Mol. R. for series different from those which furnished the data, numbers are obtained which do not agree with the observed numbers.

Nor can a constant value be found for the atomic rotatory power of chlorine; the value varies according to the series of compounds considered, according as one or two hydrogen atoms are replaced by one or two chlorine atoms, according as the hydrogen replaced is in one part of the molecule or in another part, and so on.

The general conclusion is that change of molecular rotatory power of carbon compounds under magnetic influence is intimately connected with changes in molecular structure, so that any cause which alters this structure also alters the rotatory power.

Perkin attempts to use determinations of Mol. R. for various compounds formed by the action of water on other compounds for throwing light on the question whether these compounds are hydrates, i.e. compounds of water, or compounds of oxygen and hydrogen with other elements.

In all measurements of Mol. R. the molecular rotatory power of water under the magnetic influence is taken as unity; if therefore a compound is formed by addition of water to another, Mol. R. for the new compound might be expected to be equal to that for the original compound *plus* one for each molecule of water added; if the observed Mol. R. is less than Mol. R. thus calculated, the difference may be explained by supposing that the formation of the new compound has involved a rearrangement of the atoms of the reacting molecules. Here are a few examples of the application of this method:—

$HCO_2H.H_2O$	Mol. R. observed = 2·666		Mol. R. HCO_2H + 1 = 2·671
$CH_3CO_2H.H_2O$	„	„ 3·554	„ CH_3CO_2H + 1 = 3·525
$CH_3CH_2CO_2H.H_2O$	„	„ 4·512	„ $CH_3CH_2CO_2H$ + 1 = 4·462.
H_2SO_4	„	„ 2·315	
$H_2SO_4.H_2O$	„	„ 3·188 = Mol. R.	H_2SO_4 + ·873
$H_2SO_4.2H_2O$	„	„ 4·113 = „	$H_2SO_4.H_2O$ + ·925
$H_2SO_4.3H_2O$	„	„ 5·064 = „	$H_2SO_4.2H_2O$ + ·951.

Perkin considers that the bodies formed by adding water to formic acetic and propionic acids are either hydrates of these acids, or only mixtures; but that a compound of sulphur oxygen and hydrogen [perhaps $SO(OH)_4$], and not a hydrate of sulphuric acid, is produced when sulphuric acid and water react in the ratio $H_2SO_4 : H_2O$. The difference between Mol. R. for some organic anhydrides and Mol. R. for the corresponding acids averages about ·74; in other words, the combination of a molecule of water with an anhydride to form an acid raises Mol. R. by about ·74; hence, Perkin argues, when H_2O is added to H_2SO_4 the change which occurs is so far analogous to that of the conversion of an anhydride into an acid that it cannot be regarded as a simple hydration of sulphuric acid.

The following data lead to the conclusion that chloral hydrate is not a compound of chloral and water, but that the reaction between these compounds involves a rearrangement of some of the atoms of the reacting bodies:—

Mol. R. of $CCl_3.CHO$ liquid = 6·591
Mean Mol. R. of liquid $CCl_3.CHO.H_2O$ = 7·037
Increase in Mol. R. for combination of H_2O = ·446.

149 Researches on the relations between the composition and the absorption-spectra of carbon compounds have been conducted by Hartley[1]. From the results thus obtained, Hartley concludes, that the normal alcohols $C_nH_{2n+1}.OH$ are remark-

[1] *Phil. Trans.* **170.** 257. See also *C. S. Journal* **Trans.** for **1881.** 153 *et seq.* See also report of the B.A. committee on Spectrum Analysis; *Brit. Ass. Reports* for **1880.** 258 *et seq.*

ably transparent to the ultra-violet rays—methylic alcohol transmits all rays up to wave-length 2000, but octylic alcohol transmits nothing beyond 3464; that a normal acid of the $C_nH_{2n+1}CO_2H$ series always exhibits a greater absorption of the more refrangible rays of the ultra-violet spectrum than the normal alcohol with the same number of carbon atoms; and that in both alcohols and acids addition of CH_2 is accompanied by increased absorption.

From an examination of the absorption-spectra of very many carbon compounds, Hartley concludes, that *absorption-bands* are never present in the ultra-violet part of the spectrum obtained by passing light through a compound in the molecule of which the carbon atoms are arranged in an 'open chain', but that such bands are present in the absorption-spectra of all benzene derivatives. Inasmuch, however, as benzene hexachloride $C_6H_6Cl_6$ is very transparent, and exhibits no bands, it would appear that the mere closing of the chain of carbon atoms is not the sole condition necessary for the production of absorption-bands. Hartley thinks that each carbon atom must be in direct union with at least three other carbon atoms.

This supposition is in accordance with the observation that solutions of naphthalene, anthracene, and phenanthrene, in transparent media, shew absorption-bands, similar to, but lower in refrangibility than, the benzene bands; and that these solutions likewise exhibit much more intense absorption than benzene.

Terpenes ($C_{10}H_{16}$) and camphor ($C_{10}H_{16}O$) exhibit more intense absorption than compounds of the paraffinoid group, but no bands appear in the spectra of the light transmitted by these compounds; hence their molecular structure appears to be related on the one hand to the paraffinoid and on the other hand to the benzenoid group of compounds.

By taking advantage of the differences in the character of the absorption exhibited by different compounds—e.g. the character of the absorption-spectrum of cymene is very different from that of the terpenes—it is possible to detect minute quantities of certain compounds in presence of large

quantities of others, and also broadly to classify carbon compounds into groups. Further, by taking advantage of the differences in the positions of the bands in the spectra of the light transmitted by isomeric compounds, it will be possible, when sufficient data have been obtained, to determine the class to which this or that isomeride belongs. Moreover, the gathering together of this data will doubtless be the means of gaining much precise knowledge regarding the relations between the molecular structure and the actinic properties of compounds[1]. For the experiments of Hartley[2] tend to the conclusion that although greater or less absorption is connected with molecular vibrations, yet the special selective absorption characteristic of benzenoid compounds is rather to be connected with atomic vibrations. These experiments also shew that the mean rate of vibration of the rays absorbed by molecules of naphthalene and anthracene is less than that of the rays absorbed by benzene molecules, and hence, remembering the similarity of the character of the absorptions in these three cases, it is concluded that the amplitudes of the vibrations of the naphthalene and anthracene molecules are greater, and the rates of vibration are slower, than those of the benzene molecules. Hence it would follow that the atomic vibrations which probably give rise to the observed selective absorption are closely dependent on the vibrations of the molecules as wholes.

Now if a connexion between the vibrations of molecules and the vibrations of parts of these molecules is established, and if this connexion is elucidated by precise data, we shall certainly have made an important advance in solving the fundamental problem of chemistry, which is to trace the relations between the composition and the properties of bodies.

A further step in this direction has been made by Abney and Festing[3], who have mapped the absorption which occurs in the infra-red region of the spectrum, and have thus been

[1] For the application of his general conclusions to essential oils, quinoline, hydrocyanic and cyanuric acids, &c., see Hartley, *C. S. Journal* **Trans.** for **1880.** 676; do. for **1882.** 45; and *Chem. News*, **40.** 269.

[2] *C. S. Journal* **Trans.** for **1881.** 165—167.

[3] *Proc. R. S.* **31.** 416, and *Phil. Trans.* for **1881.** 887.

able to shew that there is a definite connexion between the nature of the atomic groups in the molecules of many carbon-compounds, and the vibrations of the rays stopped by these compounds[1].

SECTION III. *Methods based on determinations of the molecular volumes of compounds*[2].

150 The quotient obtained by dividing the formula-weight by the specific gravity of a compound (referred to water at 4°) is generally called the *specific volume* of that compound. The term *specific volume*, however, evidently expresses the relative volume of unit weight of the substance. The quotient in question is sometimes called the *molecular volume* of the compound formulated. This expression strictly interpreted implies that the formula-weight is identical with the molecular weight, and that the specific gravity and formula-weight are

[1] Kruss and Oeconomides (*Ber.* **16.** 2051), and Kruss (*Ber.* **18.** 1426, 2586), have traced some connexion between the shifting of absorption towards or away from the less refrangible part of the spectrum and the substitution of hydrogen in benzenoid compounds by CH_3, Br, NH_2, NO_2, &c. Reference may here be made to a paper by G. Kruss [*Ber.* **15.** 1243, and **16.** 2051] on an optical method for determining whether or not chemical action has occurred between two substances in solution, all the possible products of the reaction being also soluble under the experimental conditions. The method consists, essentially, in comparing the sums of the absorption-spectra of the original liquids with the absorption-spectrum of a mixture of these liquids.

[2] It may be well to gather together here references to the most important articles and papers on the subject of this section:—KOPP, *Annalen* **96.** 153, 303; **100.** 19, &c. BUFF, *Annalen* **Supplbd. 4.** 129, and *Ber.* **4.** 647. THORPE, *C. S. Journal*, **Trans.** for **1880.** 141, 327. L. MEYER, *Annalen* **Supplbd. 5.** 129; also *Die modernen Theorien* (4th Ed.), 284–292; *English Ed.* pp. 259–267. ELSASSER, *Annalen* **218** 302. STAEDEL, *Ber.* **15.** 2559. WEGER, *Annalen* **221.** 61. RAMSAY, *C. S. Journal*, **Trans.** for **1879.** 463; do. for **1881.** 49. 66. LOSSEN, *Annalen* **214.** 81. Compare also SCHIFF, *Ber.* **14.** 2761; **15.** 1270; **19.** 560; *Annalen* **220.** 71, 278; **223** 247. SCHALFEJEW, *Ber.* **15.** 2209; **16.** 1853. ZANDER, *Annalen*, **224.** 56. LOSSEN and ZANDER, *Annalen*, **225.** 109. LOSSEN, *Annalen*, **243.** 64. GARTENMEISTER, *Annalen*, **233.** 249. HORSTMANN, *Ber* **19.** 1591; **20.** 766. ISCHERMAK, *Annalen*, **112.** 129; **114.** 25. SCHRÖDER, *Wied. Ann.* **11.** 997; **14.** 656; KRAFFT, *Ber.* **15.** 1687. VOLLMAR, *Ber.* **15.** 2560. WILSON, *Proc. R. S.* **32.** 457. NEUBECK, *Zeitschr. fur physikal. Chemie*, **1.** 649. See also O. E. Meyer's *Die Kinetische Theorie der Gase*, 216—221: and WATTS' *Dict.*; **1.** 440 *et seq.* and (more especially) **3rd Supplt.** 2117 *et seq.*

expressed in terms of the same standard. The value of $\frac{\text{formula-weight}}{\text{spec. gravity}}$ is equal to the product of specific volume multiplied into molecular weight, assuming the latter to be the same as the formula-weight; or we may say that, if the weight expressed by the formula is taken in grams, the quotient $\frac{\text{formula-weight}}{\text{spec. gravity}}$ represents the number of cubic centimetres occupied by an amount of the substance in grams proportional to its molecular weight. Now we can determine the molecular weights of gaseous compounds only: if the specific gravities of compounds are referred to hydrogen as unity, then, $\frac{\text{molecular weight}}{\text{spec. gravity}} = const. = 2$. Nevertheless, if the quotient $\frac{\text{formula-weight}}{\text{spec. gravity}}$ is obtained for a number of liquid compounds, we shall have a series of comparable values, which—if formula-weight of liquid is a simple multiple of molecular weight of gas—represent the volumes occupied by quantities of various liquid compounds proportional to the molecular weights of the same compounds in the state of gases.

The meaning to be attached to the expression 'volume occupied by a quantity proportional to molecular weight' will be discussed in paragraph 156.

The name *atomic volume* is generally applied to the quotient $\frac{\text{atomic weight}}{\text{spec. gravity of solid element}}$ (water = 1).

The determinations of the specific gravities of liquids necessary for finding values for the quotient we are discussing, should be made under comparable conditions; this is roughly fulfilled by determining the specific gravities at the boiling points of the liquids[1].

[1] It would be advisable to compare those volumes of liquids for which temperature and pressure are equal fractions of their critical values. (See Ostwald's *Lehrbuch*, 1. 336.) Full details regarding the methods used for determining the spec. grav. of liquids at their boiling points will be found in Thorpe's paper, *loc. cit.*; see also Ramsay (*loc. cit.*); Schiff (*loc. cit.*); and Neubeck (*loc. cit.*).

151 Let the *molecular volume*, i.e. the quotient

$$\frac{\text{formula-weight of liquid compound}}{\text{spec. gravity referred to water}},$$

be expressed by the symbol (V). Then the value of (V) for a compound is in some cases equal to the sum of the values of (V) for the elementary atoms which form the molecule of that compound. But is (V) always the sum of the atomic volumes of the constituent elements, and has each elementary atom a constant value?

For many carbon compounds Kopp has shewn that

$$(V)\ C_xH_yO_z=(x.\,11)+(y.\,5{\cdot}5)+(z.\,7{\cdot}8).$$

But in some cases the observed value of (V) does not agree with that calculated by this formula; thus

			diff
Aldehyde C_2H_4O :	calculated $(V)=(2.11)+(4.5{\cdot}5)+7{\cdot}8=51{\cdot}8$		
	observed (V)	$=56{\cdot}5.$	$+4{\cdot}7$
Acetic acid $C_2H_4O_2$:	calculated $(V)=(2.11)+(4.5{\cdot}5)+(2.7{\cdot}8)=59{\cdot}6$		
	observed (V)	$=63{\cdot}5.$	$+3{\cdot}9$

The value of (V) for a compound $C_xH_yO_z$ is conditioned, according to Kopp, by the value of (V) for the oxygen atom, or atoms, in the molecule. Kopp gives the following two values, according as the oxygen atom acts as a monovalent or divalent atom in the given molecule[1];—

$$(V)\,O^{I}=12{\cdot}2;\quad (V)\,O^{II}=7{\cdot}8.$$

Applying these values to the case of aldehyde, we have

$$(V)\ H_3C-\underset{\displaystyle H}{\overset{\displaystyle |}{C}}-O=(2.11)+(4.5{\cdot}5)+12{\cdot}2=56{\cdot}2;$$

a result which agrees very closely with the observed value, viz. 56·5. For acetic acid we have

$$(V)\ H_3C-C\begin{cases}=O\\ -OH\end{cases}=(2.11)+(4.5{\cdot}5)+7{\cdot}8+12{\cdot}2=64{\cdot}0:\ \text{observed}=63{\cdot}5.$$

[1] Kopp used the expression 'oxygen within the radicle' as synonymous with what is now called divalent (singly-linked) oxygen atoms; and 'oxygen without the radicle' as synonymous with monovalent (doubly-linked) oxygen atoms.

Or again, for ethylic acetate,

$$(V)\ H_3C-C\begin{matrix}O\\ \diagdown\\ O-C_2H_5\end{matrix} = (4.11)+(8.5{\cdot}5)+12{\cdot}2+7{\cdot}8 = 108{\cdot}0:$$

observed = 107·8.

Or, once more, for acetone and its isomeride allylic alcohol,

(1) $(V)\ H_3C-\underset{\underset{O}{\|}}{C}-CH_3 = (3.11)+(6.5{\cdot}5)+12{\cdot}2 = 78{\cdot}2$: observed = 78·0;

(2) $(V)\ H_2C-\underset{H}{C}-\underset{H_2}{C}-OH = (3.11)+(6.5{\cdot}5)+7{\cdot}8 = 73{\cdot}8$: observed = 73·8.

Instead of assigning two values to the oxygen atoms in compounds of the form $C_xH_yO_z$, it would probably be better to employ the value $(V)\ CO = 23{\cdot}2$ (i.e. $11+12{\cdot}2$), which attributes the influence on the total value of (V) due to the presence of the group CO to both the atoms which comprise this group.

Schiff (*loc. cit.*) concludes that the value of $(V)\ O^{II}$ varies according to the nature and arrangement of all the constituents of the molecule; and also, that the value of $(V)\ X-C-O$ is always greater than that of $(V)\ C-O-X$, where X represents a radicle.

Kopp[1] deduced two values for (V)S; thus $(V)S^{I} = 28{\cdot}6$, $(V)S^{II} = 22{\cdot}6$: but only one value for (V)C, and one for (V)H and (V)Cl. Many and very varying values have been found by different observers for (V)N: thus Kopp assigns the value 2·3 to (V)N when N occurs in amines, and 17 when N occurs in CN and in some nitro-compounds; Ramsay gives $(V)N = 3{\cdot}6$ in amines, $= 9{\cdot}0$ in pyridine, lutidine, &c., and $= 7$ in aniline, toluidine, and dimethylaniline.

If the influence exerted by the oxygen in a carbon compound on the value of (V) for that compound varies according to the actual valencies of the oxygen atoms in the molecule, it appears probable that the total value of (V) will also depend on the actual valencies of the carbon atoms in the molecule. Buff[2] thought that his determinations shewed that the value of (V) for compounds containing trivalent (doubly-

[1] See also Ramsay, *C. S. Journal* **Trans.** for **1879.** 471—2.

[2] *Annalen*, **Supplbd. 4.** 143 *et seq.*

linked) carbon atoms is greater than the value calculated on the assumption that $(V)C^{III} = (V)C^{IV} = 11$. Thus,

(1) Dichlorethylene $Cl_2 = C^{III} - C^{III} - H_2$, $(V) = 79{\cdot}9$:
(V) calculated $= 78{\cdot}6$; diff. $= +1{\cdot}3$.

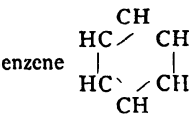
(2) Carbon dichloride $Cl_2 = C^{III} - C^{III} = Cl_2$, $(V) = 115{\cdot}4$:
(V) calculated $= 113{\cdot}2$; diff. $= +2{\cdot}2$.

(3) Amylene $H_3C^{IV}\diagdown H_3C^{IV}C^{III} - C^{III}H - C^{IV}H_3$, $(V) = 112$:
(V) calculated $= 110$; diff. $= +2{\cdot}0$.

(4) Valerylene $H_3C - C^{III}H - C^{II} - C^{III}H - C^{IV}H_3$, $(V) = 104{\cdot}0$:
(V) calculated $= 99$; diff. $= +5{\cdot}0$.

(5) Diallyl $H_2C^{III} - C^{III}H - C^{IV}H_2 - C^{IV}H_2 - C^{III}H - C^{III}H_2$, $(V) = 126{\cdot}8$:
(V) calculated $= 121$; diff. $= +5{\cdot}8$.

No trustworthy conclusions regarding the values to be assigned to $(V)C^{III}$ or $(V)C^{IV}$ can however be drawn from these data, because when we tabulate the values of (V) for a number of hydrocarbons we find no apparent regular connexion between these values and the valencies of the carbon atoms. Thus,

		Diff.
(1) Hexane $H_3C - (CH_2)_4 - CH_3$	$(V) = 140$: (V) calculated $= 143$;	-3.
(2) Diallyl $H_2C - CH - CH_2 - CH_2 - CH - CH_2$	$(V) = 126{\cdot}8$: (V) calculated $= 121$;	$+5\,8$.
(3) Benzene 	$(V) = 96$: (V) calculated $= 99$;	-3.

If we associate the increase in the value of (V) for diallyl over the calculated value with the presence of trivalent carbon atoms, then we must conclude that the presence of trivalent carbon atoms in the molecule C_6H_6 is connected with a decrease in the calculated value of (V), or that all the carbon atoms in this molecule are tetravalent.

153 Not only may the values to be assigned to carbon and oxygen atoms in determining the total value of (V) for a carbon compound vary according to the actual valencies of these atoms in the molecule of the compound in question, but they may

also vary, apparently, in accordance with the distribution of the interatomic reactions in molecules wherein all the carbon atoms are tetravalent, and all the oxygen atoms are divalent. Thorpe (*loc. cit.*) has given some examples of such variations; but Zander[1] has extended the number of examples considerably. Thus a comparison of (V) for propyl and isopropyl compounds shews that the normal compounds always exhibit a smaller value than the iso-compounds:—

	C_3H_7OH	C_3H_7I	C_3H_7Br	C_3H_7Cl
highest value of (V) obtained for normal compound $\left(H_3C-\underset{H_2}{C}-\underset{H_2}{C}-X\right)$	81·4	108·2	97·5	91·7
lowest value of (V) obtained for iso-compound $\left(X-CH\begin{matrix}\nearrow CH_3\\ \searrow CH_3\end{matrix}\right)$	82·3	108·3	99·0	93·0

But the molecules of both classes of compounds contain only tetravalent carbon atoms[2].

Lossen[3] has collected the most trustworthy data bearing on the question as to whether or not a constant value can be assigned to $(V)CH_2$. Kopp gave 22 as the mean value for this group. Lossen shews that the differences between the values of (V) for successive homologues of the acid series $C_nH_{2n+1}CO_2H$ nearly agree with the differences calculated on the basis of $(V)CH_2 = 22$; but that in the series of alcohols $C_nH_{2n+1}CH_2OH$ the value of $(V)CH_2$ varies from 18·7 to 21, assuming that the other atoms exert a constant influence on the total value of (V). Apparently then a variable value must be assigned to $(V)C^{IV}$, or to $(V)H$, or to both of these quantities.

Some light is thrown on this point by Zander's comparison (*loc. cit.*) of (V) for propyl, isopropyl, and allyl, compounds, which leads to the conclusion that the difference between (V) for a normal propyl and the corresponding allyl compound, i.e. between two compounds differing in composition by H_2, varies from 5·7 to 8·9 (having a mean value of 7·1): hence, if

[1] *Annalen* **214.** 138: **224.** 56.

[2] See also Brown *Proc. R. S.* **26.** 238. Also Elsässer, *Annalen* **218.** 302.

[3] *Annalen* **214.** 81 *et seq.*

we assume that the difference in question is wholly due to the difference in empirical composition, we appear forced to conclude that the value of the influence exerted on (V) by the monovalent atom H is variable[1].

Thorpe (*loc. cit.*) got these results for compounds containing only tetravalent carbon atoms in their molecules:—

H_2CCl_2 (V) = 65·12; hence (V) Cl = 21·6; (assuming (V) C = 11, and (V) H = 5·5)

$HCCl_3$ (V) = 84·53; „ (V) Cl = 22·7

CCl_4 (V) = 103·68; „ (V) Cl = 23·2

Taking the mean value for (V)Cl, viz. 22·5, and applying this to calculate the values of (V) for each of the preceding compounds, we have

(V) H_2CCl_2 = 67·0	observed = 65·12	diff. = − 1·88
(V) $HCCl_3$ = 84·0	„ = 84·53	„ = + ·53
(V) CCl_4 = 101·0	„ = 103·68	„ = + 2·68

Hence the value of (V)Cl appears to be variable. This is more strikingly illustrated by Stædel's comparison[2] of the differences in the values of (V), and also the differences in the boiling points, at various pressures, of chlorine compounds derived from C_2H_4.

The differences in (V), and also in B.P., between the following pairs of compounds, viz.

ClH_2C-CH_2Cl and H_3C-CH_2Cl,

$ClH_2C-CHCl_2$ and $H_3C-CHCl_2$,

ClH_2C-CCl_3 and H_3C-CCl_3,

[1] Besides the empirical difference of H_2, there is a difference in the actual valencies of some of the carbon atoms in propyl and allyl compounds; thus, normal propylic alcohol is $H_3C-\overset{H_2}{C}-\overset{H_2}{C}-OH$, and allylic alcohol is $H_2C^{III}-\overset{H}{C^{III}}-\overset{H_2}{C}-OH$. See also Weger, *Annalen* **221.** 61, who gets different values for (V) CH_2 in different series of compounds. See *Ber.* **16.** 2458, where Kopp reminds us that this number was given by him as a *mean value*, and nothing more. Schiff (*Annals* **220.** 286, and 291) concludes that (V)C almost certainly varies according to the nature and the arrangement of the constituents of the molecule in which C occurs. Horstmann (*Ber.* **20.** 766) collects many data which lead him to the conclusion that 'unsaturated compounds with closed chain formulæ have considerably smaller molecular volumes than those with open chain formulæ and multiple linkings of atoms'. Neubeck (*Zeitschr. für physikal. Chemie*, **1.** 649) shews that (V) for benzene derivatives is modified according to the position [ortho, meta, or para] of the replacing groups.

[2] *Ber.* **15.** 2559.

express differences corresponding with change of CH_3 into CH_2Cl, i.e. with the introduction of the first chlorine atom in place of an atom of hydrogen into the hydrocarbon residue CH_3.

The differences in the values of the same quantities between the following pairs of compounds, viz.

$$Cl_2HC-CH_3 \text{ and } H_2ClC-CH_3,$$
$$Cl_2HC-CH_2Cl \text{ and } H_2ClC-CH_2Cl,$$
$$Cl_2HC-CHCl_2 \text{ and } H_2ClC-CHCl_2,$$
$$Cl_2HC-CCl_3 \text{ and } H_2ClC-CCl_3,$$

express differences corresponding with the introduction of the second chlorine atom (in place of an atom of hydrogen) into the residue CH_3.

And lastly, by comparing (V) and B.P. for the following pairs of compounds, viz.:

$$Cl_3C-CH_3 \text{ and } Cl_2HC-CH_3,$$
$$Cl_3C-CH_2Cl \text{ and } Cl_2HC-CH_2Cl,$$
$$Cl_3C-CHCl_2 \text{ and } Cl_2HC-CHCl_2,$$
$$Cl_3C-CCl_3 \text{ and } Cl_2HC-CCl_3,$$

the differences corresponding with the introduction of the third chlorine atom into the group CH_3 are determined.

Now the differences in question are:

for the first chlorine atom (V) = 14·20: B.P. = 56°·22;
„ second „ (V) = 16·37: B.P. = 31°·30;
„ third „ (V) = 19·16: B.P. = 16°·04.

Hence each chlorine atom has a different 'volume-value' and a different 'boiling-point-value'. If we choose to attribute the observed differences to the carbonaceous parts of the molecules, i.e. to C_2H_4 in $C_2H_4Cl_2$, to C_2H_3 in $C_2H_3Cl_3$, &c., we seem still obliged to admit that carbon *and* hydrogen atoms have varying 'volume-values', and varying 'boiling-point-values', in the molecules formulated.

154 The remark made in paragraph 151 that the value of (V) for a compound is equal to the sum of the values of (V) for each of the elementary atoms in the molecule of that compound, must evidently be supplemented by the statement, that in the case of carbon compounds, at any rate, the value of (V) is not constant for C or O, and probably not for H or

Cl, but varies in accordance with (1) the actual valencies of the atoms of carbon and oxygen, and (2) the distribution of all the atomic interactions in the molecule. The precise character of the connexion between the values of (V) for C, O, H, and Cl, and the valencies on the one hand, and the nature of the atoms (or atomic groups) in direct union within any molecule on the other hand, cannot be ascertained until much more experimental data has been accumulated[1]. The known data regarding the values of (V) cannot therefore be applied in other than a very tentative way to the selection of one from among several possible structural formulæ[2].

155 The values of (V) for many solid compounds have been compared, and attempts have been made to generalise the relations between these values; but, as might be expected from considering how little comparable are the conditions under which the relative densities of solids have been determined, the conclusions are either vague and difficult of precise application, or represent only interesting relations between certain numbers, without much, if any, connexion with chemical facts.

By considering the difference between (V)MO and (V)M, a fairly constant value for (V)O in the oxides is sometimes obtained: thus for PbO and Fe_2O_3, the difference in question is about 5·5. But in other oxides the value of (V)O appears to be very variable; thus,

$$(V)\,CuO - (V)\,Cu = 5{\cdot}1\,;\ \text{but}\ (V)\,Cu_2O - (V)\,Cu_2 = 10{\cdot}5.$$

Brauner and Watts[3] have drawn the following conclusions

[1] It is pointed out by Lossen (*loc. cit.*) that careful determination of (V) for many series of carbon compounds and for many individuals in each series, are now required.

[2] An illustration of the difficulties which are met with, and of the uncertain nature of the results obtained, is furnished by the contradictory conclusions of Thorpe (see Watts's *Dict.* **3rd Supplt.** 2117—18) and of Masson and Ramsay (see *C. S. Journal* **Trans.** for **1881**, 51 *et seq.*) regarding the structural formula of $POCl_3$. Thorpe concludes that the formula ought to be written $Cl_2 = P - O - Cl$, Masson and Ramsay think that $Cl_3 \equiv P - O$ more nearly represents the facts. In connexion with the formula of this compound see the experiments of Michaelis and La Coste (*Ber.* **18.** 2118).

[3] *Phil. Mag.* [5] **11.** 60.

from comparisons of (V)MO and (V)M for different series of oxides.

(1) In strongly basic oxides the value of (V)O is negative; the more basic the oxide, and the greater the value of (V)M in the oxide, the more negative is the value of (V)O.

(2) In oxides of heavy metals and non-metals the value of (V)O is positive.

(3) In oxides of the earth metals the value of (V)O is *nil.*

The values of (V) for isomorphous compounds generally vary little; thus,

(V) $MgO . Al_2O_3 = 41{\cdot}4$	(V) $ZnO . Fe_2O_3 = 47{\cdot}0$
(V) $ZnO . Al_2O_3 = 40{\cdot}2$	(V) $MnO . Cr_2O_3 = 46{\cdot}4$.

The greater the agreement between the angles of crystals belonging to the same class, the less do the values of (V) differ, e.g.

(V) $SrCO_3 = 41{\cdot}0$
(V) $PbCO_3 = 41{\cdot}2$ } crystals are almost identical.

(V) $BaCO_3 = 45{\cdot}8$ crystals exhibit differences[1] from those of $SrCO_3$ and $PbCO_3$.

Kopp[2] has concluded that if D, the difference between what he calls the 'molecular volumes' of two isomorphous compounds, is represented as $D = \frac{(V) - (V_1)}{\frac{1}{2}[(V) + (V_1)]}$, then the value of D may attain a maximum, equal to 0·328, without isomorphism being impossible.

Determinations of (V) for anhydrous and hydrated salts promise to throw some light on various questions implied in the commonly used expressions 'water of crystallisation' and 'water of constitution'.

Graham distinguished 'saline' water from 'basic' water in salts and acids; the replacement of the former by another salt, or by an oxide, produced a double salt, or in the case of acids

[1] For more details see Naumann's *Handbuch der Allgemeinen und Physikalischen Chemie*, 360—362.

[2] *Annalen* **36.** 1. *Pogg. Ann.* **52.** 262; **53.** 446; **56.** 371. See also article "Isomorphie", in the *Neues Handwörterbuch der Chemie.*

a normal salt; the replacement of the 'basic' water in an acid produced a basic salt. Thus,

$$MgSO_4\ \underset{saline}{H_2O}\ \underset{basic}{6H_2O}\ \text{gave}\ MgSO_4\ K_2SO_4\ 6H_2O;$$

$$N_2O_5\ \underset{saline}{H_2O}\ \underset{basic}{3H_2O}\ \text{gave}\ \begin{cases} N_2O_5\ CuO\ 3H_2O & \text{normal nitrate of copper.} \\ N_2O_5\ CuO\ 3CuO & \text{basic} \quad \text{,,} \end{cases}$$

Graham further distinguished *basic* water from *water of constitution;* e.g.

$$H_2SO_4.\underset{basic}{H_2O},\ \text{from}\ C_2O_3.\underset{constitutional}{H_2O}.$$

Thorpe and Watts[1] have determined (V) for the salts MSO_4, when M = Mg, Zn, Cu, Mn, Fe, Co; and for the hydrated salts MSO_4xH_2O when M = Mg, Zn, &c. and x varies from 1 to 7.

The value of $(V)MSO_4$ was found to be independent of the nature of M for the dehydrated salts. The difference $(V)MSO_4.xH_2O - (V)MSO_4$ gave the increase in (V) for xH_2O added to the salts. The following results were obtained.

Mean difference between values of

$(V)S$	and	$(V)S.H_2O = 10{\cdot}7$
$(V)S.H_2O$	,,	$(V)S.2H_2O = 13{\cdot}3$
$(V)S.2H_2O$	,,	$(V)S.3H_2O = 14{\cdot}5$
$(V)S.3H_2O$	,,	$(V)S.4H_2O = 15{\cdot}4$
$(V)S.6H_2O$	,,	$(V)S.7H_2O = 16{\cdot}2$

$$[(V)S = (V)MSO_4,\quad (V)S.xH_2O = (V)MSO_4.xH_2O.]$$

Hence the value of $(V)MSO_4.xH_2O$ is changed to a different amount by each of the molecules of water which combines with the salt; or, it may be said, that the water molecules contribute in unequal degrees towards the total value of (V).

Clarke[2] has compared the differences between (V) for hydrated and (V) for dehydrated salts, belonging to two classes of compounds.

In the first class, when M = Ca, Sr, Ba, Mg, Cu, Fe, or Co, and x varies from 2 to 6, the mean value of

$$\frac{(V)MCl_2.xH_2O - (V)MCl_2}{x}$$

[1] *C. S. Journal* **Trans.** for **1880.** 102.

[2] *Amer. Journal of Sci. and Arts,* (3). **8.** 428.

was found to be = 13·76 (with a maximum value of 15·0, and a minimum of 12·5).

The second class comprised various hydrated oxides and hydroxides, viz.

$$B_2O_33H_2O,\ I_2O_5H_2O,\ K_2OH_2O,\ CuOH_2O,\ SrOH_2O,\ BaOH_2O,$$
$$Al_2O_3H_2O,\ Mn_2O_3H_2O,\ Fe_2O_3H_2O.$$

In this class the value of the difference

$$\frac{(V)\text{ oxide }xH_2O - (V)\text{ oxide}}{x}$$

varied from 7·4 to 19·4.

If S represent one of the chlorides belonging to the first class, or one of the oxides belonging to the second class, then, for class I, the formula $(V)S\ xH_2O = (V)S + (x.\ 13{\cdot}76)$ gives numbers which agree fairly well with the observed results; but no such simple relation between $(V)S\ xH_2O$ and $(V)S$ can be traced among the results obtained for compounds belonging to class II.

But the hydrates of class I belong to the group of compounds containing 'water of crystallisation', whereas those of class II, or most of them at any rate, belong to the group containing 'water of constitution'; hence, although the results obtained by Thorpe and Watts (*loc. cit.*) lead to the conclusion that the value of $(V)H_2O$ in the salts MCl_2xH_2O is probably different for each addition of H_2O, nevertheless Clarke's numbers, taken as a whole, emphasise the difference between 'water of crystallisation' and 'water of constitution', and shew that the chemical difference implied in these expressions is connected with the relative magnitudes of the spaces occupied by chemically comparable quantities of the hydrated salts belonging to each class of compounds.

156 The quotient $\frac{\text{formula-weight}}{\text{specific gravity}}$ has been treated as an empirically determined quantity; incidentally it has been regarded as expressing the volume occupied by a quantity of the compound formulated proportional to the mass of the molecules which form the vapour of that compound. The question is often propounded in papers on '*Specific volumes*', whether the

volume of an element in the free state is, or is not, identical with the volume of the same element in combination. This question, it seems to me, may be better put in another form. What is the connexion between the value of (V) for a given compound, and the nature and arrangement of the atoms which constitute the molecule of that compound? It has been shewn (pars. 152, 153) that the partial value to be assigned to each atom is not a constant quantity; in other words that (V) varies with variations in the arrangement, no less than in the nature, of the atoms which form the molecule of the compound for which (V) has been determined. But is there any connexion between the variations of (V), the valencies of the atoms on the one hand, and the distribution of the interatomic reactions on the other? From the data concerning isomeric carbon compounds, firstly, containing only saturated polyvalent atoms, and secondly, containing also unsaturated polyvalent atoms, we may conclude, I think, that both connexions exist. It seems probable that a decrease in the actual valency of an atom, other things remaining the same, is attended by an increase in the value of (V). But Stædel's investigation (par. 153) shews that the latter value is also modified by the nature of all the atoms in the molecule. If these connexions can be made precise, and their nature ascertained by careful investigation, it may become possible to trace relations between the volumes occupied by molecules of defined structure and the energy-differences of these molecules, and perhaps to connect with these the differences in the values of the refractive, and the rotatory, powers of the same molecules[1].

If the value of (V) for a compound is regarded from the point of view of the molecular theory, a connexion may be traced between this value and the partial value of (V) for each atom in the molecule of the compound. For it has been shewn

[1] We should thus gain clearer conceptions of the properties of atoms as these are exhibited in atomic interactions, and also be able to connect these interactions, in a more precise manner than is yet possible, with the properties of the systems thereby formed. If this view is accepted it is evident that the results obtained by the various physical methods discussed in this and the preceding section must have kinetical as well as statical aspects (see Book II.).

by L. Meyer[1], and by Loschmidt[2], that the spaces occupied by gaseous molecules (calculated from data based on the transpiration-coefficients of the substances) are connected with the atomic structure of these molecules, in the same general way as has been shewn by Kopp and others to hold in the case of liquid compounds[3]. The Clausian sphere-of-action (*wirkungssphare*) of a molecule is the smallest space which the molecule can occupy under given conditions. Changes in these conditions (e.g. change of temperature), changes in the form of the molecule, or changes in the arrangement of the atoms in the molecule, will be accompanied by changes in the space occupied by the molecule. The relations between the values of these smallest spaces (spheres-of-action) occupied by the molecules of two gases can be calculated, by means of a formula deduced from the general principles of the molecular theory, from observations of the transpiration-coefficients of the gases. Putting the experimentally determined value of (V) as the value of the molecular sphere-of-action of one of the gases, the values of the molecular spheres-of-action of other gases can be found, and compared with those calculated from Kopp's, Meyer's, and Loschmidt's, values for $\frac{\text{atomic weight}}{\text{specific gravity}}$ of nitrogen, oxygen, hydrogen[4], &c., and from the partial values assigned, by different chemists, to various atoms in determining the total value of (V) for molecules containing these atoms. This is done by O. E. Meyer (*loc. cit.* pp. 219—221). The observed and calculated values of (V) agree as closely as could be expected, considering that regard has been paid in the calculations solely to volume, whereas the molecular spheres-of-action must be conditioned by the form, the diameter, and the length, of the molecular systems. Hence there is a well-established probability in favour of the conclusion that the partial values assigned to the different atoms, in determining

[1] *Annalen*, **Supplbd. 5.** 129.

[2] *Sitzberichte der K. Akad. zu Wien (math.-naturwiss. classe).* **52.** (2nd part) 395.

[3] See O. E. Meyer's *Die Kinetische Theorie der Gase*, 216—221.

[4] For a description of the determination of this constant for oxygen and other gases from measurements of the transpiration-coefficients of these gases, see L. Meyer, *Annalen*, **Supplbd. 5.** 129.

the total value of (V) for a liquid compound, are proportional to the volumes occupied by these atoms in the gaseous state. But this is just the conclusion drawn from an empirical study of the values of (V) determined for series of liquid compounds. Much work must however be done before precise connexions can be traced between the total value of (V) and the partial values assigned to the various atoms in any molecule.

It has generally been assumed that the volumes of different liquids are under comparable conditions at the boiling points of the liquids; but van der Waal's investigations[1] have shewn that those volumes of liquids are comparable for which temperature and pressure are equal fractions of their critical values. In order therefore to compare molecular volumes—i.e. to compare values of (V)—it would be advantageous to determine by experiment the critical temperature and pressure of the liquid compounds examined. This has been done in very few cases; but until it is done, considerable doubt must be thrown on the value of the elaborate deductions which have been drawn from the data regarding molecular volumes[2].

SECTION IV. *Method based on the determination of 'Etherification-values.'*[3]

157 The rate of formation of ethereal salts by the mutual actions of alcohols and carbon-containing acids has been

[1] *Die Continuitat des gasformigen und flussigen Zustandes.* (Leipzig, 1881). Comp. Ostwald's *Lehrbuch*, **1.** 336—339.

[2] Neubeck's results (*Zeitschr. fur physikal. Chemie*, **1.** 649) shew that the relations which exist between the molecular volumes of various benzene derivatives at ordinary pressures also hold good at pressures of 450 and 200 mm.

[3] The papers by Menschutkin, of which this section is a very condensed summary, will be found in *J. fur prakt. Chemie*, (2) **24.** 49: *do.* **25.** 193, and 203 (abstracts in *C. S. Journal* for **1881.** 1117; **1882.** 384, 485, and 595). Abstracts will also be found in *Ber.* **14.** 2630, 2819: **15.** 162, 248, and 721. A paper containing a summary of Menschutkin's results will be found in *Ann. Chim. Phys.* (5). **30.** 81. (Abstract in *C. S. Journal* for **1884.** 726.) See also *Zeitschr. fur physikal. Chemie*, **1.** 611.

studied by Menschutkin: many of his results have a more direct bearing on the questions of chemical kinetics, some of them however may find a place here. The standard reactions in terms of which determinations are stated are these:

(1) $HCH_2OH + CH_3CO_2H = CH_3CO_2(CH_3) + HOH$;

(2) $HC(CH_3)_2CH_2OH + HCO_2H = HCO_2(C_4H_9^{\beta}) + HOH$.

By varying the alcohol in (1) and the acid in (2), comparable series of values are obtained for (1) alcohol-acetic system, and (2) acid-isobutylic system. The number of molecules of HCH_2OH decomposed in reaction (1), and the number of molecules of HCO_2H decomposed in reaction (2), when equilibrium is established, are taken as 100, and the results with other alcohols and acetic acid, or with other acids and isobutylic alcohol, are stated in terms of this unit.

The expression 'etherification-velocity' is used to denote the amount of action during one hour; the expression 'etherification-limit' is used to denote the amount of action when equilibrium is established. Thus the statement 'the *etherification-velocity* of CH_3CH_2OH is 67·3, and the *etherification-limit* is 95·6' means, that when equal numbers of molecules of CH_3CH_2OH and CH_3CO_2H react, 67·3 molecules of CH_3CH_2OH are decomposed during the first hour, and 95·6 when the action ceases, the number of molecules of HCH_2OH decomposed under similar conditions (at the close of the reaction) being taken as 100[1].

The following, among many other numbers, were obtained by Menschutkin.

Alcohol-acetic system.

Formula of Alcohol.	Velocity.	Limit.
HCH_2OH	80·0	100·0
$CH_3 . CH_2OH$	67·3	95·6
$C_2H_5 . CH_2OH$	66·9	96·0

[1] The process is conducted at 153°—154°; the residual acid is determined by titration. Two to five grams of alcohol are sufficient, and the process is always applicable except the ethereal salt produced should be unstable at the temperature of experiment.

Hence, the substitution of CH_3 for H in the primary alcohol $H.CH_2OH$ appears to be accompanied by a decrease in the *etherification-velocity* of about 12·5, and in the *limit* of about 4·5.

The following conclusions are drawn by Menschutkin from his determinations of the reaction-values of the system $R.CH_2OH + CH_3CO_2H$.

(1) The reaction-values (i.e. velocity and limit) of the normal group C_nH_{2n+1} in the alcohols $C_nH_{2n+1}CH_2OH$ are practically the same.

(2) Isomerism in the C_nH_{2n+1} radicles of primary alcohols influences only the velocity-value, not the limiting value.

(3) Unsaturated alcohols ($R\ CH_2OH$) exhibit lower reaction-values than saturated alcohols; e.g. the values for $C_2H_3 - CH_2OH$ are smaller than those for $C_2H_5 - CH_2OH$.

From his study of the etherification of secondary alcohols R_2CHOH, the same chemist concludes that these alcohols exhibit lower values than primary alcohols; and that the same radicle has smaller values in a secondary than in a primary alcohol. The limiting value for tertiary alcohols cannot be determined on account of the occurrence of secondary changes; the velocities shew great irregularities.

Further results obtained by Menschutkin shew that definite connexions, the precise nature of which cannot yet be traced, exist between the actual valencies of the atoms, and also the distributions of the interatomic reactions, in the molecules of alcohols, and the etherification-values of these alcohols[1].

By multiplying the limiting value of each compound by the molecular weight of that compound (and dividing by 100), numbers are obtained which exhibit the influence, on the etherification-limit, of the molecular weights of the members of the system studied. Menschutkin gives the following numbers as representing *molecular limits*. In a later paper he calls these numbers simply *weight-limits*, in distinction to the *percentage limits* already explained.

[1] For a more precise statement of Menschutkin's conclusions on this point see abstract in *Ber.* **14.** 2818.

Acid-isobutylic system.

Acid.	Molecular limit.	Difference for each CH_2.	
CH_3CO_2H	40·42		
		10·41	
$C_2H_5CO_2H$	50·83		
		10·34	
$(C_3H_7^a)CO_2H$	61·17		19·81
		9·90 =	2
$(C_5H_{11}^a)CO_2H$	80·98		
		10·53 =	21·07
$(C_7H_{15}^a)CO_2H$	102·05		2

Mean difference for each increment of CH_2 = 10·29.

The value of the molecular, or weight, limit for any member of this series of acids (the alcohol being isobutylic) may be found by the formula,

$$\text{molecular limit} = 40{\cdot}42 + (n-2)\,10{\cdot}29;$$

when n = number of carbon atoms in the molecule of the acid.

Thus, in the acid $(C_3H_7^a)\,CO_2H$ $n = 4$, hence

molecular limit = 40·42 + (2 . 10·29) = 61·0; observed value = 61·17.

Menschutkin gives the expression $a + (n-2)\,d$ for finding the molecular etherification-limit for an acid in any system of alcohol and acids, when a = molecular limit for the first acid of the series, and d = mean increase, for each increment of CH_2, in the molecular limit of the acids of the series.

The rule is, to the value of the limit for the given alcohol with the first acid of the series, add $(n-2)\,d$, that is, add $(n-2)$ times the mean homologous difference (i.e. the mean difference for each increment of CH_2) between the weight-limits of the given acid and the first acid of the series, when n = number of carbon atoms in the molecule of the given acid.

Thus, required the weight-limit for the caproic-butylic system. For the acetic-butylic system $a = 40{\cdot}52$, and $d = 10{\cdot}29$; caproic acid is $C_5H_{11}.CO_2H$; therefore the weight-limit required is $40{\cdot}52 + (4 . 10{\cdot}29) = 81{\cdot}68$.

It is evident that the percentage limit can easily be found when the values of a and d are given. In the case in question we have,

$$\text{percentage limit} = \frac{81{\cdot}68 . 100}{116} = 70{\cdot}41. \quad [C_5H_{11}.CO_2H = 116].$$

Menschutkin gives the following values for a and d in various systems of alcohols and acids of the acetic series:

acid-ethylic	system;	$a=39{\cdot}94$
acid-propylic	„ ;	$a=40{\cdot}23$
acid-butylic	„ ;	$a=40{\cdot}42$
acid-amylic	„ ;	$a=40{\cdot}55$
acid-hexylic	„ ;	$a=40{\cdot}64$
acid-heptylic	„ ;	$a=40{\cdot}71$
acid-caproic	„ ;	$a=40{\cdot}77$

$d=10{\cdot}29$.

It is also possible to vary the alcohol, the acid remaining constant, and from the data obtained to calculate the weight-limit for any given system[1].

From a comparison of the etherification-values for primary secondary and tertiary acids, and also of the same values for hydroxy- and chloro-acids &c., Menschutkin draws certain conclusions regarding the connexions between the variations in these values and the molecular structures of the various acids. For instance, the velocity of etherification of the primary acids is much greater than that of the secondary acids, but the limiting values are nearly identical in both series.

A study of these conclusions shews that much is to be hoped for from the application of Menschutkin's method, but that more data must be obtained before we have precise knowledge concerning the connexions between the rate of formation of ethereal salts and the chemical constitutions of the interacting alcohols and acids[2].

SECTION V. *Miscellaneous methods.*

158 That the '*capillarity-constants*' of liquid carbon compounds are connected with the chemical constitutions of these compounds is apparent from researches by Mendelejeff[3],

[1] See details in *C. S. Journal*, **Abstracts** for **1882.** 387.

[2] See some of Menschutkin's generalisations in *C. S. Journal*, **Abstracts** for **1882.** 485, 598: and an application to the formulæ of maleic and fumaric acids in *do. do.* **1882.** 383.

[3] *Compt. rend.* **50.** 52; **51.** 97.

Wilhelmy[1], and especially Schiff[2]. The capillarity-constants are calculated from experimental data by methods which need not be discussed here (see abstracts of Schiff's papers in *C. S. Journal*, or see Ostwald's *Lehrbuch*, I. 479). Schiff's results lead to *capillarity-equivalents* for certain atoms, e.g. C = 2H, O = 3H, Cl = 7H, &c., that is, they tend to shew that n atoms of one element have the same partial value in the capillarity-constant of a series of compounds as m atoms of another element. The capillarity-equivalent of the same elementary atom seems to vary with variations in the actual valency of that atom, and also with variations in the chemical type of the compounds examined.

159 The rates of flow through capillary tubes of liquid compounds have been measured by several observers, especially by Graham[3] and by Pribram and Handl[4]. The results obtained are sufficient to establish the fact of a connexion between the *transpiration-rates* and the chemical constitution of liquid carbon compounds. But they do not elucidate the exact nature of this connexion. Ostwald[5] suggests that measurements should be made at the boiling points of various liquids, as some of the results obtained by Pribram and Handl suggest that the transpiration-rates of equal weights of analogous compounds under these conditions would be found to be nearly proportional to the molecular weights of the compounds.

160 The facts of *electrolysis* have been used as arguments in discussing the constitution of chemical compounds; but the questions on which electrolytic data throw light rather belong to the domain of chemical kinetics than to that of statics[6].

[1] *Pogg. Ann.* **121.** 55.

[2] *Annalen*, **223.** 47; *Gazetta*, **14.** 368 (abstracts in *C. S. Journal*, **Abstracts** for **1884.** 808, and **1885.** 717.)

[3] *Phil. Trans.* **1861.** 373.

[4] *Sitzungsberichte der K. K. Acad. zu Wien*, **1878** (June part); **1879** (June part).

[5] *Lehrbuch*, **1.** 507.

[6] See Book II. chap. III.

Faraday's laws of electrolysis, translated into modern chemical language, assert that the parts or ions into which a compound is separated by electrolysis are chemically equivalent and carry with them equal quantities of electricity.

Electrolytes belong to the type of salts, using the term in its widest meaning. Metallic salts are generally good conductors when molten, and they readily undergo electrolysis. But most, if not all, single liquid compounds,—e.g. water, alcohol, ether,—are nearly dielectrics. Aqueous solutions of most salts are electrolytes; and the nature of the electrolytic decomposition is clearly connected with the quantity of the solvent. Hence it is probable that a chemical action of some kind occurs between the salt and the water; and the true electrolyte may be a molecular aggregate, or aggregates, formed by the union of the two kinds of molecules. This view is confirmed, on the whole, by the electrolytic behaviour of many double salts, some of which are decomposed by the current in the same way as a mixture of their constituents, while others give distinctive products. The behaviour of concentrated aqueous solutions of cadmium iodide and chloride points to the existence and electrolytic decomposition of aggregates, probably Cd_3X_6, in these solutions, while the behaviour of dilute solutions of the same salts is explained by supposing that the body undergoing electrolysis is the ordinary molecule CdX_2. Whatever be the exact nature of the connexion between the passage of the current through a solution of a salt and the electrolysis of the salt, there can be little doubt that the process is intimately conditioned by the nature and amount of the solvent; and the most probable explanation of this conditioning effect is that which assumes the formation of more or less unstable compounds of the solvent with the dissolved body.

But considerations such as these are evidently better discussed when we are treating the subject of chemical change, than when we are dealing with chemical composition[1].

[1] See Book II. chap. III. The student would do well to read the chapter on Electrolysis in Ostwald's *Lehrbuch* **1.** 533—568.

Concluding Remarks on Part I.

161 The general aim of the first part of this book has been to give a fairly complete account of the present state of knowledge regarding the questions of chemical statics, indicating where such knowledge requires to be chiefly supplemented, or rendered more precise, by new experimental researches.

I have regarded those questions which are concerned with substances, or systems of substances, in equilibrium as broadly belonging to chemical statics; but I have been obliged to pay more or less attention to the kinetical aspects presented by all such questions.

It may be said that the fundamental conception of atom and molecule, stated and illustrated in chapter I., has been regarded in its applications to explain resemblances and differences between physical and chemical phenomena, nascent actions, allotropy, isomerism, and the classification of elements and compounds; and that the principal methods, both purely chemical and chemico-physical, which are employed in examining these problems, have been sketched, and their applications illustrated.

A way has thus been cleared by which we may hope to approach the more difficult problems of chemical kinetics.

BOOK II.

CHEMICAL KINETICS.

CHAPTER I.

THE LAW OF MASS-ACTION.

162 IN the introduction to Book I. I said that the term *chemical kinetics* would be used to connote the facts and principles which on the whole relate to chemical action, as contrasted with *chemical statics* which term includes those facts and principles that are chiefly connected with chemical composition.

Elements and compounds not only are, they also become.

When we study the statical aspects of chemical phenomena we inquire about the being of elements and compounds; when we examine the kinetical aspects of the same phenomena we study the becoming of these elements and compounds.

The history of chemistry, I think, establishes the fact that at some periods progress has been made rather by seeking knowledge of the composition than of the reactions of bodies, while at other times inquiries into the functions rather than the composition of different kinds of matter have been most productive. But while this is true, it is also certain, and the inquiries we have made in Book I. regarding composition suffice to shew that it is certain, that the division of chemistry into statics and kinetics can be carried out only in the broadest way. We have seen that the same facts must be

regarded now from the statical and now from the kinetical point of view.

A complete account of any chemical change must include the statement of the relations between the reacting bodies, and also of the relations between the forces concerned in the change.

163 The question of chemical kinetics is: what is the cause of chemical change? The answer to this question has always been the same: the cause of chemical change is chemical affinity[1].

To trace the history of the term *chemical affinity*, and to find a definite and quantitative meaning for this term, is to give a complete account of chemical kinetics.

The word *affinity* suggests the notion of kinship or relationship; it embodies the conception of the earliest chemists that those bodies which are ready to enter into union are akin to one another. In the sixteenth and seventeenth centuries the notion of kinship was so far modified that chemical processes were regarded as caused by the mutual attractions of bodies. After Newton had demonstrated the law of gravitation, the conception of one body attracting another with a force varying according to the masses of the bodies and their distances apart was adopted in chemistry, and was developed until it culminated in the *tables of affinity* drawn up by Bergmann in the latter part of the eighteenth century.

164 Bergmann thought that the cause of chemical combination was identical with the cause of gravitative attraction; but he said that the results differed according as the attraction was manifested between masses or between minute particles of bodies. In the latter cases the attraction was the greater the nearer were the particles; hence, said Bergmann, chemical action occurs more readily between liquids or gases than between solids.

[1] I have closely followed Ostwald (*Lehrbuch der Allgemeinen Chemie*) in dealing with the subject of chemical affinity. The second volume of Ostwald's *Lehrbuch* is devoted to this subject. Without the help of this book I could not have given a clear account of affinity.

Bergmann taught that the result of the chemical attraction, or affinity, between two bodies is to cause a change wholly in the direction of the stronger attraction, unless this should be reversed by the more powerful attractive force of heat Thus, suppose that two bodies, A and BC, are brought into conditions such that chemical action is possible; if the attraction, or affinity, of A for B is greater than that of B for C, then BC will be decomposed and the only products of the change will be the new bodies AB and C; but if the attraction, or affinity, of B for C is greater than that of B for A, no chemical change will occur.

By applying this conception experimentally Bergmann was able to determine the order of the affinities of series of bodies. Thus, it was required to determine the order of the affinities of three bodies, A, B and C, towards the body D. A compound AD was formed and this was caused to interact with B and C, respectively; if AD was decomposed by B forming BD and A, then the affinity of B for D was said to be greater than that of A for D; if AD was decomposed by C forming CD and A, and if BD was also decomposed by C forming CD and B, then C was said to have a greater affinity for D than either A or B. These results were then tabulated in a table of affinity as follows:—

Order of affinities towards D.

C
B
A.

But it was frequently found that a body which had no action on another when the two were mixed in solution at the ordinary temperature would decompose that other when the two were fused together at a high temperature. Hence Bergmann found it necessary to perform a vast number of experiments, and to draw up at least two tables of affinity for each substance, one shewing its affinities at ordinary temperatures in solution, and the other shewing its affinities at high temperatures when fused with other substances. Bergmann's table for potash, for instance, was constructed thus:—

ORDER OF AFFINITIES FOR POTASH.

Wet way (ord. temp.).	**Dry way** (high temp.).
Sulphuric acid	Phosphoric acid.
Nitric „	Boric „
Hydrochloric „	Arsenic „
Phosphoric „	Sulphuric „
Arsenic „	Nitric „
Acetic „	Hydrochloric „
&c. &c.	&c. „

This table conveyed the information that a solution of a compound of potash with any acid in the left-hand column would be decomposed by a solution of any acid placed in the same column above the acid which was combined with potash; and that a solid composed of potash with any acid in the right-hand column would be decomposed by heating with any acid placed in the same column above the acid which was combined with potash.

In Bergmann's view, affinity acted in one direction only.

165 The publication by Berthollet in 1803 of the *Essai de Statique Chimique* marked the next great step in advance in the study of affinity.

Berthollet, like Bergmann, regarded chemical action as the result of attractions between the small particles of bodies. When conditions are favourable, this attraction results, according to Berthollet, first in cohesion and then in combination. But other forces may come into play which are opposed to the attraction called affinity; heat may cause the expansion of substances which would otherwise combine; solution may weaken, or destroy, the cohesion of the particles of a solid. Whether combination occur or not, and if it occur, whether the products remain unchanged or not, depends, on Berthollet's view, upon the relative magnitudes of the opposing forces. If the attraction between the particles of different kinds of matter is greater than the action of the forces which tend to separate these particles, then a new compound or compounds will be formed. Should these compounds be solids under the experimental conditions, the cohesion of their particles will act in the same direction as the attraction of affinity which is the immediate agent in

their production. The final arrangement of the particles of two kinds of matter depends, according to Berthollet, not only on the relative magnitudes of the different attractions between them, but also on the relative masses of the reacting bodies; thus, a relatively small attraction may be made to overcome a greater, by largely increasing the mass of one of the two kinds of matter.

Berthollet regarded a liquid holding a solid in solution as a system in a state of more or less unstable equilibrium; by removing some of the liquid by evaporation, or by lowering the temperature, or in other ways, this equilibrium might be overthrown, and crystals might separate containing particles both of the solid previously in solution and also of water changed from the liquid to the solid state. Such a system, said Berthollet, will present two extreme cases; in one case all the solid is held in solution by the liquid, and in the other all the liquid is changed to the state of solid. Between these extremes there may be many states each marked by a certain definite relation between the amounts of solid and liquid compounds; for Berthollet regarded the solution, no less than the crystals which separated, as a compound, or a series of compounds, of water and salt.

Combination and solution were looked on by Berthollet as analogous actions. He said

"In solution, one pays attention chiefly to the liquidity acquired by the solid by combining [with the solvent], and especially to the uniformity of the parts of the liquid compound....In a combination one principally considers the other properties of the compound which is produced, comparing therewith the properties of the substances which produced it. In most cases solution is due to a combination so feeble that the properties of the dissolved substance do not disappear".[1]

Again;

"Chemical action is reciprocal; its effect is the result of a mutual tendency to combination. One ought not, strictly speaking, to say that a liquid acts upon a solid, rather than that the solid acts upon the liquid; it is more convenient however to ascribe the whole of the action to one of the substances, when one wishes to examine the products of the action, rather than the action itself."[2]

[1] *Essai*, 1. 59—60.

[2] *Essai*, 1. 36—37.

When lime is placed in water, mutual action, said Berthollet, begins at once, but the cohesion of the particles of the solid is so great that the dissolving action of the water does not produce any marked effect for some time; but water is being absorbed by the lime, and thus the effect of the cohesion of the particles of the lime is slowly overcome by that of the solvent action of the water, until finally the lime dissolves. During this process two combinations of lime and water are formed, one solid, the other liquid; the effect of one force, cohesion, is to increase the amount of the former; the effect of another force, solution, is to increase the amount of the latter combination. A state of equilibrium is established, and continues so long as the conditions are unchanged; but alteration of temperature, or changes in the relative masses of water and lime, suffice to overthrow this equilibrium and to establish another[1].

Berthollet not only formed a clear mental image of a system as held in equilibrium by the actions and reactions of its various constituents, but he had also what I think must be regarded as a very clear conception of the chief forces concerned in maintaining this equilibrium. In the summary to Part I. of the *Essai*, he says:

"The chemical qualities of different substances depend (1) on their tendencies to combine, whereby they mutually saturate each other, and which tendencies remain more or less dominant in the compounds produced; (2) on their relations to heat, which modify their combining powers, by causing variations in the quantities of the substances coming within the spheres of mutual action, and also by opposing elasticity (*élasticité*[2]) to condensation, the latter of which is one of the effects of combination; (3) on the mutual actions of their small particles (*molécules*[3]), acting in the same direction as the affinity which has produced combination, but opposed to actions and reactions between these particles and those of other substances; (4) on their relations to other substances, which combine with them, but not so as to produce a mutual saturation

[1] *Essai*, 1. 37.

[2] *Élasticité.* Berthollet uses this word as meaning nearly the same as *dilatation*, or perhaps we might now say *disgregation.*

[3] *Molécules.* This word as employed by Berthollet means only a small particle; I have thought it better not to use the term *molecule*, as this is now employed with a more definite meaning than *small particle.*

(*saturation*[1]), but rather a division and varying distribution of properties, and chiefly of those properties which depend on the constitution (*constitution*)."[2]

166 Berthollet's conception of affinity as an attractive force acting between the minute particles of bodies, and modified in its results by the action of other forces, led him to pay great attention to the influence of the masses of the bodies taking part in any chemical change. Just as the cohesion, and elasticity, &c., of the members of a system of bodies are dependent, among other conditions, on the masses of the bodies, so, in Berthollet's view, is affinity dependent on mass:

"Every substance," said Berthollet, "which enters into combination reacts by its affinity and its mass."[3]

The conception which the great French chemist formed of a chemical reaction was radically opposed to that upheld by his illustrious Swedish predecessor.

Let two acids interact with a base in aqueous solution. Bergmann asserted that the acid with the stronger affinity combined with the whole of the base, and the other acid remained uncombined. Berthollet declared that both acids interacted with the base, and that the mass of the base which remained combined with either acid when equilibrium was established depended partly on the intensity of the attraction between the particles of the base and of the acids, and partly on the relative masses of the three bodies present in the reacting system.

Bergmann taught that a chemical change proceeds in one direction only, and that the direction is entirely dependent on the relative affinities of the interacting bodies; but he was obliged to acknowledge that the affinities of some bodies for

[1] *Saturation.* By *saturation of properties* Berthollet means that merging of the properties of the constituents in those of the new compound which is so characteristic of chemical change.

[2] *Constitution.* The *constitution* of a substance is conditioned according to Berthollet by its condensation and dilatation: 'the properties which depend on the constitution' of a substance may be taken as meaning, broadly, the ... properties of the substance. *Ostwald, Lehrb. d. allgem. Chem. 2te Aufl. 1te prakt.*

[3] *Essai*, **1.** 2.

another are sometimes so nearly balanced that a compound of all the reacting bodies is produced; and he was also forced to admit that the order of the affinities of a series of bodies for one and the same body may be changed or even reversed by changing the physical conditions under which the chemical reaction proceeds.

Berthollet, on the other hand, taught that a chemical change may, and often does, proceed in two directions; that is to say, that certain bodies may react to produce others which may then by their interactions reproduce the original bodies; that the equilibrium which is finally attained by a system of interacting bodies is the result of the action and reaction of all the members of the system; and that the conditions which chiefly affect this equilibrium are the affinity and the mass of each body, and also the physical conditions under which the change proceeds and the physical properties of the different possible products of the change.

Berthollet's researches established three points of fundamental importance:—chemical action is conditioned not only by the intensities of the affinities, but also by the relative masses, of the reacting bodies; a chemical change is generally more or less reversible by changing the masses of the reacting bodies, it is only in extreme cases that a chemical change proceeds wholly in one direction; the forces which come into play in chemical occurrences are of the same kind as those which we call physical.

167 The period of sixty years following the publication of Berthollet's *Essai* is not marked by any great advance in the study of chemical affinity; nevertheless various important researches were conducted in this period the results of which served to emphasize the importance of Berthollet's fundamental conception of the influence of the relative masses of chemically reacting bodies on the course of a chemical change and on the equilibrium finally attained by the system.

In 1853 Bunsen[1] examined the change which occurs when a mixture of carbon monoxide and hydrogen is exploded

s *Mc*

I have thou quantity of oxygen less than sufficient for the com-

a more defi[1] *Annalen*, 86. 131; see also Horstmann, *Annalen*, 190. 228.

plete combustion of both gases. Bunsen shewed that some of the oxygen enters into combination with the carbon monoxide and some with the hydrogen, and that the quantity of each of these gases burnt depends on the relative masses of the combustible gas and the oxygen.

In 1855, Gladstone[1], by studying the amount of change which occurs when potassium sulphocyanide and ferric chloride react in aqueous solution, exhibited very clearly the influence of mass on chemical change. Gladstone shewed that when ferric chloride and potassium sulphocyanide react, only a portion of each salt is changed unless the mass of one is made 600 or 700 times as great as that of the other; he also shewed that the quantity of ferric sulphocyanide formed increases continuously with an increase in the quantity of potassium sulphocyanide used.

It is important to note that Gladstone used determinations of physical properties, such as depth of colour, as indications and measurements of the chemical change which occurred.

Berthollet and P. de Saint Gilles[2] in 1862—63 made a large number of measurements of the amount of change which occurs when an alcohol and an acid react to form an ethereal salt and water, and established the influence of the masses of the reacting bodies on the change in question.

168 The year 1867 is marked in the history of chemistry by the publication of a most important memoir on affinity by Guldberg and Waage entitled *Études sur les Affinités Chimiques*[3].

Guldberg and Waage restate Berthollet's law of mass-action in a form in which it is capable of quantitative application; they assert that

[1] *Phil. Trans.* **1855**. 179; and *C. S. Journal*, **9**. 54.

[2] *Ann. Chim. Phys.* (3). **65**. 385; **66**. 5; **68**. 225. Among other memoirs on the influence of mass may be mentioned Margueritte *Compt. rend.* **38**. 304; Tissier, *Compt. rend.* **41**. 312; Dulong, *Ann. Chim. Phys.* **82**. 275; Rose, *Pogg. Ann.* **94**. 481; **95**. 96, 284, 426; Malaguti, *Ann. Chim. Phys.* (3). **37**. 198; Chiczynski, *Annalen*, **Supplbd. 4**. 226; Morris, *Annalen*, **213**. 253.

[3] Published by the University of Christiania; continuation in *J. für prakt. Chemie* (2). **19**. 69.

Chemical action is proportional to the active mass of each of the bodies taking part in the reaction.

The *active mass* of a specified body taking part in a reaction is the mass of that body stated in equivalent weights, present in unit volume of the chemical system. Thus if solutions of hydrochloric acid, sulphuric acid, and caustic soda are mixed in the ratio $2HCl : H_2SO_4 : 2NaOH$, the active masses of the hydrochloric acid, sulphuric acid, and soda are 1, 1, and 1, respectively, H_2SO_4 being taken as one equivalent of sulphuric acid.

Guldberg and Waage's law of mass-action states that the action of each substance in a system of interacting bodies is proportional to the active mass of that substance, and that the total action is proportional to the product of all the active masses.

But the amount of chemical change which occurs when two or more substances react is not dependent solely on the active masses of the substances, it is also conditioned by the chemical nature, and the state of aggregation, of the substances, the temperature, and other variables. Guldberg and Waage group together these variables and express them by a coefficient called by them the *coefficient of affinity*, and represented by the symbol k.

Let two substances P and Q react, and let the active masses of these be represented by the symbols p and q; further let the coefficient of affinity for the reaction between P and Q be represented by k; then the amount of chemical change which occurs will be proportional to the product $k.p.q$. Let the products of the interaction of P and Q be two new bodies P' and Q', and let the active masses of these bodies be represented by the symbols p' and q', and the coefficient of affinity for the reaction between P' and Q' be represented by k', then the amount of chemical change which occurs between P' and Q' will be proportional to the product $k'.p'.q'$. Now when P and Q interact certain quantities of P' and Q' will be formed, and these will at once interact to re-form P and Q; this will proceed until equilibrium is established, after which no further change will occur in the

active masses of the various bodies nor in the values of the coefficients of affinity of either the direct or the reverse change. When equilibrium is attained the product $k.\ p.\ q$, will be equal to the product $k'.\ p'.\ q'$. Hence the conditions of equilibrium are expressed by the equation

$$k.\ p.\ q. = k'.\ p'.\ q'.$$

But as the reaction between P and Q proceeds the active masses of these bodies will be decreased, and the active masses of the products of the change, P' and Q', will be increased. Let P, Q, P', and Q' represent the masses of the four bodies present in the chemical system at the beginning of the change, these masses being stated in equivalent weights; when equilibrium is established x equivalents of P and x of Q will disappear and x equivalents of P' and x equivalents of Q' will simultaneously be formed; let p, q, p', and q' represent the active masses of the four bodies present when equilibrium results, then the values of these active masses will be as follows :—

$$p = \frac{P-x}{v},\quad q = \frac{Q-x}{v},\quad p' = \frac{P'+x}{v},\quad q' = \frac{Q'+x}{v},$$

where v = the total volume of the system, taken as unity.

By substituting the values for p, q, p', and q' in the equation of equilibrium we have

$$(P-x)(Q-x) = \frac{k'}{k}(P'+x)(Q'+x).$$

This equation holds good for all values of P, Q, P', and Q'. The ratio $\frac{k'}{k}$ can be calculated from a determination of x for one special case, and from the value of this ratio values can be found for x, and therefore for the distribution of the four reacting bodies when equilibrium results, starting with any specified quantities of P, Q, P', and Q'.

Guldberg and Waage thus put Berthollet's conception of the influence of mass into an exact form. They consider the masses of the several bodies comprising a chemical system present at the moment when equilibrium is established. The

attempts made to formulate the influence of mass on chemical change previous to the work of the Norwegian naturalists had been implicitly based on measurements of the masses of the reacting bodies present when the reaction began.

169 In their first memoir (*Études* &c.) Guldberg and Waage regard the occurrence of a chemical change as caused by 'chemical force'; they say that when equilibrium results in a system of four bodies, P, Q, P', and Q', the force bringing about the formation of P' and Q' is held in equilibrium by the force which causes the re-formation of P and Q. They also attempt to take into account the possibility of secondary changes among the reacting bodies and to express these in equations. But the formulæ thus arrived at are too complicated for practical application; and moreover the conception of chemical force is vague and unsatisfactory.

In their second memoir[1] Guldberg and Waage follow the example of van't Hoff[2], and, abandoning the notion of chemical force, attempt to find formulæ which may be applied in practice by starting with the clear conception of chemical equilibrium being dependent on the equality of the rates of the direct and reverse chemical changes; i.e. they consider that equilibrium results in a chemical system when the quantity of substance changed in one direction is equal to that formed in the other direction in a given time. Many measurements had been made of the rates of chemical actions, but Guldberg and Waage were the first to establish clearly the connexion between the velocity of a chemical change and the attainment of equilibrium by the system. This was done in their memoir of 1867, but the formulae given in that memoir are complicated and scarcely suited for accurate application. The equation arrived at in the second memoir as representing the connexion between reaction-velocity and equilibrium is identical with that we have already considered; viz. $k.p.q = k'.p'.q'$.

Let there then be a chemical system of four bodies, P, Q, P', and Q'; let P and Q react to produce P' and Q', and P' and Q' react to re-produce P and Q; equilibrium results

[1] *J. für prakt. Chemie*, (2). **19**. 69. [2] *Ber.* **10**. 669.

when the velocity of the direct change (i.e. the production of P' and Q') is equal to that of the reverse change (i.e. the production of P and Q). The conditions of equilibrium are expressed by the equation

$$k.p.q. = k'.p'.q',$$

or, as before,

$$(P-x)(Q-x) = \frac{k'}{k}(P'+x)(Q'+x).$$

It is important to note here that the ratio $\frac{k'}{k}$ is not analysed; it is simply the ratio of the affinity of P and Q to that of the affinity of P' and Q'; and the term affinity is used as a short expression for the unknown cause of the chemical reaction between the reacting bodies.

170 Guldberg and Waage tested their equation of equilibrium both by using the results obtained by other chemists and also by experiments which they themselves conducted.

Thus the results of Berthollet and P. de Saint Gilles[1] on the etherification of alcohols by reacting with organic acids were used by Guldberg and Waage. The members of the reacting system are alcohol, acid, ethereal salt, and water; the direct change results in the production of ethereal salt and water, and the reverse change produces alcohol and acid. The following numbers shew the close agreement between the observed and calculated values of x, i.e. the number of equivalents of acid or alcohol transformed into ethereal salt and water when equilibrium is established.

		x	
SERIES I.	Q	*Observed.*	*Calculated.*
One equivalent acid +	1	·665	·668
Q equivalents alcohol.	1·5	·779	·772
	2	·828	·827
	2·8	·856	·870
	3	·882	·878
	12	·932	·930
	500	1·000	1·000
SERIES II.	P		
One equivalent alcohol +	1	·665	·668
P equivalents acid.	2	·858	·856
	5	·966	·972

[1] *Ann. Chim. Phys.* (3). **65**. 385.

		x	
SERIES III.	P'	*Observed.*	*Calculated.*
One equiv. acid +	0	·665	·668
one equiv. alcohol +	0·13	·626	·648
P' equivs. ethyl acetate.	0·85	·563	·550
	1·6	·521	·487
SERIES IV.	Q'		
One equiv. acid +	0	·882	·871
three equivs. alcohol +	1	·809	·803
Q' equivs. water.	2	·739	·744
	8	·468	·512

Guldberg and Waage themselves examined the reaction which occurs between barium sulphate and potassium carbonate in presence of water. In this case two of the four members of the system are insoluble, viz. barium sulphate and barium carbonate. Guldberg and Waage shewed that if the absolute masses of the insoluble members of a reacting system are fairly large, and the volume of the liquid is kept constant, the changes in the absolute masses of the insoluble bodies do not appreciably affect the active masses of these bodies[1]; and this result was fully confirmed by Ostwald[2].

In the reaction between potassium carbonate (P) and barium sulphate (Q) producing potassium sulphate (P') and barium carbonate (Q'), let the active mass of the potassium carbonate be p, that of the barium sulphate q, that of the potassium sulphate p', and that of the barium carbonate q', then, as q and q' are constant, the equation of equilibrium becomes

$$(p - x) = \frac{k'}{k}(p' + x).$$

The following numbers shew how closely the values of x calculated for the condition that equilibrium is attained agree with the observed values:—

		x	
SERIES I.	Q	*Observed.*	*Calculated.*
1 equiv. barium sulphate +	3·5	·719	·715
500 equivs. water (at 100°) +	2·5	·500	·500
Q equivs. potassium carbonate	2	·395	·391
	1	·176	·178

[1] *J. für prakt. Chemie*, (2). **19**. 469. [2] *J. für prakt. Chemie*, (2). **22**. 256.

SERIES II.	Q	Q'	*Observed.*	*Calculated.*
1 equiv. barium sulphate +	2	·25	·20	·198
500 equivs. water (at 100°) +	3	·25	·408	·409
Q equivs. potassium carbonate +	2	·50	trace	·000
Q' equivs. potassium sulphate.				

171 Experimental evidence in favour of Guldberg and Waage's law of mass-action has been obtained by various observers using different methods. One of the great difficulties consists in finding suitable methods for measuring the distribution of the members of a reacting system all of which remain in solution when equilibrium is established. Very many of the methods which have been found to give trustworthy results are based on the same principle, which is that the amount of chemical change in a homogeneous system is deducible from measurements of some definite physical property of the system and determinations of the changes in the value of this property.

Thomsen[1], in 1869 and subsequent years, shewed that when two acids and a base react in aqueous solution, the distribution of the base between the acids can be determined by thermo-chemical methods. Let the heat of neutralisation of the acid A by the given base be x gram-units, and let the heat of neutralisation of the other acid B by the same base be y gram-units; then if both acids simultaneously react with the base the quantity of heat produced may be x units, in which case the whole of the base has combined with the acid A, or y units, in which case the whole of the base has combined with the acid B, or a number between x and y, in which case the base has divided itself between the two acids; in the last case the proportion of base which has combined with each acid may be calculated from the observed thermal value of the reaction[2].

In 1876 Ostwald[3] shewed that the distribution of a base between two acids can be determined from measurements of the specific volume of a solution of each acid, of the base, of the liquid formed by mixing each acid separately with the base, and of the liquid formed by mixing both acids simul-

[1] *Pogg. Ann.* 138. 65. [2] See *post* par. 183.

[3] *Pogg. Ann.* Ergzbd. 8. 154.

tancously with the base[1]. The results obtained by Thomsen and by Ostwald have fully confirmed the law of mass-action enunciated by Guldberg and Waage; and this law has also been upheld by other series of experiments conducted by various chemists[2].

The law of mass-action may then be regarded as well-established; this law asserts that the amount of chemical change which occurs when a system of interacting bodies attains equilibrium is proportional to the product of the active masses of all the bodies taking part in the change and the coefficient of affinity of the change.

[1] See *post* par. 184.

[2] These experiments will be described in some detail later; see pars. 185, 186.

CHAPTER II.

CHEMICAL DYNAMICS.

172 A DETAILED examination of the applications of the law of mass-action, which was stated and briefly illustrated in Chap. I., leads to the consideration of the forces which come into play in chemical changes[1].

As forces are measured in dynamics either by measuring the velocity produced in a specified mass in unit of time, or by opposing the unknown force by another of known amount until equilibrium is attained, so may measurements of chemical forces be obtained by determining the amount of change which occurs in unit of time, or by opposing the direct change by another in the opposite direction and determining the conditions of equilibrium.

It is important to notice that when we speak of *chemical force* the term force is used with a meaning different from that in which it is employed in dynamics: by chemical force we mean the product of the active masses of the various bodies comprising the changing system and the constant of velocity of the change. And by *velocity* we mean, not the ratio of space traversed to time used as in dynamics, but the ratio of material chemically changed to time used in the change.

Using the term chemical force with this meaning, we shall find that a chemical change is conditioned by changes in the chemical force in much the same way as an electric current is conditioned by changes of potential.

[1] In this Chapter I have again closely followed Ostwald's *Lehrbuch der Allgemeinen Chemie*, Bd. II. The present chapter is a condensed account of the greater part of the second book of Ostwald's *Verwandtschaftslehre*.

Those methods of measuring what we have called chemical forces which are based on determinations of the velocities of chemical changes may be called *kinetical methods*, while the term *statical methods* may be applied to those which are founded on determinations of the conditions of equilibrium.

The methods whereby measurements have been made of the velocities of chemical changes, with the view of determining the intensities of the chemical forces, have usually been chemical; whereas both physical and chemical methods have been used for determining the conditions of equilibrium of chemical systems.

I shall begin by considering some of the kinetical methods.

SECTION I. *Velocity of Chemical Change.*

173 Wenzel[1], in 1777, measured the times required by different acids to dissolve equal quantities of the same metal, and he attempted to draw inferences from the results as to the relative affinities of the acids. Thus, he says:—

"If an acid dissolves one drachma of copper or zinc in an hour, then an acid of half the strength requires two hours to dissolve the same amount of copper or zinc, the surfaces exposed and the temperature being constant."

Berthollet[2] made observations somewhat similar to those of Wenzel. He said that the velocity of a chemical change is greater the greater is the chemical force; but he noticed that the velocity diminishes as the change approaches completion, and that reactions which begin rapidly often finish very slowly.

174 Wilhelmy[3], in 1850, gave a mathematical form for the fundamental connexion between the quantity of material changed and the time required in a chemical reaction.

Wilhelmy examined the inversion of cane sugar in aqueous solution in the presence of acids; $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. The amount of change at any moment can be determined by measuring the specific rotatory power of the liquid.

[1] *Lehre von der Verwandshaft* [Dresden, 1777], 28.

[2] *Essai*, 1. 409.

[3] *Pogg. Ann.* 81. 413, 499.

The assumption made by Wilhelmy was that the mass of sugar changed in unit-time is proportional to the mass of sugar remaining unchanged in the reacting system.

Let A = mass of sugar originally present; let x = mass of sugar changed in time θ; then the ratio of the amount changed, dx, to the time, $d\theta$, is given by the equation

$$\frac{dx}{d\theta} = (A - x)c,$$

where $A - x$ is the amount of unchanged sugar and c is a constant.

The ratio $\frac{dx}{d\theta}$ expresses the velocity of the chemical change, or, in shorter words, the *reaction-velocity.*

Ostwald[1] integrates the above equation to get it into a form in which it may be applied; he counts the time from the moment when the sugar solution is brought into contact with the acid, i.e. when $\theta = 0$ and $x = 0$. The final form in which the value of the constant appears is

$$c = \frac{1}{\theta} \log \frac{A}{A - x}.$$

The numbers shew that $\frac{1}{\theta} \log \frac{A}{A - x}$ is nearly constant for values of θ varying from 15 to 630 minutes.

Later experiments conducted by Ostwald[2] on the inversion of cane sugar have confirmed the result of Wilhelmy, that the reaction-velocity at each moment is proportional to the mass of sugar capable of undergoing change.

175 Experiments conducted by different chemists with different changing systems have shewn that the result obtained by Wilhelmy holds good in very many and very different cases. This result may be stated in these words:—

The amount of chemical change at any moment is proportional to the mass of the changing body in the system.

Among the more important researches which have established the accuracy of this statement may be mentioned, Harcourt and Esson's examination of the reaction between

[1] *Lehrbuch*, 2. 617. [2] *J. fur prakt. Chemie* (2). 29. 385.

potassium permanganate and a large excess of oxalic acid[1], and the reaction between peroxide of hydrogen and hydriodic acid[2]; Ostwald's examination of the catalytic change of methylic acetate to methylic alcohol and acetic acid in presence of different acids[3]; van't Hoff's examination of the change of dibromosuccinic acid (from fumaric acid) to bromomaleïc acid and hydrobromic acid by boiling with water, and of monochloracetic acid to glycollic acid and hydrochloric acid in presence of water[4].

In all these cases the value of the expression $\frac{1}{\theta}\log\frac{A}{A-x}$ is nearly constant[5]. The fact, that the velocity of the early stages of a chemical change is often different from the velocity when the change has proceeded for a little time, introduces a possible source of error into the observations on which the statement concerning the proportionality between the rate of change and the mass of the changing body is based. But this error may be obviated by counting the time from the moment when the velocity of the change becomes regular, or by determining the reaction-velocity for definite intervals while the change proceeds[6].

The outcome of these experiments then is to establish a simple relation between the quantity of a body undergoing chemical change and the time occupied in accomplishing the change. In all cases only one body was undergoing change, or if more than one actually underwent change then the masses of all except one were made so large that changes in these masses could practically be neglected. It is also to be noted that all the changing systems examined were homogeneous; no separation of gases or solids occurred during the various processes. With these limitations, it appears that chemical change obeys the same law as gravi-

[1] *Phil. Trans.* for **1866**. 193. [2] *Phil. Trans.* for **1867**. 117.

[3] *J. für prakt. Chemie* (2). **28**. 449.

[4] *Études de dynamique chimique* [Amsterdam, 1884], 14.

[5] For details of the methods used for measuring the velocities of these changes, and for tables shewing the actual and observed values of the constant, see Ostwald's *Lehrbuch*, **2**. 616—624.

[6] See Ostwald, *loc. cit.* 624.

tative, electrostatic, electrodynamic, electromagnetic, and other physical changes.

176 But we must now proceed to cases where more than one body undergoes chemical change at the same time.

If we assume that the amount of change which each member of the system undergoes is proportional to the active mass of that body, then the product of the active masses of all the changing bodies gives the function which expresses the velocity of the complete reaction.

In order to find whether this assumption is justified by facts, Ostwald[1] begins by finding an expression for the reaction-velocity when two bodies only are concerned. Let A and B represent the masses of the bodies originally present, and let $x =$ the portion of each changed in the time θ, these masses being measured in equivalents; then the reaction-velocity is

$$\frac{dx}{d\theta} = (A - x)(B - x)\, c,$$

where c is a constant.

If equal numbers of equivalents of the two bodies are concerned in the change then $A = B$, and

$$\frac{dx}{d\theta} = (A - x)^2 c.$$

By integration, taking x and θ simultaneously equal to zero, the equation

$$\frac{x}{A - x} = Ac\theta$$

is obtained.

If the fundamental assumption is correct, the product Ac must remain constant when x varies: $Ac = \frac{1}{\theta} \cdot \frac{x}{A - x}$.

The experiments made by Hood[2] on the change of potassium chlorate and ferrous sulphate in acid solution to potassium chloride and ferric sulphate, are used to test the accuracy of the equation. In these experiments θ varied from 20 to 520 minutes, and Ac was almost constant, ranging from ·00737 to ·00760; when θ became 628 and 639 mins.

[1] *Lehrbuch*, 2. 626–634. [2] *Phil. Mag.* (5). 6. 371.

Ac became ·00726 and ·00725, but in these cases $A - x$ was so small that the calculation of Ac is uncertain.

Among other determinations whereby values are found for the function $\frac{1}{\theta} \cdot \frac{x}{A-x}$ are (1) Warder's measurements of the rate of saponification of ethylic acetate by caustic soda[1]; (2) Ostwald's determination of the rate of change of acetamide in presence of an acid into acetic acid and the ammonium salt of the acid used[2]; and (3) van't Hoff's experiments on the velocity of the reaction wherein sodium monochloracetate and soda are changed to sodium glycollate and sodium chloride[3]. In the first set of experiments the rate of change was determined by titrating from time to time with a standard acid; in Ostwald's experiments the rate of change was determined by decomposing the unchanged acetamide by sodium hypochlorite and measuring the nitrogen evolved; and in the third case van't Hoff measured the amount of change in specified times by titrating the residual soda by means of a standard acid.

In each set of experiments Ac has a nearly constant value; the value varies from ·106 to ·113 in Warder's experiments where θ varies from 5 to 120 minutes; in Ostwald's experiments Ac varies from ·0087 to ·0092, θ varying from 15 to 240 minutes; and in van't Hoff's experiments, where θ varies from 9 to 374 minutes, Ac varies from ·00551 to ·00633.

The expression already given for the reaction-velocity when the two bodies undergoing change are present in equal numbers of equivalents is applicable with some modification when an excess of one of the reacting bodies is employed[4]. In this case A is not equal to B and on integrating the equation $\frac{dx}{d\theta} = (A-x)(B-x)c$, we obtain the expression

$$\log \frac{B(A-x)}{A(B-x)} = (A-B)c\theta.$$

Hood[5] determined the rate of the change occurring

[1] *Amer. C. Journal* for 1882. No. 5.
[2] *J. fur prakt. Chemie* (2). 27. 1.
[3] *Études de dynamique chimique*, 20.
[4] See Ostwald, *loc. cit.* 631.
[5] *Phil. Mag.* (5). 6. 378.

between ferrous sulphate and potassium chlorate when an excess of one of the salts was used. In one case there was twice as much chlorate employed as was required for the reaction; and in the other case four times as much ferrous sulphate as was required. If $A = FeSO_4$ and $B = KClO_3$, then in the first case $A = 2B$, and

$$\log \frac{A - \frac{x}{2}}{A - x} = Ac\theta;$$

and in the second case $B = 4A$, and

$$\log \frac{A - \frac{x}{4}}{A - x} = 3Ac\theta.$$

The actual value found for Ac in the first set of experiments varied from ·001965 to ·00202, θ varying from 30·5 to 360 minutes; and the actual value found for Ac in the second case varied from ·00411 to ·00431, θ varying from 24 to 231 minutes.

There is then ample experimental evidence in support of the assertion that when more than one body is simultaneously undergoing chemical change the rate of the change is proportional to the product of the active masses of all the bodies in the changing system[1].

177 The foregoing treatment of the relation between the rate of a chemical change and the amount of the changing bodies implies, that if more than one substance is undergoing change, each obeys the law of mass-action, and each change proceeds as if it were independent of the others. The truth of this proposition is rendered apparent by the close agreement between the observed rates of many different chemical reactions and the values calculated on the assumption that the amount of change at any moment of any one member of the system is proportional to the active mass of this body, and the total change at any moment is proportional to the product of the active masses of all the changing bodies.

[1] Ostwald, *loc. cit.* 632—634, develops the necessary equations for more complex reactions than those we have considered, but these equations cannot yet be applied for lack of experimental data.

This proposition is called by Ostwald *the principle of the co-existence of reactions.*

Many of the reactions considered in the previous paragraphs have been regarded as more simple than they really are; small secondary changes have been overlooked. For instance, when methylic acetate reacts with water in the presence of an acid to produce acetic acid and methylic alcohol, the rate of change is influenced by the acetic acid produced. If these secondary changes are taken into account in the calculation of the theoretical constant of each reaction, the total change being treated as made up of the primary change and one or more small secondary changes, the values obtained for the constant shew smaller variations than if the small secondary changes are overlooked. But this is exactly what ought to be if the principle of the co-existence of reactions is true[1].

178 When a solid and a liquid interact we have a heterogeneous system. The amount of change in a given time is here also proportional to the product of the active masses of the changing bodies. But the active mass of the solid is proportional to the surface exposed, and not to the total mass of the solid. The equation by which the reaction-velocity can be calculated must therefore be modified. If w = the surface of the solid the equation becomes

$$\frac{dx}{d\theta} = (A - x)\, cw;$$

and by integration

$$\log \frac{A}{A - x} = cw\theta.$$

It is difficult to apply this equation; the results of experiments shew a certain amount of variation in the value of what ought to be a constant. But it is almost impossible to get a constant surface of a solid; the solution of the solid in the liquid causes the action to slacken; gases are sometimes formed on the surface and the surface is diminished, and so on[2].

[1] Ostwald, *loc. cit.* 2. 636, puts the principle of the co-existence of reactions into a mathematical form.

[2] See Ostwald, *loc. cit.* 2. 638—640.

SECTION II. *Chemical Equilibrium.*

179 We must now glance at the statical methods whereby it has been attempted to measure chemical forces. In these methods a chemical system is brought into equilibrium by opposing a change in one direction by a change in the opposite direction, and the distribution of the various members of the system is determined when equilibrium results.

The methods which are applicable here are either chemical or physical. Chemical methods may be used in cases where the system is heterogeneous and one or more of the members of the system can be measured by some ordinary analytical process without disturbing the equilibrium which the system has attained; for instance, an acid reacts with an insoluble salt of another acid forming a soluble salt and a new acid—e.g. calcium oxalate and hydrochloric acid produce calcium chloride and oxalic acid—the soluble acid or salt may be determined in a portion of the system when equilibrium has been reached. Physical methods may be used in cases where the system is homogeneous and where the removal of any portion of a member of the system would disturb the equilibrium of the system: in these methods either a physical change which accompanies and forms the measure of the chemical change is measured; or a physical property is measured the value of which is dependent on the distribution of the chemically reacting bodies[1].

180 If a body A is changed to A', and if A' is changed to A, the system will attain equilibrium when the velocity of the primary change is equal to that of the reverse. Let p be the active mass of A, and p' the active mass of A'; let x be the number of equivalents of A changed to A', and let x' be the number of equivalents of A' changed to A, at any moment;

[1] Steinheil (*Annalen*, **48**. 153 [1843]) was the first to give a general statement of the theory shewing the dependence of physical properties of a chemical system on changes in the arrangement of the members of the system. The theory is given in detail in Ostwald's *Lehrbuch*, **2**. 753—759.

then the velocity of the direct change $\left(\frac{dx}{d\theta}\right)$ is

$$\left(\frac{dx}{d\theta}\right) = (p - x)\, c;$$

and the velocity of the reverse change $\left(\frac{dx'}{d\theta}\right)$ is

$$\left(\frac{dx'}{d\theta}\right) = (p' - x')\, c'.$$

But x must equal $-x'$ and $dx = -dx'$; so that

$$\left(\frac{dx}{d\theta}\right) = -(p' + x)\, c'.$$

And therefore the reaction-velocity of the whole change, $\frac{dx}{d\theta}$, is expressed as

$$\frac{dx}{d\theta} = (p - x)\, c - (p' + x)\, c'.$$

The condition of equilibrium is $\frac{dx}{d\theta} = 0$; therefore, if ξ is the value obtained by x when equilibrium results

$$(p - \xi)\, c = (p' + \xi)\, c',$$

and

$$\frac{c}{c'} = \frac{p' + \xi}{p - \xi}.$$

Now as $p - \xi$ is the mass (in equivalents) of the body A, and $p' + \xi$ is the mass of A', present in the system when equilibrium results, and as these masses are independent of the original values of p and p', the equation shews equilibrium to result in a system of two chemically interacting bodies when the active masses of the bodies are in the same ratio as the velocity-constants of the primary and reverse changes.

The value of ξ can be determined experimentally, and from this the ratio of the velocity-constants of the two parts of the change can be calculated.

If one of the two bodies is in a different state of aggregation from the other, then the active mass of one is constant; thus if the system is composed of a solid and a liquid or a gas, the active mass of the solid is constant towards the liquid or gas; hence, in such a case the active mass of the other

constituent must also be constant in order that equilibrium may result. Such cases are comparatively simple; and they comprise by far the greater number of cases in which the equation of equilibrium for a system composed of two changing bodies can at present be applied.

The case of water in contact with ice at 0° is a typical one. Equilibrium is independent of the mass of the ice; and as the mass of water in unit volume of the system is independent of the absolute mass, it follows that a mixture of ice and water, in any proportion, remains in equilibrium at 0°. But if the system is compressed the active mass of the water is increased, and therefore equilibrium is upset, and is restored again only at a temperature lower than 0°. If a solid expands on melting, then equilibrium between this solid and its own liquid is attained under pressure only at temperatures higher than that of the normal melting point of the solid.

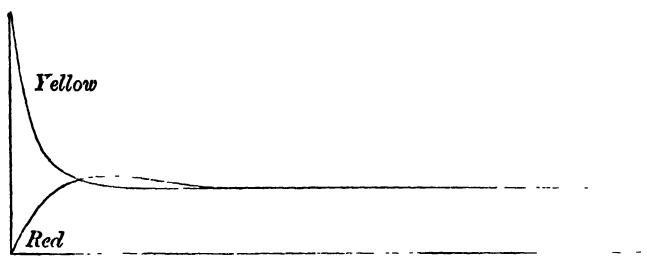
So also in cases of evaporation of liquids, equilibrium results at a definite temperature when the active mass of the vapour bears a certain constant ratio to that of the liquid; to maintain the constancy of this ratio the active mass of the vapour must remain constant, but this is done by keeping the pressure constant. The constancy of the pressure of a vapour over a liquid is therefore a function of the temperature, and not of the relative quantities of vapour and liquid.

Cases of solution belong to the category we are now discussing. When a salt dissolves in water the active mass of the solid is constant, and therefore equilibrium must result when a definite mass of the solid has dissolved, and must be independent of the relative masses of dissolved and undissolved salt but dependent on the temperature.

The attainment of equilibrium in many cases of allotropic change is also conditioned by the constancy of the ratio of the active masses of the changing bodies. For instance, in the change of paracyanogen $(CN)_n$ to gaseous cyanogen $(CN)_2$ equilibrium results when the gas attains a certain pressure which is independent of the mass of paracyanogen present but varies as the temperature varies.

So also with red and yellow phosphorus[1]. If red phosphorus is heated to 440° the pressure of the vapour increases up to a limit which is independent of the mass of solid phosphorus present; but on continued heating the pressure falls until it again attains a constant value. If yellow phosphorus is heated to 440° the pressure of the vapour is much greater than that from red phosphorus at the same temperature; but the pressure falls until it attains the same value as that which marks the final equilibrium between red phosphorus and its vapour at the same temperature. The results are represented graphically in the accompanying curve.

Troost and Hautefeuille have shewn that red phosphorus exhibits different properties according to the temperature at



which it is prepared. Red phosphorus at 440° gives a certain vapour-pressure; equilibrium results when the active mass of the gas has attained a certain value, and this value depends on the pressure; but on continued heating another variety of red phosphorus is produced, and therefore the active mass changes, and therefore the pressure changes until equilibrium again results. Yellow phosphorus at 440° gives a certain vapour-pressure; but the composition of the vapour is changing, and therefore the pressure changes until the vapour attains a definite composition, when its active mass becomes constant and equilibrium results[2].

[1] Hittorf, *Pogg. Ann.* **126**. 193; Troost and Hautefeuille, *Ann. Chim. Phys.* (5). **2**. 153; Lemoine, *Ann. Chim. Phys.* (4). **24**. 129.

[2] For a more detailed discussion of these and other cases of equilibrium in heterogeneous systems composed of two constituents, see Ostwald's *Lehrbuch*, **2**. 643—650.

181 Let us now briefly consider the equilibrium of a system comprising four changing bodies.

Let the two bodies A and B be changed to A' and B'; let the active masses (in equivalents) of the four bodies originally present be p, q, p', and q', respectively; and let x be the number of equivalents of A and B changed to A' and B', and x' the number of equivalents of A' and B' changed to A and B, at any moment; then the velocity of the direct change is expressed by the equation

$$\left(\frac{dx}{d\theta}\right) = (p-x)(q-x)c,$$

and the velocity of the reverse change by the equation

$$\left(\frac{dx'}{d\theta}\right) = (p'-x')(q'-x')c';$$

and therefore the velocity of the complete change is

$$\frac{dx}{d\theta} = (p-x)(q-x)c - (p'+x)(q'+x)c';$$

and the condition of equilibrium, i.e. the condition under which $\frac{dx}{d\theta} = 0$ and $x = \xi$ (*s.* par. 180) is given by the equation[1]

$$(p-\xi)(q-\xi)c = (p'+\xi)(q'+\xi)c'.$$

The simplest case in which to apply this equation is obtained by using equivalent quantities of A and B and allowing these to react without the addition of either A' or B'; in this case $p = q = 1$ and $p' = q' = 0$, and therefore $(1-\xi)^2 c = \xi^2 c'$, hence

$$\frac{c}{c'} = \left(\frac{\xi}{1-\xi}\right)^2.$$

The value of ξ, i.e. amount of A and B changed, and that of $1-\xi$, i.e. amount of A and B remaining unchanged, is determined experimentally, and from these values the ratio of the velocity-constants is calculated.

[1] This equation is identical with that obtained by Guldberg and Waage for the equilibrium of a system of four bodies, but the constants c and c' appear here as reaction-velocities, not as 'forces.'

Ostwald calls the ratio $\left(\frac{\xi}{1-\xi}\right)^2$ the *partition-coefficient* of the reaction; the ratio of the velocity-constants in this case is equal to the square root of the partition-coefficient.

182 Three important series of experiments with homogeneous systems have given results to which the equation

$$\frac{c}{c'} = \left(\frac{\xi}{1-\xi}\right)^2$$

can be applied: these are Thomsen's measurements of the quantities of heat produced by the interaction between an acid and the neutral salt of another acid; Ostwald's measurements of the specific volumes of the solutions obtained by mixing an acid with the neutral salt of another acid; and Berthelot and P. de Saint Gilles' determinations of the amount of ethereal salt formed when equilibrium results between an acid and an alcohol.

183 Thomsen's experiments are based on the proposition that if the heat of neutralisation of an acid by a base is x units, and the heat of neutralisation of another acid by the same base is y units, the heat produced on mixing equivalent masses of the two acids with the base will be z units, and z will be equal to x, or equal to y, or will be a number between x and y, and that from observations of x, y, and z just conclusions can be drawn as to the partition of the base between the acids.

The acids chosen to begin with were nitric and sulphuric, and the base was soda. Whether nitric acid is added to an equivalent quantity of sodium sulphate, or sulphuric acid to an equivalent quantity of sodium nitrate, or equivalent quantities of soda, nitric acid, and sulphuric acid are mixed, the distribution of the reacting bodies when equilibrium results will be the same, and the thermal value of the change will be the same[1].

Sulphuric acid and soda were mixed in equivalent quantities in dilute aqueous solution ($SO_3 + 200H_2O$ and

[1] This proposition may be deduced from the principles of thermal chemistry; it has also been experimentally proved by Thomsen; see *Pogg. Ann.* **138.** 65; or *Thermochemische Untersuchungen*, **1.** 98.

$Na_2O + 200H_2O$), the quantity of heat produced was 31,380 gram-units. The quantity of heat which disappeared when sulphuric acid was added to sodium sulphate in dilute aqueous solution was determined for different proportions of the acid and salt; the result can be expressed by the equation

$$[nH^2SO^4Aq,\ Na^2SO^4Aq] = -\frac{n}{n+8}\,3300 \text{ gram-units.}$$

If therefore $1+n$ equivalents of sulphuric acid react with an equivalent of soda the thermal value of the change may be expressed thus

$$[1+n\,H^2SO^4Aq,\ Na^2OAq] = 31{,}380 - \frac{n}{n+8}\,3{,}300.$$

Nitric acid and soda were then mixed in dilute solution ($N_2O_5 + 200H_2O$ and $Na_2O + 200H_2O$); the quantity of heat produced was 27,230 gram-units. The quantity of heat which disappeared when nitric acid was added to sodium nitrate in dilute solution was 80 gram-units; this is so small that it may be neglected, and the reaction between equivalent quantities of nitric acid and soda may be expressed thermally as

$$[H^2N^2O^6Aq,\ Na^2OAq] = 27{,}230.$$

Equivalent quantities of nitric acid and sodium sulphate in dilute solution were then mixed; the quantity of heat which disappeared was 3,500 units. Now if the sole products of the reaction between equivalent quantities of nitric acid and sodium sulphate in dilute solution were sulphuric acid and sodium nitrate, the quantity of heat which would disappear in this reaction would be equal to the difference between the heat of neutralisation of nitric acid and that of sulphuric acid by soda[1]; this quantity is

$$27{,}230 - 31{,}380 = -4{,}150.$$

But the quantity of heat which was actually used was 3,500; therefore the whole of the sodium sulphate had not been changed to sodium nitrate, and therefore the system when in equilibrium contained sodium nitrate and sulphate and also nitric acid and sulphuric acid. And moreover, if the

[1] $[Na^2SO^4\,Aq,\ N^2O^5\,Aq] = [Na^2OAq,\ N^2O^5Aq] - [Na^2OAq,\ SO^3Aq]$.

only reaction which occurred between sodium sulphate and nitric acid were formation of sodium nitrate and sulphuric acid, we might conclude that $\frac{3500}{4150}$ (= ·84) parts of the sulphate had been changed.

But we know that the sulphuric acid produced in the change would react with the unchanged sodium sulphate with disappearance of heat; this must be taken into account in the calculation.

Let ξ be the number of equivalents of sodium sulphate which have been decomposed by the nitric acid, then ξ will also be the number of equivalents of sodium nitrate formed, and also the number of equivalents of sulphuric acid formed, and $1-\xi$ will be the number of equivalents of sodium sulphate remaining; the total thermal change will therefore consist of three parts;—

(1) decomposition of ξ $Na_2SO_4 = -\xi\, 31{,}380$,

(2) formation of ξ $Na_2N_2O_6 = +\xi\, 27{,}230$,

(3) reaction between ξ H_2SO_4 and $1-\xi$ Na_2SO_4.

The thermal value of (3) will be found by using the equation already given; this equation will now assume the form

$$-(1-\xi)\frac{\frac{\xi}{1-\xi}}{\frac{\xi}{1-\xi}+\cdot 8}\,3{,}300.$$

As the observed thermal value of the complete reaction was $-3{,}500$ we have the equation

[Na^2SO^4Aq, $H^2N^2O^6Aq$]

$$=-3{,}500=\xi(27230-31380)-(1-\xi)\frac{\frac{\xi}{1-\xi}}{\frac{\xi}{1-\xi}+\cdot 8}\,3{,}300.$$

Thomsen found that if ξ is taken as $\frac{2}{3}$, the calculated value of the equation is -3550, which is almost identical with the observed value.

Applying the equation of equilibrium given in par. 182 to the reaction between sodium sulphate and nitric acid, the

value of ξ is found to be $\frac{2}{3}$; hence, as

$$\frac{c}{c'} = \left(\frac{\xi}{1-\xi}\right)^2,$$

it follows that $\frac{c}{c'} = 4$; i.e. the ratio of the velocity-constants of the direct and reverse changes is 4.

By substituting these values for $\frac{c}{c'}$ and ξ in the equation of equilibrium given in par. 181, viz.

$$(p-\xi)(q-\xi)c = (p'+\xi)(q'+\xi)c',$$

equations are obtained which can be applied to find the thermal values of the change occurring between different quantities of nitric acid and sodium sulphate in presence of varying masses of sulphuric acid or sodium nitrate. Thus, to take one case, let p, q, p', and q' represent the masses (in equivalents) of nitric acid, sodium sulphate, sulphuric acid, and sodium nitrate, respectively; let $q = 1$, $p' = q' = 0$, and let p be variable; we have

$$4(p-\xi)(1-\xi) = \xi^2, \text{ and } \xi = \tfrac{2}{3}(1+p-\sqrt{(1+p)^2-3p}).$$

Thomsen measured the thermal change when p varied; the following table presents the observed and calculated values:—

		Gram-units of heat disappeared.	
p	ξ	*Calculated.*	*Observed.*
$\frac{1}{8}$	·121	920	900
$\frac{1}{4}$	·232	1660	1620
$\frac{1}{2}$	·423	2660	2580
1	·667	3550	3500
2	·849	3950	4050
3	·903	4040	4100

The differences are within the limits of the experimental errors.

Other series of experiments were conducted, (1) in which $p = 2$, $q = 1$, $q' = 0$, and p' varied from 0 to 3; (2) in which $q = q' = \frac{1}{2}$, $p' = 0$, and p varied from $\frac{1}{4}$ to 1; and (3) in which $p = q = 0$, $q' = 1$, and p' varied from 1 to 2; in all these ex-

periments the observed values agreed well with the calculated values.

Thomsen also conducted experiments with sodium sulphate and hydrochloric acid; here also it was found that $\frac{2}{3}$ of the sodium sulphate was decomposed, and therefore in this reaction also $\frac{c}{c'} = 4$. The proportions of the reacting bodies were then varied and numbers were obtained which agreed well with those calculated by the use of the equation of equilibrium.

Thomsen's thermochemical investigation of the partition of a base between two acids fully confirms the accuracy of the equation

$$(p-\xi)(q-\xi)c = (p'+\xi)(q'+\xi)c'.$$

184 Ostwald's experiments are based on measurements of the specific gravities of solutions of equivalent quantities of acids and bases and of the salts obtained by the reactions of these acids and bases, and also of the liquids formed when two of the acids are mixed with an equivalent quantity of one of the bases. The following example illustrates Ostwald's method:—

(i) Sp. gr. of solution of caustic soda (approx. normal) [1 vol.]
(ii) Sp. gr. of an equivalent solution of sulphuric acid [1 vol.]
(iii) Sp. gr. of solution of sodium sulphate [2 vols.]

(i)	1·04051		1·04051
(ii)	1·02970	Nitric acid [1 vol.]	1·03083
Sum	2·07021	Sum	2·07134
(iii)	2·05918	Sodium nitrate [2 vols.]	2·05266
Diff.	−0·01103	Diff.	−0·01868

The increase in spec. grav. accompanying the neutralisation of soda by nitric acid is greater by ·00765 than the increase which accompanies the neutralisation by sulphuric acid.

Now if sodium sulphate and nitric acid do not react when mixed, the spec. gravity of the mixed solution would be

	Sodium sulphate [2 vols.]	2·05918
	Nitric acid [1 vol.]	1·03083
	Sum	3·09001
But the observed spec. grav. was	[3 vols.]	3·08343
	Diff.	−0·00658

If the nitric acid and sodium sulphate had been completely changed to sodium nitrate and sulphuric acid, the change in spec. gravity would have been −·00765; thus

Sodium nitrate [2 vols.]	2·05266
Sulphuric acid [1 vol.]	1·02970
Sum	3·08236
Sod. sulphate [2 vols.]+nitric acid [1 vol.]	3·09001
Diff.	−0·00765

Therefore when sodium sulphate and nitric acid react in equivalent quantities the greater part, but not the whole, of the soda goes into combination with the nitric acid.

Before the exact distribution of the soda between the two acids can be determined, it is necessary to measure the changes in spec. gravity which may accompany secondary reactions. Ostwald's measurements shewed that the observed spec. gravity agreed with the calculated, within the limits of experimental error, (1) when solutions of nitric and sulphuric acids were mixed, (2) when sodium nitrate was mixed with sodium sulphate, (3) when sodium nitrate was mixed with nitric acid. But when sodium sulphate was mixed with sulphuric acid the observed spec. gravity was greater than that calculated on the assumption that no chemical change occurred; the increase in spec. gravity was found to agree very closely with that calculated by the interpolation-formula $\frac{n}{n+\cdot 8}\,\cdot 00555$.

Ostwald then applied this correction, and arrived at the result that when sodium nitrate and sulphuric acid interact in equivalent quantities in dilute aqueous solution, two-thirds of the soda remains combined with the nitric acid, and one-third enters into combination with the sulphuric acid. This result is identical with that obtained by Thomsen. A similar examination of the reaction between sodium chloride and sulphuric acid gave a result the same as that which Thomsen obtained.

Hence Ostwald's volumetrical investigation of the partition of a base between two acids fully confirm the accuracy of the equation $(p-\xi)(q-\xi)c=(p'+\xi)(q'+\xi)c'$.

185 Van't Hoff[1], in 1877, used the results of the experiments of Berthelot and P. de Saint Gilles on the etherification of alcohols, in order to test the accuracy of the equation of equilibrium which he had deduced independently of Guldberg and Waage. The experiments shewed that equilibrium was established in a mixture of equivalent quantities of alcohol and acetic acid when two-thirds of the alcohol and the acid were transformed into ethereal salt and water; therefore here also $\frac{c}{c'} = 4$; and the equation for calculating ξ when p varies is

$$4(p-\xi)(1-\xi) = \xi^2, \text{ and } \xi = \tfrac{2}{3}(1+p-\sqrt{p^2-p+1}),$$

where p = active mass of alcohol, q = active mass of acetic acid, p' = active mass of ethereal salt, q' = active mass of water; initial conditions being $q = 1$ and $p' = q' = 0$.

The following table gives some of the results:—

p	ξ	
	Calculated.	*Observed.*
·05	·049	·05
·08	·078	·078
·18	·171	·171
·28	·232	·226
·33	·311	·293
·50	·423	·414
·67	·528	·519
1·0	·667	·673
1·5	·785	·816
2	·845	·87
2·80	·895	·892
3	·902	·90
8	·945	·97

In another set of experiments $p = q = 1$, $p' = 0$, and q' was variable; the calculated values of ξ agreed well with the observed values.

By these experiments the equation of equilibrium is again verified.

186 The equation of equilibrium

$$(p-\xi)(q-\xi)c = (p'+\xi)(q'+\xi)c'$$

[1] *Ber.* **10.** 669.

may be applied to heterogeneous systems. For dealing with systems composed of solids and liquids or gases, we must distinguish cases in which one, two, or three, of the interacting bodies are solids [1].

When one of the four bodies is a solid, the equation becomes

$$(p-\xi)(q-\xi)c=(p'+\xi)hc',$$

where h = active mass of the solid.

If the initial conditions are such that $p=q=1$ and $p'=0$, we have the equation

$$\frac{c'}{c}h=\frac{(1-\xi)^2}{\xi}:$$

by means of which the ratio of the reaction-velocities can be calculated from observations of h, or h can be calculated if $\frac{c'}{c}$ is known.

The simplest case is that in which one body reacts with the solid, the other two bodies being absent at the beginning of the reaction; we have $p=q=0$, and

$$\frac{c'}{c}h=\frac{\xi^2}{1-\xi}.$$

This last case is considered by Ostwald (*loc. cit.*) in detail, the reacting bodies being hydrochloric acid and solid calcium oxalate; the values obtained for $\frac{c'}{c}h$ are not constant. This reaction therefore shews divergences from the results which ought to follow if the law of mass-action held good. But it is possible to reconcile the results to some extent with deductions from this law; at any rate the experiments of Ostwald do not require us to reject the law of mass-action, but they rather open a path which will probably lead to fresh discoveries concerning chemical equilibrium. (See Ostwald, *loc. cit.*)

When two of the interacting bodies in a system of four bodies are solids, the other two being liquids or gases, the active masses of the solids may be put as h and h', re-

[1] Ostwald, *Lehrbuch*, 2. 658—670.

spectively, and the equation of equilibrium then assumes the following form;—

$$(p-\xi)\,hc=(p'+\xi)\,h'c',$$

and therefore $$\frac{c'h'}{ch}=\frac{p-\xi}{p'+\xi}=\text{constant};$$

or in words, equilibrium is attained when the active masses of the two liquid or gaseous constituents of the system are in a fixed ratio which is independent of the absolute or relative masses of the two solid constituents.

In 1871, Deville conducted a series of experiments on the reaction between iron, iron oxide, water-gas, and hydrogen[1]. In these experiments water was heated in a retort connected with a tube containing iron, the other end of the tube being in connexion with a mercury-pump and a manometer. A vacuum having been obtained, the contents of the retort, as also those of the tube, were raised to a constant temperature, and the pressure was measured by the manometer; the pressure was composed of the partial pressures of the water-gas and the hydrogen formed by the reaction between the iron and the steam. As the reaction consisted of a direct change of steam + iron to hydrogen + iron oxide, and a reverse change of hydrogen + iron oxide to steam + iron, equilibrium ought to have been attained when the active masses of the steam and hydrogen bore a constant ratio to each other at a specified temperature. As the active mass of a gaseous constituent of a system is conditioned by the pressure, it follows that if p_1 = the partial pressure of the hydrogen and p_2 = the partial pressure of the water-gas, the ratio $\frac{p_1}{p_2}$ ought to have been constant at each temperature. The temperature of the water in the retort was kept at 0° in one series of experiments, and at 10° in the other series; the temperature of the tube varied from 200° to 1600°. Small errors might readily be made in the measurements of the pressures, especially at the higher temperatures, and at these temperatures small errors would considerably affect the

[1] *Compt. rend.* **70.** 1105; **71.** 30.

values of $\frac{p_1}{p_2}$. The following table shews that Deville's results confirm the equation of equilibrium.

t	p_1	p_2	$\frac{p_1}{p_2}$	p_1	p_2	$\frac{p_1}{p_2}$
200°	·46	9·59	·048	·97	19·53	·05
265	·46	6·42	·072	1·57	23·51	·067
360	·46	4·04	·114	·95	7·63	·124
440	·46	2·58	·178	1·01	5·79	·174
860	·46	1·28	·36	1·30	2·39	·54
1040	·46	·92	·50	1·27	1·91	·66
1600	·46	·51	·90	1·63	1·17	1·40

The experiments of Guldberg and Waage on the reaction between a solution of potassium carbonate and solid barium sulphate (referred to in par. 170) present the conditions of equilibrium of a system composed of two solid and two liquid constituents. Expressing the active masses of the soluble bodies, potassium carbonate and sulphate, by p and p', the equation of equilibrium asserts that the ratio $\frac{p-\xi}{p'+\xi}$ should remain constant independently of the masses of the barium carbonate and sulphate. The following numbers exhibit the values actually obtained for this ratio;—

p	p'	ξ	$\frac{p-\xi}{p'+\xi}$
200	0	39·5	4·06
250	0	50·0	4·0
350	0	71·9	3·87
250	25	30·0	4·0
300	25	40·8	3·94
200	50	·5	3·95

There are as yet but few data by which may be tested the correctness of the deduction from the equation of equilibrium, that when three of the four bodies constituting a reacting system are solids, the equilibrium must be conditioned by the active mass of the liquid or gaseous constituent and must be independent of the masses of the three solid bodies.

Isambert[1] has examined the equilibrium of the system obtained by heating together solid ammonium chloride and

[1] *Compt. rend.* **102**, 1313.

lead oxide; his results shew that when equilibrium is attained for a specified temperature, the pressure of the ammonia gas produced in the reaction is constant and is independent of the masses of the solid ammonium chloride, lead oxide, and lead chloride (or oxychloride).

187 We have now passed in review a large amount of varied experimental evidence which establishes on a firm basis the law of mass-action, and the principle of the co-existence of reactions. These two generalisations assert that the amount of change undergone by a chemically reacting system is proportional to the product of the active masses of the constituents of the system and the coefficient of affinity of the change, and that when several changes take place simultaneously the total change is equal to the sum of the particular changes. We have found that in place of the phrase *coefficient of affinity* we may use the expression *reaction-velocity;* but we have not attempted as yet to analyse the conception underlying these expressions.

The law of mass-action and its applications to different cases of chemical change have been treated so far in a purely empirical manner. The law was gained by determining the distribution of the reacting bodies in certain systems which had attained equilibrium, and it was applied to determine the conditions of equilibrium in other systems and the velocities of the reactions which occurred before equilibrium was attained.

Besides the particular methods considered in the preceding paragraphs of this chapter, there are two general methods which may be used in attempts to solve the problems of chemical dynamics; one of these is thermodynamical, and the other is molecular.

SECTION III. *Thermodynamical methods applied to chemical equilibrium*[1].

188 Horstmann[2], in 1873, propounded a thermodynamical theory of dissociation which is also generally applicable to other cases of chemical equilibrium, inasmuch as the processes which occur in a system before it attains chemical equilibrium are generally reversible processes. Horstmann's method consisted in applying the second law of thermodynamics to the phenomena of dissociation; he concluded that these processes, like all other reversible processes, tend to bring the system to that condition wherein the entropy of the system has attained its maximum value under the given conditions. To determine the conditions under which the entropy of a specified system undergoing a reversible change becomes a maximum is therefore to determine the conditions of equilibrium of that system.

Let Q = quantity of heat added to a body at constant temperature T, then $\frac{Q}{T}$ = gain of entropy to the body; let Q_1 = quantity of heat lost by a body at constant temperature T_1, then $\frac{Q_1}{T_1}$ = loss of entropy to the body. All chemical and physical changes occurring spontaneously are accompanied by an increase in the entropy of the system. This statement holds good for non-reversible changes; but as no actually occurring change is completely reversible the statement holds for all changes.

Suppose that one of two bodies is hotter than another and loses heat to the colder; the hotter body at temperature T_1 loses heat Q, therefore its entropy is decreased by $\frac{Q}{T_1}$; the colder body at temperature T_2 gains heat Q, therefore its

[1] In this section I have again followed Ostwald; but the methods discussed in this section are so largely physico-mathematical that I have attempted only the briefest outline, referring the student to Ostwald's *Lehrbuch*, **2**. 702—728, and to the original memoirs.

[2] *Annalen*, **170**. 192.

entropy is increased by $\frac{Q}{T_2}$; but as $T_1 > T_2$, it follows that $\frac{Q}{T_1} < \frac{Q}{T_2}$; in other words the entropy of the system is increased by the passage of heat from the hotter to the colder body.

Changes of state involving changes of pressure and volume are also accompanied by changes of entropy; if the temperature is constant the entropy-change is easily found; if volume and temperature change simultaneously with pressure the total change may be regarded as partly adiabatic until the final temperature is reached, and then isothermal until the system attains equilibrium; the latter part of the change is alone accompanied by a change of entropy. As it is possible to pass from any given state of a system to any other by a path which is partly adiabatic and partly isothermal, it is possible to lay down the principles on which the entropy-change accompanying any material change may be determined.

189 The application of thermodynamical methods to the study of chemical equilibrium has been much developed by Willard Gibbs[1].

Gibbs shews that the criterion of the equilibrium of a system is contained in the following statement;—

> For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive; or, in other words, in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

As the masses of the constituents of a system undergoing chemical change do not remain constant, an equation which is to express the conditions of equilibrium of such a system must take into account the changes of energy produced by changes

[1] *Amer. Journ. of Sci. and Arts*, (3). **16.** 441; **18**, 277. See also Clerk Maxwell, *South Kensington Science Conferences* [1876].

in the masses of the constituents. This is done by Gibbs by introducing into his equations a term which represents the *potential* of each constituent. If an infinitesimal mass of a body is introduced into a homogeneous system without disturbance of the homogeneity and without change in the entropy and volume of the system, then the increase in the energy of the system divided by the infinitesimal mass of the substance added is the potential of that substance in the system.

The energy of the entire system is a function of the entropy and the volume of the system, and the masses of its constituents; if the energy is known in terms of these variables, then the absolute temperature and the pressure of the system, and the potentials of its constituents, can be calculated in terms of the same variables. In this way all the independent relations between the seven variables, energy, entropy, volume, masses of constituents, temperature, pressure, and potentials of constituents, can be found; and on these relations depend most of the properties of the system, including its chemical properties. A single equation from which all these relations are deducible is called by Gibbs a *fundamental equation.*

Gibbs shews how such fundamental equations are found. He then applies these equations to ideal gases, and then to ideal gas-mixtures, i.e. mixtures of ideal gases which obey the law of Dalton[1], and so he deduces the conditions of equilibrium of such mixtures of gases. Assuming that the laws of ideal gas-mixtures apply to cases in which chemical change occurs in the mixtures themselves, at certain temperatures, resulting in the formation of one kind of components from another kind, Gibbs deduces a formula for finding the specific gravity of a gas-mixture from its temperature and pressure[2]. He applies this formula to the gas-mixtures obtained by heating nitrogen peroxide (N_2O_4), phosphorus

[1] For convenience' sake, Gibbs states this law in these terms;—"The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential."

[2] See *post*, par. 205.

pentachloride, formic acid, and acetic acid, and finds that the calculated results agree on the whole very well with the observed values for the specific gravities of these gases. Hence it is probable that the fundamental equations obtained by purely thermodynamical reasoning are applicable to all cases of gaseous dissociation. But dissociation-processes are instances of chemical equilibrium; hence it is to be expected that each of the classes into which the problems of chemical equilibrium may be divided has its appropriate fundamental equation by the use of which a full thermodynamical explanation can be given of this class of cases of equilibrium.

190 One of the forms in which the criterion of stability is stated by Gibbs involves the use of a certain function, ψ, which is defined by the equation

$$\psi = \epsilon - t\eta,$$

where ϵ = energy of the system, η = entropy of the system, and t = absolute temperature; then equilibrium results when in all possible variations of the state of the system which do not alter its temperature, the variation of ψ either vanishes or is positive.

This form of stating the criterion of stability is in many cases more convenient than that given in par. 189 for deducing the conditions of equilibrium of any system. The meaning of the function ψ has been developed by von Helmholtz[1] on lines different from those adopted by Gibbs. Helmholtz divides the internal energy of a system into two parts; the *free energy* which can be completely changed into other forms of energy, and the *bound energy* which is that portion of the total energy required for establishing the state of the system conditioned by the entropy of the system; as every stable state corresponds to a maximum entropy, the bound energy cannot be changed to other forms within the system, nor without external action on the system. The bound energy is measured by the difference between the total and the free energy. Helmholtz's free energy is identical with Gibbs' function ψ.

[1] 'Die Thermodynamik Chemischer Vorgange,' *Sitzber. der Wiss. Akad zu Berlin*, 1882, also Helmholtz's *Wissenschaftliche Abhandlungen*, 2. 958.

All the properties of a system may be represented in equations as functions of the free energy of the system. Such equations have been deduced for some of the chemical properties of a system in equilibrium, e.g. for dissociation-processes of different orders of complexity, and for reciprocal actions when some members of the system are gases and some solids. These equations lead to results identical with those already obtained by the use of the empirical method of Guldberg and Waage[1].

The transformability of the chemical energy of a system into other forms of energy is measured by the free energy, and not by the total energy, of the system. For instance, the energy obtained from a chemical reaction in the form of heat does not measure the electrical energy obtainable from the same system; for the latter is obtained by the transformation of the free energy only and not of the total energy. So also in a chemical change, the direction of the change is determined by the free energy of the changing system, and this is not measured by finding the quantity of the heat produced in the change.

191 One of the consequences of the general criterion of stability deduced from the second law of thermodynamics is, that Berthelot's so-called 'law of maximum work' is inaccurate.

Berthelot's law asserts that 'every chemical change accomplished without the addition of energy from without tends to the formation of that body or system of bodies the production of which is accompanied by the development of the maximum quantity of heat.'[2]

Now a system is in equilibrium when its entropy has attained the maximum value possible under the conditions. But inasmuch as entropy is measured by a quantity of heat divided by a temperature, it is only at the absolute zero of temperature that $dS = dQ$ (S = entropy, Q = quantity of heat); hence it is only at the absolute zero that thermal

[1] See Ostwald, *Lehrbuch*, **2**. 716—724; also P. Duhem, '*Le potentiel thermodynamique*' [Paris, 1886—7].

[2] See *ante*, Book I., par. 133 for a discussion of the practical applications of this statement.

changes directly measure changes of entropy. When a chemical change is accompanied by the production of much heat, and the change occurs at a low temperature, the thermal change will roughly measure the entropy-change; therefore if such a change be possible it will occur. But if the quantity of heat produced in a chemical process is small, the entropy-change which the system undergoes may be largely conditioned by changes other than the thermal change. Indeed in some cases heat may be lost to the system, and yet the total change in the entropy may be positive; in such cases chemical change will occur with the disappearance of heat, because the decrease in the entropy of the system caused by the loss of heat will be more than balanced by the increase in the entropy caused by the changes of state which the system undergoes.

Such chemical changes are analogous to the physical change of water *in vacuo* into water-gas; in this case the water loses heat, but the loss of entropy thus suffered is more than balanced by the gain of entropy accompanying the change from liquid to gaseous water.

So far as the law of entropy has been applied to chemical processes, it has led to the same conclusions regarding the equilibrium of chemical systems as have been gained by the application of the law of mass-action. The general conception of chemical change which is given by both methods of investigation is that of a system attaining equilibrium as the result of processes occurring in opposite directions. According to van't Hoff[1], the directions of chemical processes which result in equilibrium vary with variations of temperature in such a way that the lower the temperature the more is equilibrium established with the production of heat, but the change can occur in one direction only at the absolute zero. Berthelot's 'law' would then hold good for the limiting case that the change should occur at $-273°$. As the temperature at which most chemical changes occur is not very high very many changes are accompanied by production of heat.

Berthelot's 'law of maximum work' is the modern form

[1] *Dynamique chimique*, 153.

assumed by the old Bergmannic view of affinity. Berthelot, like Bergmann, regards chemical affinity as acting in one direction only. But the outcome of all recent investigation is to negative this view, and to confirm the conception of affinity which was first clearly introduced into chemistry by the great French naturalist Berthollet.

SECTION IV. *Molecular methods applied to chemical equilibrium.*

192 In 1851 Williamson[1] suggested that the amount of chemical change which occurs between two interacting bodies is dependent on the velocities of the atomic interchanges which take place between the molecules of the bodies. He extended this conception to molecules all of the same kind, and concluded that "in an aggregate of molecules of any compound there is an exchange continually going on between the elements which are contained in it." He supposed, for instance, that in a vessel filled with hydrochloric acid the molecules HCl are continually exchanging hydrogen and chlorine atoms; if then a solution of copper sulphate is added to hydrochloric acid "the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces one atom of copper, forming chloride of copper and sulphuric acid." When one product of a chemical change is insoluble it is removed, and so almost the whole of one of the original substances is decomposed; but if all the products remain in solution, the atomic interchanges proceed in both directions and equilibrium is thus established.

In 1857 Clausius[2] developed a conception similar to that put forward by Williamson, and applied it especially to explain the phenomena of electrolysis. He supposed that the movements of the molecules of a liquid result in the production of such a condition of some of the molecules as makes these molecules ready to exchange their constituent parts. As increasing temperature is equivalent to increasing

[1] *C. S. Journal*, **4**. 110; 229. Also *Phil. Mag.* (3). **37**. 350.

[2] *Pogg. Ann.* **101**. 338.

the kinetic energy of the molecules, increase of temperature will bring about further separation of molecules into parts, and will therefore increase the chances of the exchange of parts of molecules.

Clausius' hypothesis postulates differences in the conditions of the molecules forming a liquid compound at any specified temperature, and asserts that some of the molecules will be more ready to exchange parts than others[1].

Pfaundler[2], in 1867 and 1874, developed the hypothesis of Clausius and Williamson and applied it to many chemical reactions, and more particularly to explain the phenomena of dissociation[3].

Pfaundler considers the motion of agitation of the molecules of a gas, and also the motion of parts of the molecules; according to the kinetic theory of gases, the sum of the kinetic energies due to these two motions is constant at a constant temperature, and the sum of each is constant, but the two motions may be very differently distributed among the individual molecules. The results of collision between two molecules will depend on the ratio between the energy of agitation, and the energy of rotation of the parts, of the molecules; the limiting cases are when both energies are at a maximum, or both are at a minimum, or either is at a maximum compared with the other at a minimum.

193 Guldberg and Waage[4], in 1879, brought the hypothesis of chemical action being due to differences in the states of the molecules of a gas or liquid into a form in which it could be quantitatively applied. Let the molecules of two substances which react chemically with one another be represented by A and B; let these molecules be composed of the atoms (or atomic groups) aa, and bb, respectively, performing certain vibrations within the molecules A and B. At certain points in these vibrations the atoms aa on the one hand, and the

[1] For some account of the applications of the hypothesis of Clausius, see *post*, par. 204.

[2] *Pogg. Ann.* **131.** 55 *et seq.* (especially, pp. 66—71); do. **Jubelbd.** 182.

[3] See Section v. of the present Chapter.

[4] *Journal fur prakt. Chemie*, (2). **19.** 75.

atoms *bb* on the other hand, will be so far separated from one another that the attraction between them will be very small; a molecule the atoms of which are in this condition will be ready to undergo chemical change. Suppose that a molecule A comes near to a molecule B at the moment when each is ready to undergo change, chemical action will occur with the production of two new molecules, C, each composed of the atoms *ab*. If the number of molecules of A which are in this condition of readiness to undergo change be a, the total number of molecules of A in unit volume of the system being p, and if the number of molecules of B ready to undergo change be b, the total number of molecules of B being q, then the frequency of collision of the molecules which are ready to change will be represented by the product $(apbq)$, and the velocity of formation of the new molecules, C, will be represented by $\phi apbq$, where ϕ is a velocity-coefficient which depends on the temperature and the chemical nature of the substances A and B. The nature of this dependence must be experimentally determined. An expression, similar to that given, can be found for the velocity of re-formation of A and B; and hence the amounts of A, B, and C, which are present when equilibrium is attained can be calculated for any initial state of the system.

The equation of equilibrium thus found is

$$\phi apbq = \phi' a' b' p' q'.$$

If k is put as $= \phi ab$ and k' as $= \phi' a' b'$, the equation becomes

$$kpq = k' p' q'.$$

This equation is essentially the same as that which Guldberg and Waage arrived at by the use of methods which did not involve any theory of the structure of matter. We have already traced the development and applications of this equation of equilibrium [1].

194 J. J. Thomson [2] has given a general conception of chemical equilibrium in terms of the vortex-atom theory of the structure of matter.

[1] *Ante*, pars. 172—186.

[2] *On the motion of vortex rings*. The Adams Prize Essay for 1882. (See also *Phil. Mag.* (5). **15.** 427; **17.** 233; **18.** 233.)

A compound molecule of a gas is regarded by this theory as consisting of two, or more, vortex rings. This united vortex ring will separate into its parts when subjected to a disturbing influence, such as the action due to other vortex rings in the neighbourhood. The theory thus leads to a conception of chemical combination closely resembling that enunciated by Williamson, Clausius, and Pfaundler. But for a compound gas to be more than a mere mixture of elementary gases it is necessary that 'the mean time during which an atom is paired with another of a different kind, which we shall call the paired time, should be large, compared with the time during which it is alone and free from other atoms, which we shall call the free time' (*loc. cit.* p. 115).

The ratio of *paired* to *free* time will be diminished by any disturbance to which the gas is subjected; when the diminution is carried past a certain amount, the gas is decomposed. Now 'the pairing of two atoms.....is attended by a large increase in the translatory energy;' but as these atoms are only paired for a time, 'the whole increase in the translatory energy of a large number of molecules will depend.....on the ratio of the paired to the free times' of the vortex atoms which form the molecules of the substance (*loc. cit.* p. 116). The value of this ratio in the case of an elementary gas will to a great extent condition the chemical properties of that gas; it will also determine whether chemical combination shall or shall not occur between two gases, and if it occurs, it will fix the proportions between the amounts of the various compounds produced. An elementary gas will readily enter into chemical combination, only when the ratio of free to paired time is larger for the molecule of the element, than for that of the compound produced. The value of the ratio in question may therefore afford a measure of the relative affinities for each other of the atoms of various compound molecules.

This conception of chemical change is applied by Thomson chiefly to processes of dissociation; the results obtained will be briefly considered in the next section.

SECTION V. *Dissociation.*

195 Certain changes brought about by heat and resulting in the formation of systems in equilibrium are classed together under the common term *dissociation.*

By this term is meant a change from one chemical system to another simpler system which change is caused by heat and is reversible. The composition of the constituents of the simpler system is less complex than that of the bodies which form the original system. At least one member of the simpler system is gaseous under the conditions of the experiment. The resolution of the compound N_2O_4 into $2NO_2$, or of $C_5H_{11}Br$ into C_5H_{10} and HBr, or of $CaCO_3$ into CO_2 and CaO, and the subsequent re-formation of the original compound on cooling the products of each action, are examples of dissociation.

In the change of N_2O_4 into $2NO_2$, both the original body and that formed by heating the original are gases; hence the change in question must be accompanied by a decrease in the spec. grav. of the gas. If it has been proved that the only change which occurs when N_2O_4 is heated is the gradual disappearance of the N_2O_4 with the simultaneous production of $2NO_2$, then the amount of this change which occurs at any specified temperature and pressure can be calculated from observations of the spec. grav. of the gas at that temperature and pressure.

There are cases where a gas becomes specifically lighter as temperature increases, without our being able to demonstrate by conclusive experiments that the decrease in spec. grav. is accompanied by dissociation of the gas into simpler components. For instance, the spec. grav. of the gas obtained by heating ammonium chloride is considerably less than the value calculated on the assumption that this gas consists of the compound NH_4Cl; and the spec. grav. decreases as temperature rises, until at about 350° it is very nearly identical with that calculated for a mixture of equal volumes of NH_3 and HCl (calcd. = ·93; observed = 1·0). We seem justified in considering the gas obtained by heating NH_4Cl to 350° to be a mixture of equal volumes of NH_3

and HCl, with perhaps a little unchanged NH_4Cl, although there is no absolutely conclusive experimental demonstration that this is so. In support of this conclusion may be mentioned Pebal's[1] proof that if the vapour obtained by heating ammonium chloride is diffused through a porous septum the diffusate contains considerable quantities of free ammonia.

Another instance of this kind is presented by acetic acid vapour. Ramsay and Young[2] have shewn that this vapour becomes specifically heavier by increasing pressure at any temperature or by decreasing temperature at any pressure. They contrast this behaviour with that of the vapour of alcohol and ether, which are almost certainly non-dissociable bodies; the spec. gravities of these vapours increase as temperature is decreased, at a fixed pressure, until a certain value is reached after which decrease of temperature does not change the spec. gravities. The conclusion to be drawn from these observations is that acetic acid vapour at low temperatures is probably composed for the most part of molecules which are more complex and heavier than those which chiefly compose this vapour at high temperatures, and that the former are dissociated into the latter as temperature rises.

When the spec. grav. of the gas obtained by heating a definite compound decreases as temperature increases, and reverts to its original value when the temperature falls to its initial value, and when the change of spec. grav. quantitatively corresponds with a change of composition which can be presented in a definite manner, and which is perfectly justifiable on other grounds, and is the only change of composition which will explain the observed variations of spec. grav., we are justified in regarding the variations of spec. grav. as indications and measures of the change of composition. For if we do not thus regard these variations of spec. grav., then we must regard the gases in question as having abnormal coefficients of expansion[3], and coefficients so abnormal as to demand a complete revision of our con-

[1] *Annalen.* **126.** 193.

[2] *C. S. Journal*, **Trans.** for **1886.** 790; *Phil. Mag.* (5). **23.** 129.

[3] Deville and Troost, *Compt. rend.* **64.** 237; **91.** 54; Berthelot, *do.* **91.** 77.

ceptions regarding the relations between the volumes of gases and changes of temperature. For instance, we should have to admit that the coefficients of expansion of such gases as ammonium chloride, phosphorus pentachloride, &c., which gases are generally regarded as undergoing dissociation on heating, increase as temperature rises, but increase rapidly until a maximum is reached and then increase slowly. But there is no conclusive proof that the coefficients of expansion of any gases change in this way; and moreover it has been experimentally shewn that the coefficients of expansion of the following elementary and compound gases are practically unchanged for a very large range of temperature; hydrogen, oxygen, nitrogen, sulphur, tellurium, mercury, carbon dioxide, hydrogen chloride, arsenious oxide[1].

196 The so-called *abnormal vapour-densities* of various gases are at once explained if we suppose that the gases in question are dissociated on heating, and that therefore the observed vapour-densities are the spec. gravities of mixtures and not of single gases. For instance the composition of sulphuric acid is undoubtedly expressed by the formula H_2SO_4; if this compound were gasified the spec. grav. of the gas must be 49 times that of hydrogen ($H_2SO_4 = 98$); but the spec. grav. of the gas obtained by vaporising sulphuric acid is considerably less than 49, and the spec. grav. decreases as temperature rises until at about 400° the value obtained is 24·5. These results are at once explained by supposing that the compound H_2SO_4 is dissociated into a mixture of equal volumes of the two gaseous compounds SO_3 and H_2O, as the spec. grav. of such a mixture would be 24·5 times that of hydrogen. As the variations in the spec. grav. of the vapour obtained by heating sulphuric acid as temperature increases and decreases are exactly similar to the variations observed in the spec. gravities of gases which undoubtedly undergo dissociation, we are justified in saying that the expression *abnormal vapour-density of sulphuric acid* should not be used, because the vapour is not sulphuric acid but is a mixture of two, and probably three, gases in variable proportions. The

[1] V. Meyer, *Ber.* **13.** 2022; see also Langer and Meyer, *Ber.* **18. Ref.** 133.

other cases of so-called abnormal vapour densities cease to be abnormal when we are prepared to admit the occurrence of dissociation.

197 The amount of dissociation which any body undergoes depends upon the temperature, and also on the pressure. As the body is heated, temperature rises, and the rate of dissociation increases until a maximum is reached, after which the rate of dissociation decreases until the change is completed; on cooling the products of dissociation in contact with each other, this process is reversed. If pressure and temperature are kept constant, the system composed of the original body and the products of dissociation settles down into equilibrium, which is disturbed either by changing the temperature or the pressure, although in some cases change of pressure does not affect the equilibrium nearly so much as it does in other cases[1].

The pressure at which equilibrium is attained for any specified temperature is usually called the *equilibrium-pressure* for that temperature[2].

198 Consider the effect of heat on a quantity of ammonium chloride enclosed in a vacuous vessel connected with an air-pump and a manometer. As the solid is heated, vapour is produced, and this vapour consists of equal volumes of ammonia and hydrogen chloride possibly mixed with small quantities of ammonium chloride gas. This change proceeds, with constant rise of temperature, and increase of pressure in the interior of the vessel. Now let the temperature be kept constant, say at 350°, dissociation proceeds until the pressure of the gases in the vessel attains a certain amount when the process of dissociation stops, and equilibrium is established between the three bodies, ammonium chloride, ammonia, and hydrogen chloride. Now let temperature be raised through a definite interval, say to 400°; dissociation proceeds, more ammonia and hydrogen chloride are produced, and pressure increases until it reaches a limit whereat the system again attains equilibrium. Now let a portion of the gases be

[1] See next page.

[2] The terms *equilibrium-tension*, and *tension of dissociation* are also used.

pumped out of the vessel, temperature being maintained at 400°; pressure falls, dissociation begins and proceeds until the former pressure is reached. Now let temperature be decreased, say to 350°; combination of ammonia and hydrogen chloride begins and pressure falls, and this proceeds until a new state of equilibrium is attained.

This is a typical and simple case of dissociation; one definite body is resolved into two others and these again recombine to form the original body. In this instance the amount of dissociation is increased either by increasing the temperature at a constant pressure, or by lowering the pressure at a constant temperature.

Now consider the effect of heat on a mixture of the two gases hydrogen and iodine[1]. Let a mixture of equal volumes of these gases be maintained at 440°, and let the pressure be kept at about six atmos.; combination occurs between the gases with production of hydrogen iodide, and this proceeds until (after about an hour) the system attains a state of equilibrium whereat 24 per cent. of the hydrogen originally present remains uncombined with iodine. Now let the pressure be decreased to 2 atmos., then to 1 atmo., and then to 380 mm., temperature remaining at 440°; the state of equilibrium is practically unchanged, the amount of uncombined hydrogen varying only very slightly from 24 per cent. of the amount originally present. Now let the temperature be decreased to 350°, the pressure remaining constant, a new state of equilibrium is attained, but more slowly than at the higher temperature, and this is practically unchanged if the pressure is varied from 4 atmos. to 760 mm.

But although the final state of equilibrium of a mixture of equal volumes of hydrogen and iodine at 350° or 440° is almost independent of pressure, yet the rate at which that equilibrium is attained at these temperatures varies almost directly as the pressure.

In this instance we have probably a more complex occurrence than the change of ammonium chloride into ammonia and hydrogen chloride.

[1] Lemoine, *Ann. Chim. Phys.* (5). **12**. 145; **26**. 289, especially pp. 304—344.

199 Now consider a case wherein a solid is dissociated into another solid and a gas. Let calcium carbonate be heated in a vacuous vessel connected with an air-pump and a manometer. The change which occurs may be represented thus

$$CaCO_3 \rightleftarrows xCaO + xCO_2 + 1 - xCaCO_3.$$

Let the temperature be kept constant; carbon dioxide accumulates until the pressure becomes constant, and the system remains in equilibrium. At 860° the equilibrium-pressure is 81 mm. and at 1000° it is 520 mm. Now let pressure be diminished by removing some of the carbon dioxide; the direct change proceeds until the former pressure is restored when the equilibrium again results. If the temperature is now decreased, carbon dioxide is absorbed, the reverse change occurs, and the pressure falls until a fresh equilibrium is attained. The whole process follows the same course as that observed in such a case as ammonium chloride. Equilibrium is conditioned by temperature and pressure and is independent of the masses of the solid members of the system, viz. lime and calcium carbonate.

200 Let us now consider a case wherein a solid and a gas react to produce more than one compound which compounds are dissociated by heat into their solid and gaseous constituents. Silver chloride and ammonia combine to form two compounds, $2AgCl.3NH_3$ and $AgCl.3NH_3$. If silver chloride is brought into contact with ammonia in an apparatus wherein temperature and pressure can be regulated, the system which is formed may be composed of the gas NH_3 and any or all of the three solids AgCl, $2AgCl.3NH_3$, and $AgCl.3NH_3$. If temperature is kept constant at about 15°, ammonia is absorbed with decrease of pressure and the compound $2AgCl.3NH_3$ is produced; if sufficient ammonia is supplied the system attains equilibrium at a constant pressure, and the only components of this system are $2AgCl.3NH_3$ and ammonia. By raising temperature equilibrium is upset, and pressure increases because of the production of more ammonia; but at a definite temperature equilibrium is again attained; this equilibrium is independent of the ratio between the

masses of the two solid members of the system, viz. AgCl and $2AgCl.3NH_3$, and is conditioned only by the temperature and the pressure.

Suppose equilibrium has been attained at say 20°, and that the system consists of $2AgCl.3NH_3$ and ammonia; let ammonia be pumped into the vessel so that the pressure is considerably increased; formation of the compound $AgCl.3NH_3$ begins, and pressure falls until equilibrium is attained in the system consisting of $x(2AgCl.3NH_3)$, $y(AgCl.3NH_3)$, and $z\,NH_3$. If the temperature is now lowered, more ammonia is absorbed, more $AgCl.3NH_3$ is formed, and pressure continues to fall until a new state of equilibrium is attained. For every temperature there is a certain pressure whereat equilibrium is established; this equilibrium is independent of the ratio between the masses of the solid members of the system, viz. $2AgCl.3NH_3$ and $AgCl\ 3NH_3$.

In this case then two processes occur; dissociation of the compound $2AgCl.3NH_3$ into silver chloride and ammonia, and dissociation of the compound $AgCl.3NH_3$ into $2AgCl.3NH_3$ and ammonia. The compositions of the two systems may be represented as

(1) $x\text{AgCl} + y(2\text{AgCl}.3\text{NH}_3) + z\text{NH}_3$,

(2) $x(2\text{AgCl}.3\text{NH}_3) + y(\text{AgCl}.3\text{NH}_3) + z\text{NH}_3$.

In each case equilibrium is independent of the ratio of x to y. At any specified temperature each system attains equilibrium at a definite pressure; the differences between the equilibrium-pressures of the two systems, at the same temperature, are so great that it is easy to study the relations between temperature and pressure on the one hand and the composition of each system on the other hand. The equilibrium-pressures for the two systems at temperatures varying from 6° to 20° are given in the following table[1]:—

[1] Horstmann, *Ber.* **9.** 749. Isambert, *Comp. rend.* **66.** 1259; **70.** 456.

Temp.	Equilibrium-pressure in mm.	
	$2AgCl.3NH_3$	$AgCl.3NH_3$
6°	22	—
7	23·4	—
8	24·9	432
9	26·5	446
10	28·2	465
12	31·9	520
16	40·9	653
18	46·6	723
20	52·6	793

201 If a solid were changed by heat into a series of other solids and a gas, and if the equilibrium-pressures of the different systems thus produced were nearly the same at any specified temperature, it would be impossible to disentangle the various processes of dissociation occurring when such a solid was heated, and to establish the connexions which certainly exist between temperature and pressure and the composition of the various members of the complete system.

Such a case occurs when certain hydrated salts are heated. For instance copper sulphate forms a series of hydrates $CuSO_4.xH_2O$; if a crystal of the ordinary hydrate $CuSO_4.5H_2O$ is heated in a closed vessel of such a size that the water of the crystal is more than sufficient to saturate the air in the vessel, water-gas is evolved, and the pressure increases; after a time the process stops. If the temperature is now allowed to fall, water is re-absorbed, and the pressure decreases. But the change of pressure is irregular and a long time must elapse before equilibrium is attained. At a moderate temperature the crystal is slowly dehydrated, but at the same time small quantities of water are re-absorbed by parts of the crystal which had before given off water. Irregularities in the form or surface of the crystal largely affect the processes of dehydration and rehydration, and cause fluctuations in one direction or the other. As these fluctuations are accompanied by changes of pressure, it is almost impossible to establish equilibrium, at a specified temperature, in the system consisting of $xCuSO_4 + yCuSO_4.5H_2O + zH_2O +$

varying quantities of other hydrates of $CuSO_4$. Several processes of dissociation are proceeding simultaneously, and the equilibrium-pressure for any one of the dissociating systems at a constant temperature is so nearly the same as that for the other systems that the establishment of an equilibrium-pressure for the whole system is not attained[1].

If hydrated sodium phosphate, $Na_2HPO_4.12H_2O$, is heated in a closed vessel, water-gas is given off, and the pressure increases. For any temperature there is an equilibrium-pressure established which is independent of the relative amounts of the dehydrated salt and the various hydrates present. This equilibrium-pressure is the same whether the salt $Na_2HPO_4.12H_2O$ or a less hydrated salt than this is used, provided the quantity of water in the salt is more than that required by the formula $Na_2HPO_4.7H_2O$. If the salt $Na_2HPO_4.7H_2O$ is heated, a series of equilibrium-pressures is obtained different from those pressures which characterise the process when a salt is used with any quantity of water more than that required by the formula $Na_2HPO_4.7H_2O$ but not exceeding that contained in the salt $Na_2HPO_4.12H_2O$. The following numbers represent the results obtained by Debray[2].

Temp.	Equilibrium-pressures	
	Salt with 7 to 12 H_2O.	Salt with less than 7 H_2O.
12°·3	7·4 mm.	4·8 mm.
16 ·3	8·9 „	6·9 „
20 ·7	14·1 „	9·4 „
24 ·9	18·2 „	12·9 „
31 ·5	30·2 „	21·3 „
36 ·4 salt melted	39·5 „	30·5 „
40 ·0	50·0 „	41·2 „

This process presents an example of dissociation of a solid body into solid and gaseous constituents intermediate in complexity between that exhibited by $CuSO_4.5H_2O$ on the one hand, and the pair of salts, $2AgCl.3NH_3$ and $AgCl.3NH_3$, on the other hand.

[1] For further details see Naumann, *Ber.* **7**. 1537; or Ibid. *Thermochemie*, 145–6. See also Lescœur, *Compt. rend.* **102**. 1466.

[2] *Comp. rend.* **66**. 195.

202 The relations between volume, temperature, and pressure, which accompany the merely mechanical absorption of a gas by a solid are different from those which mark the formation of a dissociable compound of a gas and a solid.

The absorption of ammonia by charcoal may be contrasted with the combination of ammonia with silver chloride. In the latter case ammonia is absorbed at 12° when the pressure is equal to about 31·9 mm., and absorption continues at this temperature and pressure until the silver chloride is changed into the compound $2AgCl.3NH_3$; the process then stops, and the pressure must be raised to about 520 mm. before absorption of ammonia again takes place; the result of the second process is the formation of the compound $AgCl.3NH_3$. Charcoal on the other hand absorbs ammonia at all pressures, temperature being constant, and the quantity of the gas absorbed increases regularly with increase of pressure.

Palladium absorbs large quantities of hydrogen. When temperature is kept constant, the volume of hydrogen absorbed is constant although the pressure is caused to increase considerably; but after the quantity of hydrogen absorbed corresponds approximately to that required on the assumption that the compound Pd_2H has been formed, the volume of hydrogen then absorbed increases largely as the pressure increases. In this case two processes very probably occur; the first results in the formation of the dissociable compound Pd_2H, and this follows the ordinary course of such changes; the second consists in the mechanical absorption of hydrogen by the compound previously formed, and this in turn follows the ordinary course of such occurrences.

These instances shew how observations of the relations between temperature and pressure and the process of ab-absorption of a gas by a solid, or the evolution of a gas from a solid, enable conclusions to be drawn regarding the formation or non-formation of a compound, or compounds, of the gas with the solid.

203 Processes of dissociation lead to the production of chemical systems in equilibrium. The generalisations which have been

made regarding chemical equilibrium hold good in cases of dissociation. Let us consider a few classes of dissociation-processes with the view of stating the law which expresses the conditions of dissociation in each class[1].

The cases presented by heterogeneous systems composed of solid and gaseous constituents admit of more simple treatment than those presented by homogeneous systems all the members of which are gases. The simplest case is that which presents itself when a solid dissociates into another solid and a gas, e.g. when calcium carbonate dissociates into calcium oxide and carbon dioxide.

Assuming the law of mass-action, it follows that equilibrium must result when the active masses of the members of the system bear a certain constant ratio to each other. But the active masses of the solids are constant[2]; therefore equilibrium will be conditioned by the active mass of the gas; now the active mass of the gas varies with variations of pressure and temperature; hence equilibrium will be attained at any specified temperature when the pressure exerted by the gas acquires a certain fixed value, and this pressure will be independent of the masses of the solids. The equation of equilibrium assumes the form

$$cu = c_1 u_1 u_2; \text{ and therefore } \frac{cu}{c_1 u_1} = u_2,$$

where c and c_1 are the velocity-constants of the direct and reverse changes, respectively, u = active mass of one solid, u_1 = active mass of the other solid, and u_2 = active mass of the gas.

This result is in keeping with what we have already learnt regarding this class of dissociation-processes.

When a solid dissociates into equal volumes of two gases, e.g. NH_4Cl to $NH_3 + HCl$, the equation of equilibrium is as before

$$cu = c_1 u_1 u_2;$$

where u = active mass of original solid, and u_1 and u_2 represent

[1] Here again I merely give a condensed outline of Ostwald's treatment of this subject in his *Lehrbuch*, **2**. 670—701.

[2] *Ante*, par. 170.

the active masses of the two gases when equilibrium results; hence

$$\frac{cu}{c_1} = u_1 u_2,$$

u is constant, as it represents the active mass of a solid present in excess.

Hence when a solid dissociates into equal volumes of two gases the product of the active masses of the gases is equal to a constant when equilibrium results, and is independent of the mass of the solid body.

If the space in which the dissociation proceeds is vacuous, or contains an indifferent gas, then $u_1 = u_2$, and

$$\frac{cu}{c_1} = u_1^2.$$

But if the space already contains one of the gaseous products of dissociation, then u_1 has not the same value as u_2; the greater u_1 the smaller is u_2, and *vice versa;* hence the amount of dissociation may be very much lessened by increasing u_1 or u_2; but it cannot be wholly stopped, because to make $u_1 = 0$, u_2 must be made $= \infty$.

As an example of the dissociation of a solid into two gases in presence of an excess of one of these gases, may be taken the results obtained by Isambert on the dissociation of ammonium hydrosulphide (NH_4HS) into ammonia and sulphuretted hydrogen in presence of excess first of sulphuretted hydrogen and then of ammonia[1].

When equilibrium results, the product of the active masses of the two gases must be the same in each series of experiments at the same temperature. Hence if p_1 and p_2 are the partial pressures of the two gases when neither is in excess, and p_1' and p_2' are the partial pressures when sulphuretted hydrogen is in excess, and p_1'' and p_2'' are the partial pressures when ammonia is in excess, the equation

$$p_1 p_2 = p_1' p_2' = p_1'' p_2'',$$

must be realised. Isambert's results shew a fair agreement

[1] *Comp. rend.* **92.** 919; **94.** 958.

between the values which ought to be constant[1]. Ostwald indicates a source of error overlooked by Isambert. Considering this, and also considering the difficulties in making accurate measurements of the partial pressures, the observed results must be regarded as agreeing very well with the calculated results.

If a solid dissociates into equal volumes of three gases, or into two volumes of one gas and one volume of another gas, the equation of equilibrium becomes

$$cu = c_1 u_1 u_2 u_3,$$

provided some quantity of one or other of the gaseous products of dissociation is present in the space in which dissociation occurs; but if the space is vacuous or contains only an indifferent gas, then

$$cu = c_1 u_1^3,$$

for in this case $u_1 = u_2 = u_3$.

Experiments on the dissociation of ammonium carbamate by Naumann[2] shewed that the equilibrium-pressure is independent of the mass of the solid present:—

$$CO.ONH_4.NH_2 \rightleftarrows CO_2 + 2NH_3.$$

Horstmann's experiments, wherein excess of ammonia was sometimes present and sometimes excess of carbon dioxide[3], and more particularly similar experiments by Isambert[4], have shewn that the product of the partial pressures of the two gases is constant at a constant temperature.

Cases of homogeneous dissociating systems are considered by Ostwald (*loc. cit* 693—698), and the various forms are found for the equation of equilibrium, and are applied particularly to the dissociation of nitrogen tetroxide. A convenient form for the equation is that in which it gives a method of calculating the spec. grav. of a dissociating gas from observations of pressure and temperature.

204 As processes of dissociation are caused by heat and are attended with changes of energy to the dissociating systems,

[1] For actual numbers see Ostwald, *loc. cit.* 685. [2] *Annalen*, **187**. 48.
[3] *Ber.* **4**. 779. [4] *Compt. rend.* **93**. 731; **97**. 1212.

it is necessary to examine briefly the thermodynamical aspects of these occurrences. It will also be incumbent on us to glance at the explanation of dissociation which is afforded by the molecular and atomic theory.

The general conception of a dissociable gas at a specified temperature which is presented by the kinetic theory of gases is that of a system of molecules the kinetic energy of some of which is different from that of the mean value of the kinetic energy of the whole number, and in which system the distribution of the energy of rotation of parts of molecules also varies. When heat is expended upon this system the energy of rotation of the parts of the molecules is increased, and the kinetic energy of the molecules is also increased. The result is that some of the molecules are separated into parts; as temperature rises more molecules are separated; but as the number of undissociated molecules becomes smaller the chances of any molecules undergoing dissociation also become smaller; hence the velocity of dissociation increases, as temperature rises, to a maximum, and then diminishes to a minimum when all the molecules have been separated into parts. Now suppose the temperature to be kept constant at a certain point in the process of dissociation; some molecules are being separated into parts, and this separation is accompanied by disappearance of heat; but at the same time the translatory energy of some of the portions of molecules has become such that re-combination occurs, and this process is attended with production of heat. If then no heat is allowed to enter or leave the system, the system will settle down into equilibrium when the number of molecules which dissociate in unit of time is equal to the number which is re-formed in the same time.

205 In par. 189 was given a brief statement of Willard Gibbs' thermodynamical treatment of chemical equilibrium.

A dissociable gaseous system is one some of the constituents of which can be produced from the other constituents; such a system will be in stable equilibrium when its energy has attained the minimum value possible for the entropy and volume of the system. An equation can be

found for such a system connecting the spec. grav. with the temperature, pressure, and volume. To find whether this equation holds good for actual dissociable gaseous systems, notwithstanding the occurrence of chemical action, Gibbs compares the spec. gravities of the gases obtained by heating nitrogen tetroxide (N_2O_4), formic acid, acetic acid, and phosphorus pentachloride, at different pressures and temperatures, with the spec. gravities calculated by means of the equation deduced for an 'ideal gas-mixture with convertible components.' The equation in question is

$$\log \frac{D_1(D-D_1)}{(2D_1-D)^2} = -A - B\log t + \frac{C}{t} + \log p;$$

where D = spec. grav. of the gaseous mixture, D_1 = spec. grav. of the less dense component of the mixture, t = temperature, p = pressure, and A, B, and C are constants to be determined experimentally for each dissociable system. The observed results agree very closely with the calculated numbers in most cases; but some discrepancies are observed, especially in the case of phosphorus pentachloride.

Gibbs concludes his paper with these words;—

"The constants of these equations are of course subject to correction by future experiments, which must also decide the more general question, in what cases, and within what limits, and with what degree of approximation, the actual relations can be expressed by equations of such form."

206 A very brief sketch was given in par. 194 of the applications to chemical equilibrium of the vortex-atom theory of matter by J. J. Thomson.

The mean time during which an atom is paired with another of a different kind is called the *paired time;* and the mean time during which the vortex-ring atom vibrates alone and unpaired is called the *free-time.* The conditions which determine the ratio of paired to free time in a dissociable gas will determine the amount of dissociation in that gas. The theory gives a means of investigating the effect of a disturbing influence, such as the action of heat, light, or electricity, or of other vortex-rings in the neighbourhood, on two vortex-

atoms. Whether the effect shall be to separate the atoms, or to make the connexion between them stronger, depends on the direction in which the vortex-rings are moving. If they are moving in the same direction with different velocities the effect of the disturbance will be to make them hold more firmly together; but if they are moving in opposite directions with different velocities the effect of the disturbance will be to separate the rings.

Thomson then considers the conditions under which the ratio of paired to free time is so reduced that the gas separates into its constituents. He considers cases of various degrees of complexity, beginning with that of an elementary gas the molecules of which are diatomic. He shews how an equation is arrived at for such a gas whereby the ratio of the number of free atoms to the number of molecules at any time may be determined. This equation may be expressed as an equation giving the vapour-density of the dissociated gas; and the results calculated by it can then be compared with the experimentally determined results. Further, this form of the equation varies according as it is assumed that the dissociation is produced by collisions between the molecules, or by some external agency such as heat, light, or electricity. In the simple case of iodine vapour "if the dissociation were due to the collisions of the particles, then the paired time would vary inversely as the number of collisions, and...dissociation would be the same at all pressures." But the dissociation of iodine vapour is dependent on the pressure, hence the dissociation is probably not due to collisions between the molecules, but rather to the action of some external agency. In considering the change of gaseous hydriodic acid into iodine and hydrogen it is shewn that the amount of the change, at a given temperature, should be much less dependent on pressure than in the case of iodine vapour. This conclusion follows whether the change is regarded as the effect of collisions between the molecules, or as the effect of an external agency. The experimental results obtained by Lemoine[1] confirm Thomson's theoretical deduction. Other

[1] See *The Elements of Thermal Chemistry*, par. 160.

cases are considered in the paper referred to, and equations are deduced whereby the conditions which determine the ratio of paired to free time, and therefore determine the amount of dissociation, may be obtained.

207 Dissociation-processes come under the laws which express the conditions of chemical equilibrium. In a chemical decomposition we have doubtless collisions occurring between different kinds of molecules resulting in the shattering of these molecules and the formation of molecules of other kinds. The theoretically simplest case of dissociation occurs when the molecules of one kind of matter are separated into parts by the action of heat without the occurrence of reactions between the parts of the molecules; such a separation probably occurs in the dissociation of the molecule I_2 into the atoms $I + I$. In the dissociation of molecules of the composition HI into the molecules H_2 and I_2, it is probable that two actions occur, one being represented by the equation

$$HI + HI = H + H + I + I,$$

and the other by the equation

$$H + H + I + I = H_2 + I_2.$$

Whether these changes are caused by collisions between the molecules, or by the action of an external agency causing the direct separation of the molecules HI into atoms, cannot at present be determined. But it is important to notice that Thomson's application of the vortex-atom theory to processes of dissociation leads to the recognition of dissociation being due to two causes, one of which is collisions between molecules, and the other is the direct effect of an external agency such as heat, electricity, or light.

208 We have now gained a fairly consistent conception of chemical change, and of the laws which express the conditions of this class of occurrences. The law of mass-action, and the principle of the coexistence of reactions, have been arrived at by an empirical examination of special cases of chemical change; these laws have been confirmed by deductions from thermodynamical principles, and also by the application of the molecular and atomic theory of matter.

Chemical change then follows the same laws as other classes of physical occurrences; the differences between chemical and physical occurrences are differences of degree and not of kind.

It is important to notice that although the thermodynamical treatment of chemical equilibrium provides for the consideration of the influence of temperature, nevertheless there has not as yet been any thorough examination of the effect of variations of temperature on the velocities of chemical changes.

Some chemical occurrences seem to be independent of temperature, while others are largely conditioned by changes in this variable. Various formulæ have been given for shewing the connexion between temperature and rate of change, but none is altogether satisfactory[1].

In the earlier statement of the equation of equilibrium

$$kpq = k'p'q',$$

the constants k and k' were called the *coefficients of affinity* of the direct and reverse parts of the complete process; as we proceeded it was found possible to substitute the more exact expression *reaction-velocity* for the vaguer term used at first. But no attempt has yet been made to analyse these coefficients, or to trace connexions between their values and the composition and other chemical properties of the bodies which take part in the various changes. It is necessary now to proceed to this part of our subject.

[1] See Ostwald, *Lehrbuch*, **2**. 728—740.

CHAPTER III.

CHEMICAL AFFINITY.

209 In Chapter I. of this Book I have placed before the student a sketch of the views concerning chemical affinity which prevailed before the publication of Berthollet's *Essai de Statique Chimique;* I have tried to shew the importance of Berthollet's assertion that every chemical change is conditioned not only by the affinities but also by the masses of the interacting bodies; I have passed in review the work of Guldberg and Waage, which led to an accurate statement of the law of mass-action, by incorporating the conception of equivalency with that of mass, and by considering the distribution of the members of a changing system when equilibrium is established; I have given a short account of those researches by Ostwald and others, which, while confirming the ideas of Guldberg and Waage by applying them to different classes of chemical changes and finding the expression of the fundamental law appropriate to each class, have also amplified these ideas by adding to the law of mass-action the principle of the coexistence of reactions; I have tried to help the student to form a conception of a changing chemical system as swinging in two directions until equilibrium is attained, and to regard the direct and reverse changes as conditioned by the active mass and the coefficient of affinity of each member of the system; I have sought to give proofs of the assertion that those reactions

which seem to proceed only in one direction are really limiting cases of equilibrium; and finally I have glanced at the thermodynamical and the molecular methods whereby the law of mass-action and the principle of the coexistence of reactions have met with a general confirmation.

210 The fundamental equation of equilibrium, $kpq = k'p'q'$, assumes a more workable form when written

$$(P-x)(Q-x)=\frac{k'}{k}(P'+x)(Q'+x).$$

In these equations P, Q, P', and Q' = number of equivalents of each reacting body in a system of four bodies; p, q, p', and q' = active mass of each body present in the system when equilibrium is established; x = number of equivalents of P and Q decomposed, and number of equivalents of P' and Q' formed, when equilibrium results; and k and k' = coefficients of affinity of the direct and reverse change, respectively. (*v.* par. 169.)

In applying this equation it is necessary to determine x for some special initial values of P, Q, P', and Q', hence to find the value of the ratio $\frac{k'}{k}$, to use this value in order to calculate x for various values of P, Q, P', and Q', and to compare the observed values of x with those thus calculated. (For examples, *v.* par. 170.)

The coefficients k and k' may be regarded as representing the chemical forces which respectively cause the formation of P' and Q', and the re-formation of P and Q. But the notion of chemical force is at present vague and inexact: we found it better to follow van't Hoff, Guldberg and Waage, and others, in regarding k and k' as the velocity-constants of the direct and reverse change, respectively. As thus interpreted, the equation

$$(P-x)(Q-x)=\frac{k'}{k}(P'+x)(Q'+x)$$

establishes a quantitative connexion between the equilibrium of a chemical system and the velocities of the two parts into which the complete change may be divided.

But although it is advantageous, at present, to regard $\frac{k'}{k}$ as the ratio of the velocity-constants of the two parts of the complete change, yet we cannot be satisfied with this interpretation. For $\frac{k'}{k}$ represents the value of the ratio of the affinity of the two bodies P and Q to the affinity of the bodies P' and Q' produced by the interaction of P and Q; and the elucidation of chemical affinity is the ultimate object of our inquiry. Let us then examine the results which have been obtained by applying the equation of equilibrium.

SECTION I.

Specific affinity-coefficients of acids and bases.

211 In par. 181 the application of the equation of equilibrium to a system of four bodies was considered. The bodies A and B are changed to A' and B'; the active masses of the four bodies at the beginning of the process are P, Q, P', Q', respectively; x represents the number of equivalents of A and B changed to A' and B' at any moment, and x' represents the number of equivalents of A' and B' changed to A and B at the same moment; c is the velocity-constant of the direct change, and c' is the velocity-constant of the reverse change; then the velocity of the direct change is

$$(P-x)(Q-x)c;$$

the velocity of the reverse change is

$$(P'-x')(Q'-x')c';$$

and the velocity of the total change is

$$(P-x)(Q-x)c-(P'+x')(Q'+x')c'.$$

When equilibrium results the velocity of the total change must $=0$; if then ξ = value attained by x when equilibrium results, we have the conditions of equilibrium expressed in terms of the velocities of the two parts of the total change by the equation

$$(P-\xi)(Q-\xi)c=(P'+\xi)(Q'+\xi)c'.$$

If the initial conditions are made such that one equivalent of A and one of B are present and A' and B' are absent, we have $P = Q = 1$, and $P' = Q' = 0$; the equation then becomes

$$(1 - \xi)^2 c = \xi^2 c',$$

and hence

$$\frac{c}{c'} = \left(\frac{\xi}{1 - \xi}\right)^2.$$

As ξ can be determined by experiment, the ratio of the velocity-constants, $\frac{c}{c'}$, can be calculated.

212 This form of the equation of equilibrium has been applied by Thomsen to the case of the interaction between an acid and the neutral salt of another acid in dilute aqueous solution. When equivalent masses of hydrochloric acid and sodium sulphate interact, Thomsen found that $\xi = \frac{2}{3}$; the same value was found when nitric acid was substituted for hydrochloric; these results were on the whole confirmed by Ostwald, who employed a different experimental method. (For details, *v.* pars. 183, 184.)

By repeated experiments with a neutral salt and different acids it is obvious that values can be found for ξ in each case; and from these, values are at once deduced for the ratio of the velocity-constants, $\frac{c}{c'}$. This ratio, $\frac{c}{c'}$, is the same as the ratio $\left(\frac{\xi}{1 - \xi}\right)^2$, so that to express the ratio in question we may employ either form, $\frac{c}{c'}$ or $\left(\frac{\xi}{1 - \xi}\right)^2$; the ratio $\frac{\xi}{1 - \xi}$ is identical with that formerly expressed by the symbols $\frac{k}{k'}$, and called the ratio of the affinities of the reacting bodies. Hence investigations conducted on the lines just indicated will lead to measurements of the relative affinities of different acids for the same base. Such investigations have been conducted by Thomsen, Ostwald, and others.

Suppose that equivalent masses of Na_2SO_4 and HCl interact in dilute aqueous solution; the direct change which occurs will result in production of NaCl and H_2SO_4, but these will

react to reproduce Na_2SO_4 and HCl; if measurements of ξ are made—*i.e.* if the number of equivalents of each body present when equilibrium is attained is determined—we have values for the ratio $\frac{\xi}{1-\xi}$ which is the same as $\sqrt{\frac{c}{c'}}$ or $\frac{k}{k'}$. We thus determine the ratio of the affinities of the two acids, sulphuric and hydrochloric, towards the base soda. If another series of measurements of ξ is made when equivalent masses of Na_2SO_4 and HNO_3 react in dilute aqueous solution, we shall determine the ratio of the affinities of the two acids sulphuric and nitric towards the base soda. We can thus obtain a series of ratios $k : k'$, $k : k''$, $k : k'''$, &c. which express the relative affinities of various acids towards a specified base in terms of some one acid chosen as a standard.

There is another way of looking at the meaning of the ratio we are considering. When an acid interacts with an equivalent mass of the neutral salt of another acid until equilibrium is attained, the number of equivalents of the salt remaining unchanged is $1-\xi$ (giving the same meaning to ξ as before), and the number of equivalents of the salt decomposed is ξ; but as each equivalent of salt decomposed produces one equivalent of base and one of acid, ξ is also the number of equivalents of the base which has combined with the added acid, and $1-\xi$ expresses the number of equivalents of the base which has remained in combination with the first acid. The ratio $\frac{1-\xi}{\xi}$ then expresses the distribution of the base between the acids. Thus in the case of Na_2SO_4 reacting with $H_2N_2O_6$, Thomsen found $\xi = \frac{2}{3}$; that is, $\frac{2}{3}$ of the base (Na_2O) had entered into combination with nitric acid, and $\frac{1}{3}$ of the base remained combined with sulphuric acid, when equilibrium was attained. Hence, if the affinity of an acid is measured by the quantity of a base with which it combines when competing for the base with another acid in dilute aqueous solution, the three compounds being present in equivalent quantities, it follows that the affinity of nitric acid for soda is twice that of sulphuric acid for the same base.

Thomsen uses the term *avidity* of an acid for a base, but it seems better not to introduce a new term when we have already employed the word *affinity* to express the same conception.

The following numbers are taken from Thomsen's *Untersuchungen* (I. 308):

	Relative affinity.
Nitric acid	1·0
Hydrochloric acid	1·0
Hydrobromic acid	0·89
Sulphuric acid	0·49
Dichloracetic acid	0·36
Oxalic acid	0·24
Monochloracetic acid	0·09
Acetic acid	0·03

Take the numbers for sulphuric and monochloracetic acids, ·49 and ·09; these numbers tell that when one equivalent of sulphuric acid reacts with one equivalent of sodium monochloracetate in dilute solution until equilibrium is established, the base divides itself between the acids in the ratio ·49 : ·09; or $\frac{1-\xi}{\xi} = \frac{\cdot 49}{\cdot 09}$; hence $\xi = \cdot 155$; in other words, 15·5 p. c. of the total soda remains combined with the monochloracetic acid and 84·5 p. c. enters into combination with the sulphuric acid.

213 The thermal methods employed by Thomsen, and the volumetric methods used by Ostwald, for determining the distribution of a base between two acids, when the three bodies react in equivalent quantities in dilute solutions, have already been described (pars. 183, 184). Ostwald conducted a series of experiments with the special purpose of determining whether the relative affinity of an acid varies with variations in the base[1]. The acids compared were nitric and sulphuric, hydrochloric and sulphuric, and hydrochloric and nitric; the bases were potash, soda, ammonia, magnesia, zinc oxide, and cupric oxide. The following table shews the ratio in which an equivalent of each base divided itself between an equivalent of each acid:—

[1] See *Lehrbuch*, **2.** 784; or *J. für prakt. Chemie*, (2). **16.** 385.

RELATIVE AFFINITIES.

Base.	I. $\frac{H_2N_2O_6}{H_2SO_4}$.	II. $\frac{H_2Cl_2}{H_2SO_4}$.	III. $\frac{H_2Cl_2}{H_2N_2O_6}$.
Potash	$\frac{0{\cdot}667}{0{\cdot}333}=2{\cdot}00$	$\frac{0{\cdot}659}{0{\cdot}341}=1{\cdot}94$	$\frac{1{\cdot}94}{2{\cdot}00}=0{\cdot}97$
Soda	$\frac{0{\cdot}667}{0{\cdot}333}=2{\cdot}00$	$\frac{0{\cdot}657}{0{\cdot}343}=1{\cdot}92$	$\frac{1{\cdot}92}{2{\cdot}00}=0{\cdot}96$
Ammonia	$\frac{0{\cdot}652}{0{\cdot}348}=1{\cdot}88$	$\frac{0{\cdot}644}{0{\cdot}356}=1{\cdot}81$	$\frac{1{\cdot}81}{1{\cdot}88}=0{\cdot}96$
Magnesia	$\frac{0{\cdot}638}{0{\cdot}362}=1{\cdot}76$	$\frac{0{\cdot}635}{0{\cdot}365}=1{\cdot}74$	$\frac{1{\cdot}74}{1{\cdot}76}=0{\cdot}99$
Zinc oxide	$\frac{0{\cdot}617}{0{\cdot}383}=1{\cdot}61$	$\frac{0{\cdot}605}{0{\cdot}395}=1{\cdot}53$	$\frac{1{\cdot}53}{1{\cdot}61}=0{\cdot}95$
Copper oxide	$\frac{0{\cdot}591}{0{\cdot}409}=1{\cdot}44$	$\frac{0{\cdot}584}{0{\cdot}416}=1{\cdot}40$	$\frac{1{\cdot}40}{1{\cdot}44}=0{\cdot}97$

The ratio of the affinities of hydrochloric and nitric acids is evidently independent of the nature of the base, whereas in the case of sulphuric and hydrochloric, or sulphuric and nitric, acids, the ratio varies in accordance with the nature of the base. The reason for this apparent difference is to be sought for in the numbers which express the volume-changes attending the action of sulphuric acid on normal sulphates. Ostwald shews that when sulphuric acid and normal sulphates react in equivalent quantities, only a portion of the sulphate is changed into the acid salt, and that the amount of this change depends on the base present in the normal sulphate. Hence, Ostwald concludes, that

"sulphuric acid ... does not exert affinity on a base with its whole mass but only with that part which is not combined to form acid sulphate. The greater this part, the greater will the affinity of sulphuric acid appear to be."

It is probable that the true relative affinity of sulphuric acid, like that of hydrochloric and nitric acids, is independent of the nature of the base with which the acid combines.

The influence of temperature on the relative affinities of the three pairs of acids is then examined by Ostwald in the same way as has been employed for examining the influence of the nature of the base.

The results are contained in the following table.

RELATIVE AFFINITIES (for Soda).

Temp.	I. $\frac{H_2N_2O_6}{H_2SO_4}$.	II. $\frac{H_2Cl_2}{H_2SO_4}$.	III. $\frac{H_2Cl_2}{H_2N_2O_6}$.
0°	$\frac{0\cdot655}{0\cdot345}=1\cdot90$	$\frac{0\cdot659}{0\cdot341}=1\cdot93$	$\frac{1\cdot93}{1\cdot90}=1\cdot02$
20°	$\frac{0\cdot667}{0\cdot333}=2\cdot00$	$\frac{0\cdot657}{0\cdot343}=1\cdot92$	$\frac{1\cdot92}{2\cdot00}=0\cdot96$
40°	$\frac{0\cdot669}{0\cdot331}=2\cdot02$	$\frac{0\cdot666}{0\cdot334}=1\cdot99$	$\frac{1\cdot99}{2\cdot02}=0\cdot98$
60°	$\frac{0\cdot703}{0\cdot297}=2\cdot37$	$\frac{0\cdot703}{0\cdot297}=2\cdot37$	$\frac{2\cdot37}{2\cdot37}=1\cdot00$

Here again the relative affinities of hydrochloric and nitric acids remain constant, while that of sulphuric acid varies with variations of temperature. The variation in the value of the relative affinity of sulphuric acid is shewn to be inversely as the amount of acid which has combined with the normal sulphate; this confirms the provisional conclusion that the true relative affinity of sulphuric acid is in all respects comparable with the relative affinities of hydrochloric and nitric acids.

The final result of these experiments is, that *the relative affinities of the acids are expressed by constant numbers.*

In another paper[1], Ostwald extends the volumetric method to a number of acids, both monobasic and dibasic, including several carbon-acids. He has also determined the refractive indices of many of the solutions of acids, bases, and salts, already employed, and from these he has arrived at measurements of the amounts of change; so that most of the data on which his calculations are based have been gained by two independent methods. The results agree very well; Ostwald, however, thinks that the volumetric method gives more trustworthy results than the optical method. The following table presents the results of the volumetric experiments.

[1] *J. fur prakt. Chemie*, (2). **18.** 328; *Lehrbuch*, **2.** 785.

PROPORTIONS IN WHICH BASES ARE SHARED AMONG MONOBASIC ACIDS.

	Acids.	Potash.	Soda.	Ammonia.	Mean.
1	Dichloracetic : nitric	77	77	75	76
2	Dichloracetic : hydrochloric	74	75	73	74
3	Dichloracetic : trichloracetic	70, 73	71, 71	70, 72	71
4	Dichloracetic : lactic	8	9	11	9
5	Monochloracetic : trichloracetic	92	92	92	92
6	Formic : trichloracetic	97	96	97	97
7	Formic : lactic	43	46	48	46
8	Formic : acetic	25	23	23	24
9	Formic : butyric	21	21	19	20
10	Formic : isobutyric	19	19	18	19
11	Butyric : acetic	54	52	53	53
12	Isobutyric : acetic	56	51	53	53
13	Propionic : formic	78	80	79	79
14	Glycollic : formic	43	44	45	44

One equivalent of the neutral salt (of potassium, sodium, or ammonium) of the acid placed first in column 1 reacted with one equivalent of the acid placed after it in the same column; the numbers in the columns of bases represent the percentage amounts of base withdrawn from the first acid by the action of the second.

These results confirm the conclusion that the relative affinities of the acids are expressed by constant numbers.

214 This question of the constancy of the numbers expressing the relative affinities of acids is very important. Having shewn by experiment that the question, Are these numbers independent of the nature of the base? must be answered in the affirmative, Ostwald[1] proceeds to examine the subject somewhat as follows.

The absolute affinity of an acid A for a base B is a function of both; let it be represented by $f(A, B)$; then by putting A and A' as two acids and B and B' as two bases, the statement that the relative affinities of the acids are independent of the nature of the bases, may be put in the form,

$$\frac{f(A, B)}{f(A', B)} = \frac{f(A, B')}{f(A', B')}.$$

[1] *Lehrbuch*, 2. 787; *J. für prakt. Chemie*, (2). 16. 442.

And by changing the means we get

$$\frac{f(A, B)}{f(A, B')} = \frac{f(A', B)}{f(A', B')}.$$

But the second equation means that the relative affinities of the bases are independent of the nature of the acids. Hence the affinity between an acid and a base is the product of two specific affinity-coefficients, one of which belongs to the acid and the other to the base.

This conclusion is of very great importance; it rests on the experimental evidence already sketched, but it is also confirmed by a large amount of indirect evidence. An examination of this evidence leads us not only to place greater trust in the accuracy of the conclusion already stated, but it also shews how values have been found for the affinities of many acids by methods other than the thermal method used by Thomsen and the volumetric method employed by Ostwald.

215 When acetamide is brought into contact with water and an acid, it is changed to acetic acid, and ammonia, which combines with the acid.

The change may be formulated thus,

$$CH_3.CO.NH_2 + H_2O = CH_3.CO.OH + NH_3.$$

The rate of this change varies with the nature of the acid used.

If each acid possesses a specific affinity-coefficient, we might expect that the reaction under consideration would be quantitatively conditioned by the value of the coefficient for each acid used.

Now we have already seen that the ratio of the affinities of two acids may be expressed in the form $\frac{\xi}{1-\xi}$, and that this ratio is equal to the square root of the ratio of the velocity-constants of the reaction $\left[\frac{\xi}{1-\xi} = \sqrt{\frac{c}{c'}}\right]$; hence if the velocities of the change of acetamide to acetic acid and ammonia are measured, using different acids, we shall be able

to find the affinity-constants of the acids; and the values thus obtained may be expected to be the same as those deduced for the same acids by the thermal or volumetric study of the reactions which occur when these acids react with bases[1].

The course of the change was observed by decomposing the ammonium salt formed by sodium hypobromite, and measuring the nitrogen evolved. The reaction is not free from secondary changes; the ammonium salt formed causes the velocity-constant of the stronger acids to be greater, and the constant for weak acids to be smaller, than would be the case were the ammonium salt not formed. The time was determined in each case at which one-half of the total acetamide had been changed; the reciprocals of these times are the velocity-constants; and the square-root of the ratio of these is the ratio of the affinities of the acids. The occurrence of secondary reactions makes the numbers obtained rather doubtful; nevertheless the order of the affinities of the acids examined is the same as the order of the affinities determined by the more accurate volumetric method, and in the cases of the stronger acids the individual numbers agree very fairly. Ostwald also determined the velocity-constants when the reaction had proceeded for a short time only; under these conditions but little ammonium salt was formed, and the secondary changes were eliminated to a considerable extent. When the values thus obtained are compared with those formerly arrived at, the influence of the secondary reaction caused by the ammonium salts is very marked, especially with the weaker acids[2].

216 When methylic or ethylic acetate in aqueous solution is kept at a moderate temperature the acetate is very slowly changed to alcohol and acid, but if an acid is added the change proceeds more rapidly;

$$CH_3.COOCH_3 + H_2O = CH_3.COOH + CH_3.OH.$$

[1] See Ostwald, *J. für prakt. Chemie*, (2). **28**. 449; or *Lehrbuch*, **2**. 798. It has already been shewn (par. 176) that the reactions in question follow the law of mass-action and the principle of the coexistence of reactions.

[2] The numbers are given in the table on p. 421.

This reaction has been used by Ostwald[1] for determining the affinities of many acids; the velocity of the change was measured by titrating with a standardised baryta solution, as the change proceeded the amount of acid in the liquid increased.

As only a limited quantity of one body is undergoing change, the velocity-constant of the reaction should be found by the formula deduced for such cases from the law of mass-action[2], viz. $c = \frac{1}{\theta} \log \frac{A}{A - x}$ where A = number of equivalents of methylic acetate originally present, and x = number of equivalents changed in time θ. The velocity-constants of about 30 acids have been determined by Ostwald, and from these the affinity-constants have been calculated in terms of hydrochloric acid as unity; the results agree very fairly well with those previously obtained; in the cases of weak acids the values found by the methyl acetate method are considerably larger than those deduced from the observations with acetamide.

217 The inversion of cane-sugar by means of acids in dilute solution has been used by Ostwald as a third process whereby values may be found for the affinities of various acids[3];

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

The velocity of the change was determined by measuring the amount of inverted sugar by means of Fehling's solution. The same formula was employed as was used for calculating the velocity-constants of the change of methylic acetate to alcohol and acid. The results are in keeping with those formerly obtained; but as the inversion-process is more free from secondary reactions than either the acetamide-process or the methyl acetate process, the values found for the affinities of the acids by the first-named method are to be preferred to those obtained by the other methods.

[1] *J. für prakt. Chemie*, (2). **28**. 449; or *Lehrbuch*, **2**. 803.
[2] See par. 174.
[3] *Lehrbuch*, **2**. 810.

218 Some other reactions in which acids take part have been examined by Ostwald with the view of determining whether the reactions are quantitatively conditioned by the affinities of the acids.

Ammonia solution reacts with bromine to form nitrogen and hydrobromic acid; if an acid is present, an ammonium salt is produced and the change proceeds more slowly. Ostwald[1] has shewn that the stronger acids retard this change more than the weaker acids, and that the times required for a definite amount of the change to be accomplished vary approximately inversely as the affinities of the acids.

In another memoir[2], Ostwald has examined various cases of oxidation and reduction occurring in presence of free acids and has shewn that these are retarded to an amount proportional to the affinities of the acids. The reactions examined were, firstly, that occurring between bromic and hydriodic acids, $HBrO_3Aq + 6HIAq = HBrAq + 3H_2O + 6IAq$—the retarding effects of about a dozen acids being measured—and, secondly, that occurring between chromic acid and iodine,

$$2CrO_3Aq + 6HIAq = 2CrO_3H_3 + 6IAq.$$

The change which occurs when solid calcium oxalate reacts with various acids to produce a soluble calcium salt and oxalic acid has also been examined by Ostwald[3]. The amount of change which has occurred when equilibrium is established depends on the affinities of the acids employed[4].

219 A few determinations have been made of the velocity-constants of reactions brought about by bases. Warder measured the velocity of the saponification of ethylic acetate

[1] *Zeits. fur physikal. Chemie*, **2**. 124.

[2] *Ibid.* **2**. 127; see also Burchard, *Zeits. fur physikal. Chemie*, **2**. 796.

[3] *Lehrbuch*, **2**. 793.

[4] Other processes have been employed for determining the distribution of the members of a system when equilibrium results, or when a certain amount of change has been accomplished; among the more important of these are the colorimetric method, e.g. measurements of amount of $FeCl_3$ changed to $Fe(SCy)_3$ by reacting with KSCyAq (Gladstone, *Phil. Mag.* (4). **9**. 535); and optical methods, especially that founded on measurements of rotatory power (*v.* especially Jellet, *Trans. Royal Irish Acad.* **25**. 391).

by soda[1]. Reicher extended the method to potash, lime, and a few other bases[2]. Ostwald has applied the same process to ammonia, substituted ammonias, and substituted ammoniums[3]. The results can be regarded only as a starting-point for further investigations. But we shall see that the electrical method of observation is to be preferred to that based on the saponification of ethereal salts.

220 There is then a large amount of evidence in favour of the statement that many different reactions of acids are quantitatively conditioned by certain coefficients which depend only on the constitution of the acids, and the degree of dilution, and are independent of the nature of the chemical reaction. These coefficients, or affinity-constants, can be determined by different methods. Of the methods which we have considered, the most trustworthy are (1) that based on the inversion of cane-sugar, (2) that wherein the change of methylic acetate into alcohol and acid is measured, (3) that which rests on determinations of the change of acetamide into acetic acid and ammonia, (4) that which determines the division of a base between two acids either by measuring the thermal change or the volume-change which accompanies the chemical change.

The following table presents the numbers deduced by Ostwald for the affinities of various acids by the different methods.

[1] *Amer. Chem. Journal*, **1882**. No. 5.
[2] *Annalen*, **228**. 257.
[3] *Lehrbuch*, **2**. 819.

RELATIVE AFFINITIES OF ACIDS. (OSTWALD.)

Acid	I sugar inversion	II methyl acetate	III acetamide	IV division of base between two acids
Hydrochloric	100	100	100	98
Hydrobromic	105·5	99·1	98	—
Hydriodic	—	98·1	—	—
Nitric	100	95·7	98	100
Chloric	101·8	97·2	—	
Sulphuric	73·2	73 93 [1][104·56]	65·4	66
Methane sulphonic	—	100·37	—	—
Ethane sulphonic	100	99·33	—	—
Propane sulphonic	—	98 98	—	—
Isobutane sulphonic	—	98·53	—	—
Pentane sulphonic	—	97·82	—	
Hexane sulphonic	95·4	98 94	—	—
Isethionic	95·9	98·87	—	—
Benzene sulphonic	102·2	99·54	—	—
Formic	12·4	11·49	5	3·9
Acetic	6·32	5·87	2 34	1·23
Propionic	—	5·51	—	1·04
Butyric	—	5·47	—	0·98
Isobutyric	5·79	5·18	—	0·92
Monochloracetic	22	20·8	13	7
Dichloracetic	52·1	48	40·8	33
Trichloracetic	86·8	82·6	80	80
Glycollic	11·4	—	—	—
Diglycollic	16·3	—	—	—
Lactic	10·3	9·49	5	3·3
Methoxyacetic	13·5	—	—	—
Ethoxyacetic	11·7	—	—	—
Methoxypropionic	11·8	—	—	—
Hydroxyisobutyric	10·3	9·60	—	—
Trichlorolactic	—	26·3	—	—
Pyruvic	25·5	25 9	—	—
Oxalic	43	43	22·6	—
Malonic	17·5	16·9	—	—
Glyceric	13·1	—	—	—
Succinic	7·38	7·04	2·5	1·45
Malic	11 3	10 86	4·7	2·82
Tartaric	—	15·15	7·5	5·2
Pyrotartaric	10·3	—	—	—
Racemic	—	15·15	—	—
Citric	13·1	12·79	4	—
Phosphoric	24·9	—	—	—
Arsenic	21·9	—	—	—

[1] The affinity of sulphuric acid appears less than that of its derivatives obtained by replacing hydrogen by indifferent, or even basic, radicles. But it is to be noted that $\frac{1}{2}H_2SO_4$ is compared with $SO_2 . OH . OCH_3$ &c. If molecular quantities are to be compared, the observed numbers for sulphuric acid reactions must be doubled; if this is done the affinity of sulphuric acid is 104·56.

None of these numbers can be accepted as final. Some of the reactions used for finding the affinity-constants are more free from secondary changes than others. It has already been pointed out that the presence of normal salts tends to make the stronger acids appear stronger, and the weaker acids appear weaker, than they really are. This influence exerted by normal salts also depends on the dilution of the acids and on the temperature; the subject has been examined experimentally in a series of memoirs by Spohr[1]. The explanation which Spohr gives of the phenomena is based on the molecular conception of chemical action which was shortly discussed in par. 193.

221 Besides the methods described in the preceding paragraphs, there is another method for determining the relative affinities of acids and bases, which is more widely applicable, more easily applied, and more accurate, than any. This method rests on the connexion which exists between the affinities of acids and the electrical conductivities of their aqueous solutions.

The following numbers[2] shew the existence of a definite connexion between the electrical conductivities of various acids in aqueous solutions and the velocity-constants of chemical reactions conditioned by the same acids; the numbers are all referred to hydrochloric acid = 100.

[1] *J. für prakt. Chemie*, (2). **32.** 32; **33.** 265; *Zeitschr. für physikal. Chemie*, **2.** 194 (especially the last paper). *v.* also par. 237.

[2] Ostwald, *Lehrbuch*, **2.** 823. For a description of Ostwald's methods and apparatus for measuring the conductivities of electrolytes see *Zeits. für physikal. Chemie*, **2.** 561.

Acid.	*Conductivities.*	*Velocity-constants.* *Methylic acetate reaction.*	*Velocity-constants.* *Inversion of sugar.*
Hydrochloric	100	100	100
Hydrobromic	101·1	98	111
Nitric	99·6	92	100
Ethane sulphonic	79·9	98	91
Isethionic	77·8	98	92
Benzene sulphonic	74·8	99	104
Sulphuric	65·1	73·9	73·2
Formic	1·68	1·31	1·53
Acetic	1·424	0·345	0·4
Monochloracetic	4·9	4·3	4·84
Dichloracetic	25·3	23·0	27·1
Trichloracetic	62·3	68·2	75·4
Glycollic	1·34	—	1·31
Methyl glycollic	1·76	—	1·82
Ethyl glycollic	1·30	—	1·37
Diglycollic	2·58	—	2·67
Propionic	0·325	0·304	—
Lactic	1·04	0·9	1·07
Oxypropionic	0·606	—	0·8
Glyceric	1·57	—	1·72
Pyruvic	5·60	6·70	6·49
Butyric	0·316	0·3	—
Isobutyric	0·311	0·268	0·335
Oxyisobutyric	1·24	0·92	1·06
Oxalic	19·7	17·6	18·6
Malonic	3·1	2·87	3·08
Succinic	0·581	0·5	0·55
Malic	1·34	1·18	1·27
Tartaric	2·28	2·30	—
Racemic	2·63	2·30	—
Pyrotartaric	1·08	—	1·07
Citric	1·66	1·63	1·73
Phosphoric	7·27	—	6·21
Arsenic	5·38	—	4·81

The agreement between the values in the three columns for these acids shews that there is a close parallelism between the electrical conductivities and the affinities of the acids. The three sets of values were not all determined for equal dilutions of the acids used; hence the first question to be considered in inquiring more closely into the connexion

between the electrical conductivities and the affinities of acids is; how are the conductivities modified by dilution?

222 In dealing with this subject, Ostwald determines the *molecular conductivities* of the acids examined.

Let that number of grams of an acid which is equal to the molecular weight of the acid be dissolved in water, and let this solution be placed in a vessel the parallel sides of which are formed of infinite electrodes placed 1 centim. apart; then the electrical conductivity of this system, expressed in Ohms or in mercury units, is defined to be the *molecular conductivity of the electrolyte*. The molecular conductivity expresses the quantity of electricity which is conveyed across the electrolyte in 1 second when the difference of potential between the electrodes is 1 volt; inasmuch as each ion carries the same quantity of electricity with it, the quantity carried across the electrolyte measures the number of molecules which suffer electrolysis in the process. If μ = molecular conductivity, and λ = electrical conductivity as ordinarily defined (in mercury units) then $\mu = 10^7 n\lambda$, where n = number of litres to which the molecular weight of the acid taken in grams is diluted[1].

223 The molecular conductivities of solutions of acids vary greatly with dilution. This statement rests on the experiments of Arrhenius, Kohlrausch, and others. Considering first, the monobasic acids, Ostwald has arrived at the *law of dilution for monobasic acid*[2]. This law states that *the dilutions at which the molecular conductivities of monobasic acids exhibit equal values bear a constant relation to each other.* For instance the molecular conductivity of monochloracetic acid at any dilution is equal to that of formic acid when the latter is 16 times more dilute than the former, and is equal to that of butyric acid when the latter is 256 times more dilute than the monochloracetic acid.

The following table exhibits some of the data on which this statement rests. Dilution is stated in litres; it is expressed by means of the exponent p, which is defined by the

[1] Ostwald, *Lehrbuch*, 2. 824.

[2] *Lehrbuch*, 2. 825—838; or *Phil. Mag.* Aug. 1886. 104.

p	Butyric	p	Acetic.	p	Formic.	p	Monochlor-acetic.	p	Dichlor-acetic	p	Hypophos-phorous	p	Iodic.	p	Chloric.
1	0·397	1	0·520												
2	0·604	2	0·755												
3	0·876	3	1·08												
4	1·28	4	1·51												
5	1·81	5	2·12	1	1·76										
6	2·56	6	2·94	2	2·47										
7	3·59	7	4·08	3	3·43										
8	5·03	8	5·64	4	4·80	1	4·99								
9	7·02	9	7·75	5	6·33	2	6·98								
10	9·74	10	10·47	6	9·18	3	9·53								
				7	12·6	4	12·9								
				8	17·0	5	17·3								
				9	22·4	6	22·9								
				10	29·0	7	29·6	1	25·7	1	30·9				
						8	37·8	2	34·3	2	37·9				
						9	46·8	3	43·0	3	45·8	1	42·6		
						10	55·6	4	52·2	4	54·1	2	50·6		
								5	60·3	5	62·1	3	59·0		
								6	67·4	6	69·1	4	66·3		
								7	72·5	7	74·1	5	72·3		
								8	76·2	8	77·8	6	76·9	1	77·9
												7	80·2	2	80·2
												8	81·8	3	82·3
												9	83·0	4	84·0
														5	85·3
														6	86·4
														7	87·9
														8	88·7

relation, dilution $= 2^p$. The conductivities are here expressed in terms of an arbitrary unit which is 4·248 times greater than the mercury unit. The measurements have been extended to nearly 100 monobasic acids; all obey the law.

The conductivities of the stronger monobasic acids HCl, HBr, HI, HNO_3, $HClO_3$, &c. nearly reach their maxima in moderately dilute solutions; hence the conductivities of these acids vary but little with dilution. The conductivities of the weaker monobasic acids, on the other hand, increase largely as dilution increases; the rate of this increase varies; the weaker the acid, and therefore the smaller the conductivity, the greater, as a rule, is the increase for a given dilution. The molecular conductivities of the stronger monobasic acids reach a maximum equal to about 400 in mercury units, at a moderate dilution; the conductivities of the weaker acids also reach a maximum in very dilute solutions, but this maximum is not quite the same for all monobasic acids[1]. This fact opens a new inquiry; if there is a close parallelism between the chemical reaction-velocities, and therefore the affinities, of acids and the electrical conductivities of these acids, does this parallelism hold between the affinities and the maximum conductivities, or between the affinities and the conductivities at varying dilutions stated with reference to the maximum values? For instance: the maximum conductivities of hydrochloric, hydrobromic, and hydriodic, acid are practically identical, viz. 400 (in mercury units); the maximum conductivities of ethane sulphonic and methane sulphonic acids are identical, viz. 368; the maximum conductivities of isobutane sulphonic and benzene sulphonic acids are identical, viz. 356; moreover the rate at which the conductivities increase as dilution increases, stated in terms of the maximum conductivities, is practically identical in these three groups of acids. Now if the reaction-velocities of all the acids in any one of the groups are the same, but if this number is different from the value for any other of the three groups, we must conclude that the parallelism between conductivity and affinity holds

[1] Ostwald, *Zeitschr. fur physikal. Chemie*, 1. 74 and 97.

good between maximum conductivity and affinity; on the other hand if the reaction-velocities of all the acids in the different groups are the same, we must conclude that the parallelism holds good between affinity and the relative conductivities at varying dilutions stated with reference to the maximum conductivities. Should it appear that affinity is closely connected with maximum conductivity, it will only be necessary to determine the conductivity of an acid in a dilute solution in order to find its affinity; but should it appear that affinity and rate of increase of conductivity, relatively to maximum conductivity, are closely connected, it will be necessary to determine the conductivity of an acid at varying dilutions until the maximum conductivity is reached, before an approximate value is found for its affinity.

224 The following numbers shew that affinity is closely connected with relative conductivity and not only with maximum conductivity[1]:—

	Reaction-velocity.		*Max.*	
ACID.	*Methylic acetate.*	*Sugar-inversion.*	*Conductivity.*	
Hydrochloric	24·12	21·87	401	Rate of increase of conductivity practically the same for all these acids.
Hydrobromic	23·7	24·38	403	
Hydriodic	23·33	—	401	
Methane sulphonic	24·30	—	368	
Ethane sulphonic	23·80	23·44	367	
Isobutane sulphonic	23·41	—	355	
Benzene sulphonic	23·94	22·82	358	

The acids have practically identical reaction-velocities; the rate at which their conductivities increase as dilution increases is practically the same, but their maximum conductivities are different.

In order to arrive at exact determinations of the affinities of monobasic acids by the electrical method, it is therefore necessary to measure the conductivities of these acids in solutions of increasing dilution until the maximum value is obtained. But it is extremely difficult to do this; indeed the maximum conductivity of a weak acid cannot be directly

[1] Ostwald, *Zeitschr. fur physikal. Chemie*, **1**. 78.

determined, because at great dilutions the impurities in the water affect the result more than the minute trace of acid present.

Ostwald[1] has examined the conductivities of weak monobasic acids in dilute solutions. The starting-point is the generalisation made by Kohlrausch[2], to the effect that the electrical conductivity of a salt of a strong monobasic acid is the sum of two constants, one of which depends entirely on the nature of the acid, and the other entirely on the nature of the base. Ostwald's researches shew that the difference between the conductivity of a strong monobasic acid and that of its sodium salt is approximately a constant, and that this value becomes more nearly constant as the maximum conductivity is more nearly approached. Hence, he concludes, that the difference in question has a constant value when maximum conductivity is reached. Similarly the difference between the conductivity of a strong monobasic acid and its potassium salt is expressed by a constant, while another constant expresses the difference when a lithium salt is used. Further, if the conductivities of solutions of a series of sodium salts of strong monobasic acids are compared with those of a series of potassium salts, there is found to be a constant difference; e.g. the conductivity of the lithium salt is always approximately 9·7 units less than that of the sodium salt, and that of the potassium salt is always approximately 21·1 units less than that of the sodium salt. The conductivity of an alkali salt of a strong monobasic acid is therefore the sum of two constants, one of which belongs to the acid and the other to the base; Kohlrausch's generalisation is fully confirmed for the alkali salts of strong monobasic acids. The constant expressing the influence of the base may be found by subtracting the maximum conductivity of the strong acid from that of its normal salt with the base in question.

225 In a more recent paper[3], Ostwald develops the application

[1] *Zeitschr. fur physikal. Chemie*, **1**. 78, and 97.

[2] *Wied. Ann.* **6**. 167.

[3] Ostwald, *loc. cit.* **2**. 840.

of the law of Kohlrausch. Kohlrausch's law may be put in this form;

$$\mu = k\,(u + v)$$

where μ = conductivity, u = velocity of transference of one ion, v = velocity of transference of the other ion, and k = fraction of the total mass of electrolyte that is dissociated in the solution undergoing electrolysis. This way of stating the law rests partly upon the hypothesis which Arrhenius has developed from van't Hoff's law of osmotic pressure, viz. that some of the molecules of an electrolyte in solution are dissociated into their ions, and that the greater the number of dissociated molecules the greater is the conductivity of the electrolyte (*v. post*, par. 235). Electrolytic conductivity, then, seems to depend upon (1) the amount of dissociation, and (2) the velocities of motion of the ions into which the molecules of the electrolyte are dissociated. The conductivity of a binary electrolyte at infinite dilution may be stated as $\mu = u + v$. Kohlrausch[1] has shewn that the conductivities of solutions of sodium chloride, potassium iodide, and similar salts, practically reach their limiting values at a dilution of about 5000 litres; knowing then the maximum conductivity of one of these salts in solution, the velocity of transference of each ion can be found, provided we know the ratio of the velocities of the two ions (for the maximum conductivity is equal to the sum of the two velocities). The ratio in question can be determined from observations of the variations of concentration of the solution during electrolysis. In the case of potassium chloride the mean value of the ratio $\frac{u}{v}$ is ·94; the maximum molecular conductivity of the salt at 25° is 140·3 in mercury units[2]. Hence the velocities of the ions, stated in corresponding values, are

$$K = 67{\cdot}9;\ \mathrm{Cl} = 72{\cdot}4.$$

Similarly, values are obtained for the velocities of the ions

[1] *Wied. Ann.* **26**. 198.

[2] Kohlrausch, *Pogg. Ann.* **103**. 35.

of potassium nitrate, sodium chloride, and sodium nitrate; the mean values are as follows:—

$$K = 67{\cdot}9;\ NO_3 = 68{\cdot}1;\ Na = 44{\cdot}5;\ Cl = 73{\cdot}5.$$

As a mean value for the velocity of hydrogen as an ion, Ostwald takes the number 320·5 at 25°; this value may require to be somewhat altered.

The foregoing treatment of the law of Kohlrausch furnishes Ostwald with a means for finding the maximum conductivity of a monobasic acid. Let M = maximum conductivity of the acid; let μ = maximum conductivity of the sodium salt of the acid; then $\mu = 44{\cdot}5 + m$, where m is the velocity of transference of the negative ion, 44·5 being the velocity of the positive ion, viz. sodium. Then as the positive ion of the acid is hydrogen, and as the velocity of this ion is 320·5, we have

$$M = 320{\cdot}5 + m;\ \text{and therefore } M = \mu + 276.$$

In other words; to find the maximum conductivity of a monobasic acid, in mercury units at 25°, add 276 to the maximum conductivity of the sodium salt of the acid.

But it must be remembered that dilution affects the conductivities of the normal salts of weak and strong monobasic acids in the same way, e.g. dilution from 32 to 1024 litres raises the conductivity of the sodium salts of all monobasic acids about 10 units. This fact, established by Ostwald[1], gives a means for finding the maximum conductivity of the sodium salt of a monobasic acid from the observed conductivity at stated dilution, without introducing a serious error. It is only necessary to add a certain number to the observed conductivity; the value of this number is independent of the nature of the acid. The following table[2] gives the data for sodium chloride:—

Maximum conductivity at 25° (*Kohlrausch*) = 119·9.

v	μ	d	a	v	μ	d	a
32	107·6	12·3	288·3	250	113·9	6·0	282·0
64	109·9	10·0	286·0	512	115·8	4·1	280·1
128	112·0	7·9	283·9	1024	117·5	2·4	278·4
				∞	119·9	—	276·0

[1] *Zeitschr. fur physikal. Chemie*, 1. 97.

[2] Ostwald, *Ibid.* 2. 843.

In this table v = dilution in litres, μ = conductivity in mercury units at 25°, d = difference between observed and maximum conductivity, and $a = 276 + d$, in other words a = number to be added to conductivity of sodium salt at stated dilution to obtain the maximum conductivity of the acid.

In using this table it is assumed that the acid is monobasic. This assumption can be tested by finding whether the increase in molecular conductivity is approximately 10 units, when dilution is increased from 32 to 1024 litres; if the acid is n-basic, the increase will be approximately n. 10 units.

The results embodied in the preceding table may be used to determine the velocity of transference of the negative ions of monobasic acids. The method consists in determining the conductivity of the sodium salt of the given acid for a stated dilution; then adding the number required to give the maximum conductivity of the salt (d in the table); and finally deducting 44·5 (the velocity of sodium as an ion) from the result. The following table gives Ostwald's results in more convenient form: v = dilution in litres, and b = numbers to be deducted from molecular conductivity of sodium salt at dilution v, in order to get the velocity of transference of the negative ion:—

v	b	v	b
32	32·2	256	38·5
64	34·5	512	40·4
128	36·6	1024	42·1
		∞	44·5

226 The research, of which a condensed account is given in the preceding paragraph, furnishes a method for finding the maximum molecular conductivity of a monobasic acid from observations of the conductivity of its sodium salt at stated dilutions. The further development of the method of Ostwald (*loc. cit.*) makes it probable that the maximum conductivity of some acids may be calculated from a knowledge of their composition alone. Ostwald[1] calculates the velocities of the negative ions of 44 monobasic acids of very different composition; from the results so obtained he draws conclusions

[1] *Loc. cit.* 847.

regarding the connexions between the composition and the velocities of transference of these ions. These conclusions are: (1) isomeric ions travel with equal, or almost equal, velocities; (2) as the number of atoms forming the negative ions increases the velocity of transference of the ions decreases; (3) the substitution of one atom by another influences the velocity with which the ion travels, e.g. the velocity is decreased by substituting chlorine, or hydroxyl, for hydrogen, but this effect is marked only in the comparatively simple ions; (4) when the number of atoms forming the negative ions is more than about 12, the velocities of these ions seem to depend almost entirely on the number, and not at all, or hardly at all, on the nature, of the atoms. If the number of atoms in various negative ions is taken as abscissae, and the velocity of transference as ordinates, an asymptotic curve is obtained running convex to the abscissae-axis, from which the velocity of ions formed of more than about 12 atoms can be calculated, from the composition of these ions, to within $\pm$ 1 to 2 units, without any measurements of conductivity. Hence it becomes possible to find the maximum conductivity of a monobasic acid the negative ion of which is composed of not less than about 12 atoms, from the composition of the acid alone.

227 The relations between the electrical conductivities and the dilution of polybasic acids differ from those established for the monobasic acids. The polybasic acids conduct as if they were first of all separated into hydrogen and a radicle containing replaceable hydrogen, then, as dilution increases, into hydrogen and a radicle containing less replaceable hydrogen, and finally into hydrogen and the acidic radicle containing no replaceable hydrogen[1]. In other words: a dibasic acid conducts at first as if the ions were H and HR, but on further dilution the ions become H_2 and R; so the stages which can be distinguished in the conduction of a solution of a tribasic acid as dilution increases are three, the ions being (1) H and H_2R, (2) H_2 and HR, and (3) H_3 and R.

When polybasic acids form unstable and easily decom-

[1] Ostwald, *Lehrbuch*, 2. 831 *et seq.*, (or *Phil. Mag* August, 1886).

posed normal salts, e.g. selenious acid or phosphoric acid, the *molecular* conductivities of these acids follow nearly the same course, as dilution increases, as the monobasic acids. In the following table the molecular conductivities of selenious and monochloracetic acids are placed side by side; dilution is stated in litres.

Dil.	H_2SeO_3	$CH_2Cl.CO_2H$	*Dil.*	H_2SeO_3	$CH_2Cl.CO_2H$
2	32·5	21·2	256	191	161
4	41·4	29·7	512	231	199
8	53·5	40·5	1024	267	236
6	70·3	54·6	2048	295	270
32	92·3	73·4	4096	312	
64	120	97·4			
128	154	126			

The relations between the dilution and the *molecular* conductivities of the polybasic acids which form stable normal salts with neutral reaction are different from those just described. The *molecular* conductivities of the stronger dibasic acids of this class increase until a value is reached about the same as that for the stronger monobasic acids; at about this point the second replaceable hydrogen atom appears to take part in the conduction, the ions are now probably H_2 and R and conductivity increases as dilution increases, until it reaches a maximum. The following numbers give the molecular conductivities of oxalic acid, sulphuric acid, and methane disulphonic acid. Dilution is stated in litres.

Dil.	$H_2C_2O_4$	H_2SO_4	$CH_2(SO_3H)_2$.
2	120	394	569
4	152	410	622
8	187	428	651
16	224	456	674
32	261	494	694
64	293	541	711
128	319	592	727
256	339	640	740
512	355	684	751
1024	371	719	756
2048	391	741	760
4096	420	753	757

Oxalic acid reaches the maximum of the strong monobasic acids at about the dilution of 512 litres, sulphuric acid has reached this maximum at 2 litres, while the molecular conductivity of methane sulphonic acid, which is a very strong acid, is much greater even at 2 litres than the maximum value for the strong monobasic acids. Of the three acids here considered, the weakest is oxalic, and the strongest is methane sulphonic; the changes in the conductivity of oxalic acid as dilution increases follows a course somewhat similar to that noticed in the case of a fairly strong monobasic acid, say dichloracetic acid, until a dilution of 512 litres or so is reached, after which the second replaceable atom of hydrogen probably begins to be separated and the electrolysis proceeds according to the scheme $H_2 + R$. The molecular conductivities of dichloracetic acid are given in order that they may be compared with those of oxalic acid:—

Dil.	$CHCl_2.CO_2H$	*Dil.*	$CHCl_2.CO_2H$	*Dil.*	$CHCl_2.CO_2H$
2	109	32	256	512	339
4	146	64	286	1024	342
8	183	128	308	2048	343
16	222	256	324		

The changes in the molecular conductivity of sulphuric acid as dilution increases cannot be compared strictly with the changes of conductivity of a monobasic acid; some of the second replaceable hydrogen atoms are probably separated even in solutions so concentrated as 4 litres, and conductivity continues to increase until a maximum is reached which is approximately double that of the stronger monobasic acids; but the influence of either replaceable atom of hydrogen cannot be wholly separated from the influence of the other. If the *equivalent* conductivities of sulphuric acid—obtained by dividing the molecular conductivities by two,—are compared with those of a monobasic acid there is still a marked difference in the relations between conductivity and dilution in the two cases.

Methane sulphonic acid is a decidedly stronger acid than sulphuric; in this case dilution influences the equivalent conductivity (i.e. molecular conductivity divided by two) in

much the same way as it affects the conductivity of a strong monobasic acid. The numbers for nitric acid are given, and beside them are placed the *equivalent* conductivities of methane sulphonic acid:—

Dil.	HNO_3	$\frac{CH_2(SO_3H)_2}{2}$	*Dil.*	HNO_3	$\frac{CH_2(SO_3H)_2}{2}$	*Dil.*	HNO_3	$\frac{CH_2(SO_3H)_2}{2}$
2	331	285	32	367	347	512	377	376
4	342	311	64	371	356	1024	378	378
8	352	326	128	375	364	2048	375	380
16	361	337	256	376	370	4096	—	378

The behaviour of tribasic acids resembles that of dibasic acids. Phosphoric acid, for instance, resembles dichloracetic acid; dilution increases the molecular conductivity from 131 at 2 litres, to 293 at 64 litres, and 345 at 2048 litres. The maximum of a fairly strong monobasic acid is reached but not surpassed; the third atom of replaceable hydrogen probably takes very little part in the electrolysis. Strong tribasic acids would probably reach a maximum conductivity approximately equal to three times the maximum of the strong monobasic acids, and the *equivalent* conductivities of these acids would probably be very similar to the molecular conductivities, which in this case are also the equivalent conductivities, of the strong monobasic acids. But very few tribasic acids have yet been examined. (See also par. 232.)

The researches of Kohlrausch and Ostwald[1] have established a connexion between the molecular conductivities of bases and the dilution of solutions of these bases similar to that which exists between the conductivities and the dilution of acids.

228 The molecular conductivities of the strong bases, soda, potash, lithia, and thallia, increase as dilution increases in much the same way as the conductivities of the strong monobasic acids increase; the maxima for the bases seem to be about $\frac{2}{3}$ of those for the acids.

The following numbers[2] shew that there is a close paral-

[1] See Ostwald's *Lehrbuch*, **2**. 839 and 886.

[2] Ostwald, *Lehrbuch*, **2**. 839.

lelism between the electrical conductivities and the reaction-velocities of bases; the reaction-velocities were determined by observing the rate of saponification of ethylic acetate by the different bases; the numbers are stated in empirical units for convenience sake.

BASE.	*Saponification-velocities.*	*Electrical conductivities.*
Soda	162	161
Potash	161	149
Lithia	165	142
Thallia	158	156
Ammonia	·3	4·8
Methylamine	19	20·2
Ethylamine	19	20·5
Propylamine	18·6	18·4
Isobutylamine	14·4	15·2
Amylamine	18·5	18·6
Allylamine	4	6·9
Dimethylamine	22	23·5
Diethylamine	26	28·3
Trimethylamine	7·3	9·7
Triethylamine	22	20·2
Piperidine	27	27
Tetra-ethylammonium	131	128

229 It has been shewn in pars. 223 and 224 that the affinities of acids are closely connected with the relative conductivities of these acids stated in terms of their maximum conductivities; and that it is necessary to determine the conductivities of acids at varying dilutions, until the maximum is reached, in order to arrive at exact measurements of the affinities of these acids by the electrical method. Pars. 224 and 225 contain an account of Ostwald's method for finding the relative and maximum conductivities of monobasic acids.

Let us now see how the results thus obtained are applied to find the affinities of the monobasic acids. Ostwald's treatment of this subject[1] is based on the extension by Arrhenius to electrolytic phenomena of van't Hoff's law of

[1] *Zeitschr. fur physikal. Chemie*, **2**. 270.

osmotic pressure (*v. post* pars. 235, 237). The hypothesis of Arrhenius states that the molecular conductivity of an electrolyte in solution depends on the number of molecules of the electrolyte which are dissociated into their ions, and on the velocity of transference of these ions. The differences between the conductivities of different acids depend, on this hypothesis, chiefly on differences in the degrees of dissociation of the molecules of these acids. At infinite dilution, all the molecules of the electrolyte are supposed to be dissociated into their ions.

As the hypothesis rests on the identity of the laws expressing gaseous dissociation and dissociation in solution, it follows that deductions may be drawn from gaseous dissociation-phenomena and applied to dissociations in solution. Now if a gaseous body is dissociated into two gases, temperature being constant, the pressure of the undissociated portion, p, bears a constant relation to the square of the pressure of the dissociated portion, p_1, so that $\frac{p}{p_1^2} = c$. At a stated temperature, the pressure of a gas is proportional to its mass, u, and inversely proportional to the volume, v. But van't Hoff's law of osmotic pressure states that the osmotic pressure of an undissociated compound in solution is equal to the pressure which the same mass of that substance would exert did it exist as a gas occupying the same volume as is occupied by the solution; hence in the solution, this pressure, p, may be put as proportional to $\frac{u}{v'}$; and therefore from the above equation $\frac{uv'}{u_1^2} = C$.

Now let μ_∞ = molecular conductivity of a binary electrolyte at infinite dilution, and let μ_v = molecular conductivity of volume v (i.e. conductivity of v litres containing one molecular weight in grams of the electrolyte); then (by the hypothesis) the fraction $\frac{\mu_v}{\mu_\infty}$ expresses the portion of the electrolyte which is dissociated in terms of the total mass of the electrolyte taken as unity. Putting this fraction as u_1,

and the undissociated portion of the electrolyte as u, we have

$$u = 1 - \frac{\mu_v}{\mu_\infty}.$$

Then substituting these values in the equation $\frac{uv}{u_1^2} = C$, we have

$$\frac{\mu_\infty (\mu_\infty - \mu_v)}{\mu_v^2} v = C.$$

This equation may be put in the more convenient form

$$\frac{1 - m}{m^2} v = C;$$

where $m = \frac{\mu_v}{\mu_\infty}$, i.e. the molecular conductivity at any stated dilution referred to the maximum molecular conductivity. This equation states that $\frac{1 - m}{m^2} v$ must have the same value for all dilutions of any one binary electrolyte.

Ostwald has proved that the value of $\frac{1 - m}{m^2} v$ is constant for each of a great many monobasic acids[1]; in these cases m varied from ·7 to 76, and the value of C varied for different acids from ·129 to 15·3.

Now the affinity of an acid is a number which quantitatively conditions the chemical reactions of the acid, and this number is nearly proportional to the electrical conductivity of the acid in aqueous solution. The value of the affinity-coefficient of an acid, according to the hypothesis of van't Hoff and Arrhenius, depends chiefly upon the degree of dissociation of that acid, for the greater the amount of dissociation into hydrogen and a negative ion the more readily will these ions enter into chemical reactions; and inasmuch as the amount of dissociation is independent of the nature of

[1] Ostwald (*loc. cit.*) shews how the application of corrections for the changes in molecular volumes and in viscosity which accompany the concentration of solutions of binary electrolytes, brings the observed values of C yet more near to absolute constancy.

the reactions brought about by the acid, it follows that the affinity of an acid is independent of the nature of the reactions in which the acid takes part.

The constant obtained by applying the equation

$$\frac{1 - m}{m^2} v = C$$

to a monobasic acid, represents then the affinity of the acid in question.

SECTION II. *Connexions between the affinity-coefficients and the constitution of acids.*

230 Ostwald has shewn that the affinity-coefficients of many monobasic acids are very nearly proportional to their molecular electrical conductivities in solution stated as fractions of the maximum conductivities. This statement asserts that a number can be found for each acid which measures its readiness to conduct electricity in solution, and also its readiness to take part in chemical reactions, and that this number depends only on the nature of the acid, and is independent of the degree of dilution. Put into the form of an equation by which the number in question can be determined, the statement is

$$\frac{1 - m}{m^2} v = C;$$

where

$$m = \frac{\mu_v}{\mu_\infty};$$

μ_v being the conductivity of a solution of one molecular weight in grams in v litres of water, and μ_∞ being the maximum molecular conductivity at infinite dilution.

In applying this equation to the measurement of affinities of acids, Ostwald[1] prefers to put it in the following form:

$$\frac{m^2}{(1 - m) v} = k,$$

where $k = \frac{1}{C}$. The reason for this form is, that C has small

[1] *Königl. Sachsischen Gesellschaft der Wissenschaften* (*math.-physische Classe*), Bd. **26** [1889]. (Also in *Zeitschr. fur physikal. Chemie*, **3**. 170.)

values for strong acids and large values for weak acids. To avoid small fractions, Ostwald multiplies m by 100, and also k by 100; he gives values for $100k$ at dilutions varying from 8 to 1024 litres, and finally he expresses the most probable value for $100k$ as K.

231 Ostwald has determined K for more than 100 monobasic acids. The following are selections from his results for various series of acids.

ACETIC ACIDS, $C_nH_{2n+1}.COOH$ AND THEIR DERIVATIVES.

ACID.		K.
Formic	$H.COOH$	·0214
Acetic	$CH_3.COOH$	·0018
Propionic	$C_2H_5.COOH$	·00134
Butyric	$C_3H_7.COOH$	·00149
Isobutyric	$CH(CH_3)_2.COOH$	·00144
Valeric	$C_4H_9.COOH$	·00161
Caproic	$C_5H_{11}.COOH$	·00145
Monochloracetic	$CH_2Cl.COOH$	·155
Dichloracetic	$CHCl_2.COOH$	5·14
Trichloracetic	$CCl_3.COOH$	121*
Monobromacetic	$CH_2Br.COOH$	·138
Cyanacetic	$CH_2Cy.COOH$	·37
Sulphocyanacetic	$CH_2SCy.COOH$	·265
Isosulphocyanacetic[1]	$C_3H_3O_2SN$	·000024
Carbaminthioglycollic[2]	$CH_2(SCONH_2).COOH$	·0246
Thio-acetic	$CH_3.COSH$	·0469
Thioglycollic	$CH_2SH.COOH$	·0225

* Approximate only.

OXYACETIC ACIDS, $C_nH_{2n}OH.COOH$, AND THEIR DERIVATIVES.

ACID.		K.
Glycollic	$CH_2OH.COOH$	·0152
Methoxy-acetic	$CH_2(OCH_3).COOH$	·0335
Ethoxy-acetic	$CH_2(OC_2H_5).COOH$	·0234
Phenoxy-acetic	$CH_2(OC_6H_5).COOH$	·0756
o-Nitrophenoxy-acetic	$CH_2(OC_6H_4.NO_2).COOH$	·158
p- „ „	„ „	·153

[1] By action of chloracetic acid on sulphocarbamide (Volhard, *J. fur prakt. Chemie*, **1874.** 6; Claesson, *Ber.* **10.** 1352).

[2] Claesson, *Ber.* **10.** 1350.

ACIDS DERIVED FROM AMIDOACETIC, $CH_2.NH_2.COOH$.

ACID.		K.
Amidophenyl-acetic	$CH_2(C_6H_4NH_2).COOH$	·0039
Hippuric	$CH_2(C_6H_5.NH.CO).COOH$	·0222
Aceturic	$CH_2(NH.C_2H_3O).COOH$	·023

ACIDS DERIVED FROM PROPIONIC, $CH_3.CH_2.COOH$.

ACID.		K.
Lactic	$CH_3.CHOH.COOH$	·0138
Oxypropionic	$CH_2OH.CH_2.COOH$	·00311
Glyceric	$CH_2OH.CHOH.COOH$	·0228
Laevulic	$CH_2.C_2H_3O.CH_2.COOH$	·00255
Iodopropionic	$CH_2I.CH_2.COOH$	·009
Trichlorolactic	$CCl_3.CHOH.COOH$	·465

DERIVATIVES OF HIGHER ACETIC ACIDS.

ACID.		K.
Trichlorobutyric	$C_3H_4Cl_3.COOH$	10·0
Oxyisobutyric	$(CH_3)_2.CHOH.COOH$	·0106
Nitrocaproic	$C_5H_{10}.NO_2.COOH$	·0123
Dinitrocaproic	$C_5H_9.(NO_2)_2.COOH$	·0694

BENZOIC ACID AND ITS OXY-DERIVATIVES.

ACID.		K.
Benzoic	$C_6H_5.COOH$	·006
1 : 2 Oxybenzoic	$C_6H_4OH.COOH$	·102
1 : 3 "	"	·00867
1 : 4 "	"	·00286
Oxysalicylic COOH : OH : OH = 1 : 2 : 3		·114
Oxysalicylic 1 : 2 : 5		·108
" 1 : 2 : 4		·0515
" 1 : 2 : 6		5·0
Dioxybenzoic COOH : OH : OH = 1 : 3 : 4		·0033
Dioxybenzoic 1 : 3 5		·0091

HALOGEN DERIVATIVES OF BENZOIC ACID.

ACID.		K.
o-Chlorobenzoic	$C_6H_4Cl.COOH$	·132
m- "	"	·0155
p- "	"	·0093
o-Bromobenzoic	$C_6H_4Br.COOH$	·145
m- "	"	·0137
m-Fluobenzoic	$C_6H_4F.COOH$	·0136
m-Cyanobenzoic	$C_6H_4.CN.COOH$	·0199

NITROBENZOIC ACIDS.

ACID.		K.
o- Nitrobenzoic	$C_6H_4.NO_2.COOH$	·616
m- „	„	·0345
p- „	„	·0396

AMIDOBENZOIC ACIDS AND THEIR DERIVATIVES.

The values of K for the three isomeric amidobenzoic acids vary; the acids are all very weak; the meta acid is the strongest of the three.

ACID.		K.
o- Acetamidobenzoic	$C_6H_4.NHC_2H_3O.COOH$	·0236
m- „	„	·0085
p- „	„	·00517

DERIVATIVES OF OXYBENZOIC ACID.

ACID.		K.
o- Acetoxybenzoic	$C_6H_4(OC_2H_3O)COOH$	·0333
p- „	„	·00422
m- „	„	·00986
o- Methoxybenzoic	$C_6H_4(OCH_3)COOH$	·00815
p- „	„	·00302

HOMOLOGUES OF BENZOIC ACID.

ACID.		K.
o- Toluic	$C_6H_4.CH_3.COOH$	·012
m- „	„	·00514
p- „	„	·00515
Phenylacetic	$C_6H_5.CH_2.COOH$	·00556

UNSATURATED ACIDS.

ACID.		K.
Acrylic	$C_2H_3.COOH$	·0056
Crotonic	$C_3H_2.COOH$	·00204
Isocrotonic	„	·0036
Tiglic	$C_4H_7.COOH$	·0009
Angelic	„	·00501
Hydrosorbic	$C_5H_9.COOH$	·00241
Sorbic	$C_5H_7.COOH$	·00173
Parasorbic	$C_5H_7.COOH$	·00173
Methylacrylic	$C_5H_9.COOH$	·00111

CINNAMIC ACID AND DERIVATIVES.

ACID.		*K*.
Cinnamic	$CH(C_6H_5).CH.COOH$	·00355
α- Bromo-cinnamic	$CH(C_6H_5).CBr.COOH$	1·44
β- „	$CBr(C_6H_5).CH.COOH$	·093
Phenylpropiolic	$C_6H_5.C_2.COOH$	·59
o- Nitrophenylpropiolic	$C_6H_4NO_2.C_2.COOH$	1·06

DERIVATIVES OF THE BENZENOID SULPHONIC ACIDS.

The benzenoid sulphonic acids are so strong that their affinity-constants cannot accurately be determined by the electrical method; at moderate dilutions as much as 90 per cent. of an acid of this group seems to be dissociated. When the amido-group (NH_2) is introduced in place of hydrogen, the affinity of a sulphonic acid is decreased, and measurements can be made by the elcctrical method.

ACID.		*K*.
o- Amidobenzene sulphonic	$C_6H_4.NH_2.SO_3H$	·33
m- „	„	·0185
p- „	„	·0581
Diamidobenzene sulphonic $SO_3H : NH_2 : NH_2 = 1 : 2 : 3$		·005
Bromamidobenzene sulphonic $SO_3H : NH_2 : Br = 1 : 2 : 5$		1·67
Bromamidobenzene sulphonic 1 : 3 : 6		·072
Dibromamidobenzene sulphonic 1 : 2 : 4 : 5		7·9
„	1 : 2 : 3 : 5	very strong; *K* shews irregularities.
„	1 : 3 : 4 : 6	2·5
Toluidine sulphonic $SO_3H : NH_2 : CH_3 = 1 : 3 : 4$		·0236
„	„ 1 : 4 : 2	·0357

232 It has already been mentioned (par. 227) that many dibasic acids conduct as if they were separated by the current into hydrogen and a negative ion HR, and on further dilution into hydrogen and the negative radicle R. Electrolysis probably takes place in accordance with the two schemes (1) $H_2R = H + HR$, (2) $HR = H + R$; both of these occur more or less together, but until the conductivity, and hence, by hypothesis, the electrolytic dissociation, reaches about half its maximum value, the first scheme fairly accurately represents the course of the electrolysis. Dissociation-

constants can be determined for dibasic acids by the method already described, provided only those values of the conductivity are used for which m is less than ·5. If the conductivities are greater than half the maximum values for monobasic acids, the dissociation-constants cannot be accurately determined; yet even in these cases comparison of the dilutions at which the relative conductivities of the different acids are equal, or nearly equal, gives data for comparing the dissociation-constants of the acids; the constants are inversely as the corresponding dilutions[1].

Ostwald has determined the conductivities of many dibasic acids, and, by using the numbers representing relative conductivities at varying dilutions approximately up to that dilution whereat the second phase of the electrolysis begins, he has found values for K which enable the affinities of these acids to be compared.

The following numbers are selected from his results.

Oxalic Acids and Derivatives.

The constant for oxalic acid itself could not be accurately determined; even at a dilution of 32 litres, the acid is much more than half dissociated. From his observations, Ostwald concludes that K for oxalic acid may be taken in round numbers as about 10.

Acid.		K.
Malonic	$CH_2(COOH)_2$	·158
Succinic	$C_2H_4(COOH)_2$	·00665
Glutaric	$C_3H_6(COOH)_2$	·00475
Adipic	$C_4H_8(COOH)_2$	·00371
Pimelic	$C_5H_{10}(COOH)_2$	·00359
Methylmalonic	$CH(CH_3).(COOH)_2$	·087
Ethylmalonic	$CH(C_2H_5).(COOH)_2$	·127
Dimethylmalonic	$C(CH_3)_2.(COOH)_2$	·077
Methylsuccinic	$C_2H_3(CH_3).(COOH)_2$	·0086
Oxamic	$CONH_2.COOH$	·80
Oxaluric	$CONH(CONH_2).COOH$	4·5
Oxanilic	$CONH(C_6H_5).COOH$	1·21
o- Chloroxanilic	$CONH(C_6H_4Cl).COOH$	2·03
p- „	„	1·4

[1] Ostwald, *l.c.*

Malic	$C_2H_3(OH).(COOH)_2$	·0395
Inactive malic	,,	·0399
Dextro-tartaric	$C_2H_2(OH)_2(COOH)_2$	·097
Laevo-tartaric	,,	·097
Racemic	,,	·097

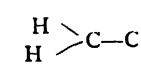
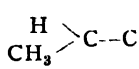
BENZENE DICARBOXYLIC ACIDS.

ACID.		*K*.
o-Phthalic	$C_6H_4(COOH)_2$	·121
m- ,,	,,	·0287
Oxyterephthalic	$C_6H_3(OH).(COOH)_2$	·25
Nitrophthalic	$C_6H_3(NO_2).(COOH)_2$	1·22
COOH : NO_2 : COOH = 1 : 2 : 5		
,,	1 : 3 : 5	·60

ACIDS DERIVED FROM PYRIDINE[1].

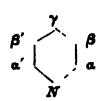
ACID.		*K*.
Picolinic	$C_5H_4N.COOH$	·0003
Nicotinic	$C_5H_4N.COOH$	·00137
Isonicotinic	,,	·00109
Lutidinic	$C_5H_3N(COOH)_2$ ($\alpha\gamma$)	·60
Cincomeronic	,, ($\beta\gamma$)	·21
Isocincomeronic	,, ($\alpha\beta'$)	·43
Quinolinic	,, ($\alpha\beta$)	·30
Pyridine dicarboxylic	,, ($\beta\beta'$)	·15
a- Methyl pyridine dicarboxylic	$C_5H_2.CH_3.N(COOH)_2$	·20
aa'- Dimethyl pyridine dicarboxylic	$C_5H(CH_3)_2N(COOH)_2$	·34
aγ- ,, ,,	,,	·55

The following results exhibit the influence of *geometrical isomerism* (*v.* pars. 93—95, Book I.). The formulae are written in accordance with the notation of Wislicenus.

ACID.		*K*.
Crotonic		·00204
Isocrotonic		·0036 (approximate).

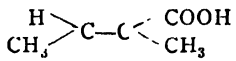
The values of *K* for isocrotonic acid vary from ·0028 to

[1] The positions of the carboxyl groups in the dicarboxyl derivatives of pyridine are indicated by the scheme

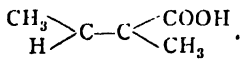


·00347; this is because of the impossibility of completely separating the acid from admixed crotonic acid. The *axially symmetric* isocrotonic acid is certainly stronger than the *plane symmetric* crotonic acid.

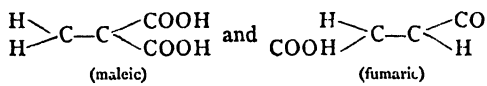
The values of K for tiglic and angelic acids, $C_5H_8O_2$, are; tiglic acid = ·000957, angelic acid = ·00501. It is therefore probable that angelic acid is analogous to isocrotonic acid, and has the constitution



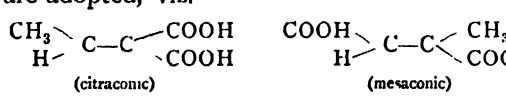
while tiglic acid is probably



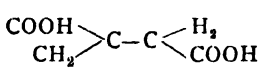
In the cases of maleic and fumaric acids, $C_2H_2(COOH)_2$, the values are; maleic acid = 1·17, fumaric acid = ·093. In maleic acid, which is about twelve times stronger than fumaric acid, the carboxyl groups are probably nearer one another than in fumaric acid; the structure is indicated by the formulae



If the formulae of Wislicenus for citraconic and mesaconic acids are adopted, viz.



we should expect citraconic to be the stronger of the two acids. The values obtained for K are, for citraconic ·34, and for mesaconic ·079. The third isomeride, itaconic acid is very weak; K = ·012. The constitution of this acid is probably



233 The results obtained by Ostwald, some of which are recorded in the preceding paragraphs, enable conclusions to be drawn regarding connexions between the constitutions and the affinities of acids. In the acetic series, for example,

affinity decreases from formic to propionic acid and then remains nearly constant until caproic acid is reached. The substitution of chlorine for hydrogen in an acetic acid is attended with an increase of affinity; the value of K is increased to a smaller extent when bromine replaces hydrogen; on the other hand the group CN increases the affinity more than chlorine does, so does the group SCN, but SCN is less energetic in this way than CN. In the benzoic acids, substitution of hydrogen by CN increases K a little more, but only a little more, than is effected by putting chlorine for hydrogen, the position of the CN group in one case being the same as that of the Cl atom in the other case. Substitution of sulphur for oxygen in the group COOH in acetic acid, raises K from ·0018 to ·0469; but if the group SH is substituted for hydrogen in the same acid, K is raised from ·0018 to ·0225 only.

The change from an acetic acid to the corresponding oxyacid, *i.e.* the substitution of OH for H, raises the affinity, but the increase is much less than when Cl is put in place of H. The group OCH_3 is more acidic than OH. The acidic character of the group OC_6H_5 is very marked. When $OC_6H_4NO_2$ is substituted for H, in an acetic acid, the increase of K is approximately equal to that which occurs when Cl is substituted for H. On the other hand, the basic character of ammonia derivatives is seen by comparing K for

$$CH_2(OC_6H_5)\,COOH\ [K = ·0756],$$

with K for $CH_2(C_6H_4NH_2)\,COOH\ [K = ·0039]$:

with this decrease may be contrasted the increase due to putting in the acidic group CO

$$[K \text{ for } CH_2(C_6H_5.NH.CO)\,COOH = ·0222],$$

or the acidic group C_2H_3O

$$[K \text{ for } CH_2(NH.C_2H_3O)\,COOH = ·023].$$

The influence of the relative positions of the different groups is apparent when we compare the affinities of propionic, oxypropionic, lactic, and glyceric acids;

$CH_3.CH_2.COOH$	$K=·00134$
$CH_2OH.CH_2.COOH$	$K=·00311$
$CH_3.CHOH.COOH$	$K=·0138$
$CH_2OH.CHOH.COOH$	$K=·0228$

The influence of relative position is well shewn in the values of K for the three oxybenzoic acids; the affinity of the ortho-acid is nearly twelve times greater than that of the meta-acid, and the affinity of the meta-acid is about three times greater than that of the para-acid. Substitution of a second OH group in benzoic acid raises the affinity a little if the second OH group is placed in the position next to the first, but if the second OH group is placed in the position next to the COOH group, the increase in the value of K is very great;

$C_6H_4.COOH.OH$	1 : 2	$K=·102$
$C_6H_3.COOH.OH.OH$	1 : 2 : 3	$K=·114$
$C_6H_3.COOH.OH.OH$	1 : 2 : 6	$K=5·0$

A comparison of the affinities of the isomeric chloro- and bromo-benzoic acids shews the influence of the arrangement of the substituting groups; the nearer the acidic groups are placed the greater is the affinity of the acid. Again the effect of replacing H by Cl, and by NO_2, exhibits at once the more acidic character of the NO_2 group, and also the influence of position :—

Cl substituted for H in $C_6H_5.COOH$ in the meta-position raises K from ·006 to ·0155.

NO_2 substituted for H in $C_6H_5.COOH$ in the meta-position raises K from ·006 to ·0345.

Cl substituted for H in $C_6H_5.COOH$ in the ortho-position raises K from ·006 to ·132.

NO_2 substituted for H in $C_6H_5.COOH$ in the ortho position raises K from ·006 to ·616.

The effect of the character and position of the replacing groups is also shewn in the change of affinity brought about by passing from benzoic acid to ortho- and para-acetoxy-benzoic acids, and from benzoic acid to ortho- and para-methoxy-benzoic acids; both groups raise the affinity when they are placed in the ortho-position, and both lower the

affinity when they are placed in the para-position; the change of position in the case of the group $O.C_2H_3O$ from ortho to para decreases the affinity to about $\frac{1}{8}$ of its value, the corresponding change of position in the case of the group $O.CH_3$ decreases the affinity to about $\frac{1}{3}$ of its value:—

$O.C_2H_3O$ substituted for H in $C_6H_5.COOH$ in the ortho-position raises K from ·006 to ·0333.

$O.CH_3$ substituted for H in $C_6H_5.COOH$ in the ortho-position raises K from ·006 to ·00815.

$O.C_2H_3O$ substituted for H in $C_6H_5.COOH$ in the para-position lowers K from ·006 to ·00422.

$O.CH_3$ substituted for H in $C_6H_5.COOH$ in the para-position lowers K from ·006 to ·00302.

That the affinity of an acid is dependent not only on the character of the radicles, but also on their relative positions, is shewn in a very marked way by comparing the values of K for the two bromo-cinnamic acids:—

$CH(C_6H_5).CH.COOH$	$K = ·00355$
$CH(C_6H_5).CBr.COOH$	$K = 1·44$
$CBr(C_6H_5).CH.COOH$	$K = ·093$

Substitution of Br for H in one case increases the affinity about 400 times, and in the other case only about 26 times.

The affinities of the pyridine dicarboxylic acids also exhibit the influence of position; what one may perhaps call the strongest position for the COOH group is that nearest the nitrogen atom, and the position para to the nitrogen atom is stronger than that which is meta to the nitrogen atom.

These results, regarded as a whole, point to a close connexion between the affinities of acids and the space-arrangements of the atoms which form the molecules of the acids. This is confirmed by the measurements of the affinities of crotonic and isocrotonic, maleic and fumaric, and citraconic, mesaconic, and itaconic, acids[1].

[1] For further data, and discussion of the data, Oswald's memoir must be consulted.

SECTION III. *Chemical change.*

234 In considering Guldberg and Waage's general equation of equilibrium

$$kpq = k'p'q'$$

the quantities k and k' were treated as the 'coefficients of affinity' of the direct and reverse changes, respectively; in a later consideration of the subject k and k' were regarded as representing the velocity-coefficients of the two parts of the complete change. In pars. 214—220 it is shewn that to each acid may be assigned a certain number which is the affinity-coefficient of that acid, and that the value of this coefficient quantitatively conditions the different reactions in which the acid takes part. Pars. 221—229 are devoted to a sketch of the electrical methods whereby values are obtained for the affinities of the acids. The explanation of these electrical methods rests on a development of the molecular dissociation-hypothesis of Williamson which was first applied to electrolysis by Clausius (*v.* par. 192).

The further development of the Clausian hypothesis is due in great measure to the labours of van't Hoff, Arrhenius, and Ostwald. An account has been given in the preceding sections of this chapter of the results of some of Ostwald's work in this direction, and reference has been made, from time to time, to the 'law of osmotic pressure' as stated by van't Hoff. It now remains to glance at the investigations whereby this law has been gained and at the extensions of the law to explain the phenomena of chemical change occurring among substances in solution. As the subject is not yet fully elucidated, and as the principles involved are rather physical than chemical, although the chemical applications are of paramount importance, a brief account of the fundamental researches will suffice.

235 In 1887 van't Hoff published an important memoir[1], in which he sought to establish similarities, and, under certain conditions, identities, between substances in dilute solution and in the gaseous state. If an aqueous solution of a sub-

[1] *Zeitschr. fur physikal. Chemie*, **1**. 481 (Translation in *Phil. Mag.*, August, 1888).

stance is contained in a vessel the walls of which are permeable by water molecules but not by the molecules of the dissolved substance, and the vessel is immersed in water, water will enter the vessel, and the pressure on the walls will increase until equilibrium results, after which no more water will enter. The pressure on the walls of the vessel is called *osmotic pressure*. If the vessel had been furnished with a movable piston, the same condition of equilibrium might have been obtained, without the entry of water, by compressing the solution with a pressure equal to the osmotic pressure. With such an arrangement the concentration of the liquid could be altered by increasing or decreasing pressure by means of the piston; as the process would be reversible, the second law of thermodynamics may be applied.

Experiments on osmotic pressure have been conducted by de Vries[1], Pfeffer[2], and others; the results shew that the osmotic pressures of dilute solutions are proportional to the concentrations of the solutions. Now the statement that the alteration of concentration of a dilute solution is proportional to the pressure exerted by the solution, is equivalent to saying that Boyle's law holds good for dilute solutions. Moreover the proportionality of concentration to osmotic pressure may be theoretically deduced. If we assume, as seems justifiable, that osmotic pressure is due to the impact of the molecules of the dissolved substance, then the number of impacts in unit time must be proportional to the number of molecules in unit volume. But this is the molecular conception of the pressure of a gas; and as in gases volume is inversely as pressure, the same proportionality should hold good in dilute solutions, in other words, Boyle's law should apply to these solutions.

van't Hoff then proceeds to deduce, by thermodynamical reasoning, that osmotic pressure is proportional to absolute temperature, provided concentration remains constant; this conclusion is equivalent to the law of Charles for gases, inasmuch as concentration in one case corresponds with volume in the other.

[1] See especially *Zeitschr. für physikal. Chemie*, **2**. 415.

[2] *Osmotische Untersuchungen* [Leipzig, 1887].

The experimental results obtained by Pfeffer, and also by Soret[1], are, on the whole, in keeping with the statement that the laws of Boyle and Charles hold good in dilute solutions.

Further thermodynamical reasoning applied to *isotonic* solutions, *i.e.* solutions exerting equal osmotic pressures, leads to the conclusion that the osmotic pressure of a stated mass of a gasifiable substance in dilute solution is equal to the pressure exerted by the same mass of the same substance existing as a gas at the same temperature. If then osmotic pressure may be substituted for gaseous pressure, Avogadro's law may be extended to substances in dilute solution. This extension of Avogadro's law is thus stated by van't Hoff,—"*Equal volumes of different solutions, at the same temperature and osmotic pressure, contain equal numbers of molecules, which numbers are the same as would be contained in equal volumes of gases at the same temperature and pressure.*"

This is van't Hoff's *law of osmotic pressure.*

The first experimental proof of the accuracy of this law is obtained from the results of Pfeffer's experiments on the osmotic pressure of sugar solutions at different temperatures, by comparing these with the pressures exerted at the same temperatures by a volume of hydrogen containing the same number of molecules as the sugar-solution. The second proof of the accuracy of the law is obtained by proving thermodynamically that the vapour-pressures of solutions containing equal numbers of molecules of different substances are equal; but this statement has already been established experimentally by Raoult (*Compt. rend.* **44**. 1431; **87**. 167). The third proof of the accuracy of the law also rests on thermodynamical reasoning; van't Hoff shews that solutions in the same solvent having the same freezing point are isotonic, *i.e.* exert equal osmotic pressures, at their freezing points; and from this he deduces the conclusion that solutions which contain equal numbers of molecules in equal volumes, and

[1] *Ann. Chim. Phys.* (5) **22**. 293.

which are therefore isotonic by the law of osmotic pressure, have the same freezing point. But this statement is identical with Raoult's *law of molecular lowering of freezing point* which was gained by laborious experimental investigation (*v.* Book I. par. 35). This third proof of the law furnishes a convenient method for finding osmotic pressures from determinations of the lowering of freezing points of dilute solutions.

But there are many exceptions to Raoult's law of molecular lowering of freezing point. These exceptions are explained, if we assume, with Arrhenius, that compounds whose behaviour is not expressed by this law are partially dissociated in solution. Here again there is a marked analogy between gases and dilute solutions; as the pressure of ammonium chloride vapour is greater than that calculated by applying Avogadro's law on the assumption that the vapour consists of molecules of NH_4Cl, but as the observed pressure agrees with the calculated pressure when it is assumed that the vapour consists of equal numbers of molecules of NH_3 and HCl, so the apparently abnormal osmotic pressures of many solutions may be reconciled with the law of osmotic pressure by assuming that the compounds in these solutions are more or less dissociated into simpler molecules.

The osmotic pressures of certain solutions agree with those calculated by van't Hoff's law from observations of the lowering of the freezing points of the solutions; these solutions are generally, if not always, non-electrolytes. The exceptions to the law of van't Hoff occur chiefly, if not wholly, among electrolytes. The hypothesis of Arrhenius (par. 237) regards such electrolytes as more or less dissociated into their ions when they are dissolved in water.

Dealing with exceptions to the law of osmotic pressures, van't Hoff calculates the ratio of the observed pressures to the pressures which would be exerted did the law fully express the behaviour of the compounds in question. This ratio he designates by the symbol i; values are obtained for i from Raoult's freezing-point determinations[1]. The law of mass-

[1] For more recent and more trustworthy determinations of i for 40 compounds *v.* Raoult, *Zeitschr. für physikal. Chemie*, **2.** 488; and Arrhenius, *ibid.* **2.** 491.

action of Guldberg and Waage is then considered by van't Hoff, formulæ being used in which the ratio i occurs; the results agree very fairly with the calculated numbers.

The law of osmotic pressure has been placed on a fairly firm basis by van't Hoff, who has also shewn that the hypothesis that many compounds, and especially electrolytes, are partially dissociated in dilute solutions, serves to explain many if not all the apparent exceptions to the law.

236 Planck, in memoirs[1] published independently of van't Hoff, by purely thermodynamical reasoning, arrived at the conclusion that, in the case of compounds which do not obey Raoult's law of lowering of freezing point, van't Hoff's coefficient i expresses the ratio of the number of molecules actually present in solution to the number which would have been present had no dissociation occurred. In other words, Planck concludes that the observed phenomena regarding the freezing points of dilute solutions can be brought into accordance with thermodynamical laws only by assuming that, in many cases, dissociation of the molecules of the dissolved body has occurred, and that the ratio of the observed to the calculated osmotic pressure of substances which do not obey the law of freezing points is also the ratio of the number of molecules actually present to the total number which would have been present if dissociation had not occurred.

237 Arrhenius[2] has developed the Clausian hypothesis of electrolytic dissociation, and in doing this he has made use of van't Hoff's law of osmotic pressure.

Arrhenius applies the term 'active' to the molecules of an electrolyte which are supposed to be dissociated in solution; the undissociated molecules he calls 'inactive'. The ratio between the number of active molecules and the sum of all the molecules, whether active or inactive, is called by Arrhenius the 'activity-coefficient' of the solution (this is the same as the 'dissociation-ratio' of Lodge[3]), and is represented by the symbol α. At infinite dilution all the molecules of an

[1] *Wied. Ann.* **32.** 462; **34.** 139; *Zeitschr. für physikal. Chemie*, **1.** 577.

[2] Especially *Zeitschr. fur physikal. Chemie*, **1.** 631; **2.** 284, 491.

[3] *Brit. Ass. Reports*, **1886.** 756.

electrolyte are supposed to be active, and therefore the activity-coefficient is equal to unity; in less dilute solutions, but still so dilute that the effects of internal friction, &c. may be overlooked, the activity-coefficient may be taken as the ratio between the observed molecular conductivity and the limiting value at infinite dilution. (For Ostwald's method of finding this ratio *v. ante*, pars. 225, 226.) The value of van't Hoff's coefficient i can be calculated if α is known[1]. Putting m as the number of inactive molecules, n as the number of active molecules, and k as the number of ions into which each active molecule is separable (e.g. KCl is separable into 2 ions, K + Cl, and K_2SO_4 into 3 ions, K + K + SO_4), we have

$$i = \frac{m + k.n}{m + n};$$

but

$$\alpha = \frac{n}{m + n};$$

hence

$$i = 1 + (k - 1)\,\alpha.$$

Arrhenius then calculates i from observations of α for a great many compounds; he also calculates i for the same bodies from determinations of the lowering of the freezing points of solutions of these bodies[2]. The two series of values for i agree very well on the whole. For non-conducting liquids such as methylic alcohol, ethylic acetate, &c., i is approximately equal to unity; for bases, acids, and salts, i varies from 1 to about 2·5.

We have already seen (pars. 225, 226) that Ostwald's measurements of the molecular conductivities of monobasic acids have led to results in keeping with those deduced from the hypothesis of electrolytic dissociation. In two memoirs[3], Arrhenius uses the same hypothesis to explain the conductivities of solutions of mixtures of different electrolytes; the

[1] See also van't Hoff and Reicher, *Zeitschr. für physikal. Chemie*, **3**. 198.

[2] Let lowering of freezing point of water produced by dissolving 1 gram-molecule of given body in 1 litre water $= t$; then $i = \frac{t}{18{\cdot}5}$; *v.* van't Hoff, *Phil. Mag.*, August, 1888, p. 100.

[3] *Zeitschr. für physikal. Chemie*, **1**. 631; **2**. 284.

results obtained agree very closely with the calculated results. To follow the reasoning here would lead us too far afield. One point however must be noted; Arrhenius shews that the hypothesis enables the retarding influence of ammonium salts on the saponification of ethylic acetate by ammonia to be quantitatively determined, and that the numbers theoretically calculated agree well with those actually observed. Arrhenius also extends the hypothesis to the case of any number of electrolytes in solution together; the equation arrived at[1] expresses the conditions of chemical equilibrium for a mixture of electrolytes, and the quantitative applications of this equation give good results.

The work of van't Hoff and Arrhenius establishes a large probability in favour of the statement that the properties of dilute solutions can be deduced from two principles, viz. the principle of the close analogy, and in some respects even the agreement, between the gaseous state and the state of dilute solution, and the principle of electrolytic dissociation[2].

238 Arrhenius[3] points out that many physico-chemical properties of salts in solution can be represented as approximately the sums of the properties of parts of the solution; such properties are the heats of neutralisation of acids by bases in dilute solution, the specific volumes and specific gravities, the specific refractive powers, and the conductivities, of dilute solutions of salts. The fact that such properties as these are *additive*, as distinguished from *cumulative* properties, is entirely in keeping with the hypothesis of electrolytic dissociation, inasmuch as this hypothesis regards a dilute solution of an electrolyte as composed, for the most part, of the ions of the electrolyte, each ion having its own characteristic properties which are generally independent of the properties of the other

[1] *Zeitschr. für physikal. Chemie*, **2**. 194.

[2] The agreements between the observed and calculated numbers do not, of course, finally establish the accuracy of these two principles.

The law of van't Hoff gives a means for determining the molecular weights of salts in solution; but the work of Arrhenius points to the existence in many salt solutions of molecules of different degrees of complexity, and suggests that in many cases we cannot speak of *the* molecular formula of a salt in solution.

[3] *Ibid.* **1**. 640.

ion. The solutions of salts which have been used for measurements of specific gravity, refractive power, lowering of freezing points, &c., have not, as a rule, been so dilute as to ensure complete dissociation of the dissolved bodies; hence the properties mentioned appear as approximately the sums of certain constants, each of which belongs to one part of the solution. When we deal with fairly dilute solutions of the salts of strong acids with strong bases, or with dilute solutions of the strong acids and bases themselves, no large errors are introduced by generally assuming that such properties as those named are the sums of the properties of the ions. The weak acids and bases, and several salts—e.g. ammonia and the amines, phosphoric, boric, hydrocyanic, and sulphhydric, acids, and many salts of mercury, cadmium, and zinc—do not appear to be largely dissociated in solution; the properties of such compounds in solution are not so distinctly additive as are the properties of the strong acids and bases and the salts formed by the interactions of these. It is then necessary to distinguish between different classes of compounds; some are almost wholly dissociated in dilute solutions into their ions, others are partially dissociated, and others are dissociated only to a small extent[1].

239 In par. 229 was given a short account of Ostwald's application of the law of osmotic pressure, and the hypothesis of electrolytic dissociation, to find the affinities of monobasic acids. The equation given by Ostwald

$$\frac{\mu_\infty (\mu_\infty - \mu_v)}{\mu_v^2} v = c$$

ought to express completely the electrical conductivity of binary electrolytes, if the hypothesis of electrolytic dissociation is well founded. Ostwald[2] notes six generalisations regarding aqueous solutions of binary electrolytes which have been established empirically. These are :—

[1] The degree of dissociation is determined from measurements of the coefficients i and α: *v.* pars. 235, 237.

[2] *Zeitschr. fur physikal. Chemie*, 2. 275.

1. The molecular conductivities of solutions of electrolytes increase with increasing dilution, and asymptotically approach maximum values.

2. The maximum values for equivalent quantities of acids, bases, and salts, are of the same order but they are not identical.

3. The maxima may be expressed as sums of two quantities, one of which depends only on the positive ion, and the other only on the negative ion.

4. The last statement does not hold good for somewhat concentrated solutions, nor for solutions of weak acids or bases.

5. The molecular conductivities of bad conductors, such as weak acids and bases, increase rapidly as dilution increases; the conductivities of monobasic acids and mono-acid bases are proportional to the square root of the dilution.

6. Increase of molecular conductivity follows the same course in solutions of all monobasic acids and mono-acid bases; the dilutions at which the conductivities of these acids and bases are equal fractions of their maximum conductivities bear a constant proportion to one another.

Ostwald then proceeds to shew that the equation already given contains these six generalisations. The equation is

$$\frac{\mu_\infty (\mu_\infty - \mu_v)}{\mu_v^2} v = c;$$

where μ_v = molecular conductivity for volume v, μ_∞ = maximum conductivity for infinite dilution, v = volume of solution.

1. If v increases without limit, the expression

$$\frac{\mu_\infty (\mu_\infty - \mu_v)}{\mu_v^2} = \frac{c}{v}$$

must approach zero. As both μ_v and μ_∞ have finite values, $\mu_\infty - \mu_v$ must become smaller, i.e. μ_v will increase continuously until it reaches the limiting value μ_∞.

2 and 3. As μ_∞ expresses the molecular conductivity of the completely dissociated electrolyte, and as the ions move in this solution independently of one another, the value of μ_∞

can be regarded as the sum of two quantities, which are measured by the velocities of the ions, quite apart from the nature of the compound which was formed by the union of these ions. If compounds are compared which have one common ion, and the other ions of which do not shew great differences in their velocities of transference, then the sums of the two velocities must be of the same order of magnitude.

4. The conductivities of fairly concentrated solutions are conditioned by the degree of dissociation of the solutions, and as this varies in different solutions, especially in weak acids and bases, the conductivities of these solutions cannot be expressed as the sums of two quantities one of which depends only on each ion. Salts, however, of similar composition are nearly equally dissociated in solutions of equal dilution; the molecular conductivities of such salts are equal fractions of their maximum values, and they can be expressed as the sums of two quantities which are the velocities of the ions multiplied into the degree of dissociation.

5. In the cases of weak acids and bases μ_v is small compared with μ_∞, and $\mu_\infty - \mu_v$ is nearly constant, and the equation gives $\mu_v^2 = v$ const. In other words, when conductivity is small, it increases proportionately to the square root of the dilution.

6. In the equation, the constant c depends on the nature of the electrolyte; if the dilutions at which the relative conductivities of various electrolytes are equal are put as $v_1\ v_2 \ldots$ then the values of

$$\frac{\mu_\infty\ (\mu_\infty - \mu_v)}{\mu_v^2}$$

are equal, and $v_1 : v_2 : v_3 \ldots = c_1 : c_2 : c_3 \ldots$;

i.e. the dilution at which the conductivities of different electrolytes are equal bear a constant relation to one another, and this relation depends only on the nature of the electrolytes.

In these six points then, there is complete agreement between the empirically determined data and the deductions from the equation which expresses the conductivity of binary electrolytes. But this equation is itself deduced from the

principles of electrolytic dissociation and of agreement between the gaseous state and the state of bodies in dilute solution. We have already seen (par. 229) how Ostwald has modified the equation expressing the behaviour of binary electrolytes so as to obtain measurements of the constant which is dependent on the nature of the electrolyte. In the case of acids, this constant expresses the affinity of the electrolyte; the agreement between the affinities of acids thus determined and the affinities determined by other physical and chemical methods, is a further proof of the trustworthiness of the principles on which the electrical method is based.

240 The hypothesis of the dissociation of electrolytes in solution is connected with van't Hoff's extension to solutions of the law of Avogadro, in much the same way as the hypothesis of gaseous dissociation is connected with Avogadro's law in its original form. Planck's thermodynamical investigations give independent support to the hypothesis. The hypothesis gives a fairly complete account of the conductivities not only of electrolytes in solution, but also of mixtures of electrolytes. The results of determinations of the molecular lowering of the freezing points of solutions strikingly confirm the hypothesis, and afford a convenient method for determining the ratio of the number of molecules actually present to the number which would have been present had no dissociation occurred. The hypothesis gives an explanation of the retarding influence of neutral salts on the rates of chemical actions brought about by weak acids. From the hypothesis of electrolytic dissociation, taken along with van't Hoff's law of osmotic pressure, an equation is deduced which enables measurements to be made of the affinities of acids, and these affinities are in keeping with the values obtained by wholly different methods, both physical and chemical[1].

241 If we accept the law of van't Hoff, and the principle of electrolytic dissociation, we must regard the chemical reactions of acids and bases in solution, as, at any rate very

[1] For a brief statement of the present position of the electrolytic dissociation-hypothesis, *v.* Arrhenius, *Zeitschr. fur physikal. Chemie*, **2**. 504 (July, 1888).

largely, dependent on the extent to which these compounds are dissociated into their ions, and on the velocities of transference of these ions. Inasmuch as hydrogen moves so much more rapidly than any of the negative ions of acids, the chemical reactions of acids in solution will chiefly depend on the degree of dissociation. The exact form in which this conception is applied in order to find the affinities of acids has been given in par. 229; it is

$$\frac{1-m}{m^2}v = c,$$

where m = molecular conductivity at any stated dilution, referred to the maximum molecular conductivity, and c = a constant = affinity of the acid.

In comparing gaseous dissociation with dissociation in solution, it is important to note that just as all gases are not dissociated by heat, so all salts, acids, and bases, are not dissociated in solution; nevertheless, if the hypothesis of dissociation is adopted, and the law of van't Hoff is taken to be true, the data shew that dissociation is a much more frequent occurrence among compounds in solution than among gases. The compounds which most readily and most completely undergo dissociation in solution are electrolytes; the greater the conductivity the more complete is the dissociation. Now if a compound is a good electrolytic conductor it is also ready to take part in chemical reactions. The strong acids and bases—*e.g.* HCl, HNO_3, KOH, NaOH —are chemically very energetic, and their conductivities are very large. Hence, if we adopt the hypothesis of electrolytic dissociation, we must regard the readiness shewn by the strong acids and bases in solution to exchange hydrogen and hydroxyl in chemical reactions, as due to the large extent to which they are dissociated in solutions, into hydrogen and negative ions on the one hand, and hydroxyl and positive ions on the other hand. At the first glance it is difficult to accept the conception of such compounds as hydrochloric and nitric acids, or soda and potash, as existing in solution dissociated into their ions. But some of the difficulty arises,

as Ostwald points out[1], partly from confounding the affinities which hold together the elements of a compound with the affinity which this compound exhibits towards other bodies, and partly from forgetting that the ions of an electrolyte which is dissociated in solution are not comparable with the same bodies in the free state, because the ions carry with them enormous electrical charges[2]. Because potassium hydroxide is chemically extremely energetic, it does not follow that 'the elements are held together in this compound' as is sometimes said 'by the strongest affinities.' The reverse of this rather is true: it is in compounds which do not readily enter into chemical reactions, such as the paraffins and their derivatives, that the elements are firmly held by strong affinities.

To meet the objection that we cannot suppose a solution of potash to contain the ion potassium, because we know that potassium and water at once react to form hydrogen and potash, Ostwald brings forward the following considerations[3]. Let two glass vessels contain potassium chloride solution; let the vessels be brought into communication by a glass tube filled with the same solution; now let a negatively electrified body be brought near one of the vessels, the contents of this vessel become positively electrified and those of the other vessel become negatively electrified; let the connecting tube be now removed, and then let the negatively electrified body be removed; the contents of the vessels remain electrified, one positively and the other negatively. Now, according to Faraday's law, electricity must travel in an electrolyte with the ions; therefore the vessel which remains positively electrified must have positively electrified potassium atoms accumulated in it, while negatively electrified atoms of chlorine must have accumulated in the other vessel. If a platinum wire, in connexion with the earth, is now

[1] *Zeitschr. für physikal. Chemie*, 2. 270.

[2] It is to be remembered that the statement, that the ions of an electrolyte are endowed with electrical charges and are thus different from the products of dissociation of a gas, does not *explain* the difference in question, because we are as yet ignorant what an electrical charge is.

[3] *Loc. cit.* pp. 271—273.

brought into the positively electrified vessel, potash and hydrogen are produced; and this is because the atoms of potassium give up their electric charges and then at once interact with the water.

From this experiment, Ostwald draws the conclusion that the electrolyte must have been dissociated in the solution before the electrified body was brought near. The measurements of Kohlrausch shew that the rates at which ions travel may be stated in not very many millimetres per second; but electrolytes take up electrostatic charges practically instantaneously; hence, in the experiment described, the chlorine atoms which accumulate in one vessel could not have been originally in combination with the potassium atoms which appear in the other vessel. A similar conclusion is drawn[1] from the results of the common experiment of placing amalgamated zinc and a platinum wire, at a considerable distance apart, in dilute sulphuric acid, and then connecting the zinc and platinum. Hydrogen instantly appears on the platinum; but this hydrogen cannot have been in combination with the negative ion, SO_4, which at the same moment combines with the zinc, because the rates at which the ions hydrogen and SO_4 travel during electrolysis are not rapid enough to have enabled the hydrogen to pass to the platinum and the SO_4 to pass to the zinc[2].

The affinity-coefficients of the acids and bases in solution are then, on this hypothesis, measures of the dissociation of these compounds; and as the amount of dissociation of an acid or base is generally independent of the body with which the acid or base chemically reacts, these affinity-coefficients have constant values which depend only on the nature of the acid or base. If however another body should be present which modifies the dissociation of the acid or base, the presence of this body will also modify the affinity of the acid or base. This explains the fact that the affinities of the acids are modified by the presence of the normal salts of these acids[3].

[1] *Zeitschr. für physikal. Chemie*, **2**. pp. 271—273.

[2] See also Ostwald and Nernst, *Zeitschr. für physikal. Chemie*, **3**. 120.

[3] Arrhenius has worked out in detail the modifying influence of normal salts,

As the molecular conductivities of the acids depend on the degree of dissociation of the acids, and also on the velocities of transference of their ions, but chiefly on the former because the positive ion hydrogen travels more than five times more rapidly than the quickest travelling negative ion, so the affinities of acids depend on the degree of dissociation of these acids and on the velocities of transference of their ions.

But the affinities are dependent on the velocities of the ions to a greater extent than the conductivities. In some reactions, *e.g.* the solution of zinc in acids, the velocity of the negative ion plays an important part; in such cases the action of acids which are all equally dissociated will vary in accordance with the velocities of their negative ions. In other reactions the negative ion will be of little importance; in these cases the actions of different acids which are equally dissociated will be equal. Generally speaking, the readiness with which acids react chemically will be chiefly dependent on the degree of dissociation of the acids, because the positive ion hydrogen travels so much more rapidly than the negative ions, and the nature of the negative ion will be of secondary importance[1].

242 The hypothesis sketched in the preceding paragraphs, whether accepted or not, presents a general conception of those chemical changes which take place between electrolysable bodies in solution. All compounds which in solution react chemically with electrolytes are regarded by the hypothesis as themselves electrolytes.

It is necessary to observe that the hypothesis, in its present form at any rate, is applicable only to substances in solution. If we regard the hydrogen chloride in a dilute aqueous solution of this compound as dissociated to the extent of about 90 per cent., and if we assign the chemical activity of the compound in this solution to the large preponderance of 'active' over 'inactive' molecules (*i.e.* by hypothesis, the preponderance of dissociated over undissociated

and has shewn that the amount of modification can be correctly deduced from the hypothesis of electrolytic dissociation; *v. Zeitschr. für physikal. Chemie*, 2. 284.

[1] Ostwald, *Zeitschr. für physikal. Chemie*, 2. 273—275.

molecules), it does not follow either that liquid hydrogen chloride should be chemically active, or that gaseous hydrogen chloride should be easily dissociated by heat. The hypothesis does not afford means for comparing the chemical activity, or the stability, of gaseous or liquid compounds with the activity of the same compounds when in solution.

It should also be remembered that the hypothesis does not assert the occurrence of dissociation in solutions of all compounds; it distinguishes between non-electrolytes, solutions of which it regards as not dissociated, and electrolytes, which it looks on as more or less dissociated in solution; and it allows a gradation from one class to the other.

243 The action of the solvent on the electrolyte dissolved in it is not yet fully explained by the hypothesis of electrolytic dissociation. The law of van't Hoff assumes that the volume of the solvent is occupied by the molecules of the dissolved body in the gaseous state. The molecules of those compounds which are apparent exceptions to this law are supposed to be dissociated; in these cases, the volume of the solvent therefore contains more molecules than if dissociation had not occurred, and, as a consequence, the osmotic pressure exceeds that calculated from the law. This explanation regards the solvent as in some way bringing about dissociation without itself being changed. If the solvent acts merely as a medium in which the dissolved electrolyte is dissociated, one would expect the amount of dissociation of an electrolyte to be independent of the composition of the solvent. But experiments shew that the conductivities of certain salts dissolved in alcohol are considerably less than those of the same salts dissolved in water[1]; Arrhenius says[2] that this decrease in conductivity is probably due to the friction which the ions must overcome being increased by the substitution of alcohol for water.

Armstrong[3] seems to think that a non-conductor, say

[1] Fitzpatrick, *B. A. Reports*, **1886**. 333.

[2] See *B. A. Reports*, **1888**; "*On Electrolysis in its Physical and Chemical Bearings.*"

[3] See the Reports of the *B. A. Committee on Electrolysis*, 1886—89.

liquid hydrogen chloride, is composed of complex molecular aggregates, which are broken down by the action of the solvent into simple molecules; that these molecules flow past one another, and that although their parts 'strain at one another,' yet the molecules are not separated into their ions until electromotive force is applied. The objection to this view lies in the fact that, so far as accurate experiment has gone, electrolytes obey Ohm's law, in other words, that electrolytes cannot resist the smallest electromotive force directly applied to them. This fact seems to require the presence of some ions in the solution of an electrolyte before the current passes.

How then are these ions produced? Energy must be obtained somewhere to effect the separation of the molecules of the electrolyte into ions. It may be that the water used as a solvent is chiefly composed of aggregates of molecules, but that some molecules, H_2O, are also present, and that the combination of these with molecules of the electrolyte is the source of the energy whereby some of the electrolytic molecules are separated into their ions[1].

Molecular aggregates are probably formed before electrolytic dissociation begins; in our present ignorance of interatomic forces, it seems enough to say that the production of molecular aggregates brings the atoms into intra-molecular relations which result in new arrangements of these atoms[2]. Or, it may be said that 'the molecular aggregates in solution' have 'an aptitude for directed decomposition,' and that when the current is applied, electrolysis results (Lodge).

244 There can be no doubt of the existence of a marked parallelism between the electrical conductivities and the chemical activities of many compounds in solution. If the former is connected with dissociation, however effected, the latter is probably due to the same cause. As pure liquid hydrogen chloride is an extremely bad conductor, if not indeed non-conductive, so is this compound very inactive chemically; the addition of water is accompanied by the

[1] *Cf.* Pickering, *C. S. Journal*, **Trans. 1889.** 23.

[2] Some such view as this seems to be favoured both by Lodge and Armstrong. See *B. A. Electrolysis Committee Reports.*

manifestation of conductivity and chemical activity. We cannot yet fully explain why the presence of water so largely changes the properties of the hydrogen chloride; but we know other cases wherein the presence of a third body is required before chemical action takes place between two bodies.

Perfectly dry chlorine and hydrogen do not combine in sunlight; the presence of a very small quantity of water suffices to start the combination[1]. A mixture of perfectly dry carbon monoxide and oxygen is not exploded by an electric spark which at once produces explosion if the gases are slightly moist[2]. Dry hydrogen chloride is unchanged when mixed with dry oxygen and exposed to sunlight, but in the presence of a little liquid water chlorine is produced; if the water present is all gaseous, chemical action does not occur[3]. A mixture of dry hydrogen iodide and oxygen is, however, said to be changed in sunlight[3].

Whether the water in these reactions acts by directly decomposing one of the gases, e.g.

$$(1)\quad 2CO + 2H_2O = 2CO_2 + 2H_2$$
$$(2)\quad 2H_2 + O_2 = 2H_2O,$$

or whether a compound of the water with the reacting bodies is first formed, e.g.

$$(1)\quad \begin{matrix} O\ H_2O\ CO \\ O\ H_2O\ CO \end{matrix} \qquad (2)\quad \begin{matrix} OH_2\ OCO \\ OH_2\ OCO \end{matrix},$$

cannot yet be decided[4]. The presence of water is required in order to render the molecules of the other bodies active.

Whether we accept the hypothesis of electrolytic dissociation or not, we must admit that the conductivities and chemical activities of many compounds are much increased by solution in water. If we say that many of the molecules of the dissolved body acquire 'an aptitude for directed decom-

[1] Pringsheim, *Wied. Ann.* **32.** 384.
[2] Dixon, *Phil. Trans.* **1884.** 617; and *C. S. Journal*, **49.** 94.
[3] Richardson, *C. S. Journal*, **51.** 801.
[4] *Cf.* Dixon, *l.c.* with Armstrong, *C. S. Journal*, **49.** 112.

position', and if we agree to call these molecules 'active', then the ratio of active to inactive molecules is the chief condition which quantitatively affects the electrical conductivity and the chemical activity of the compound in solution. Ostwald has shewn us how to put this conception of chemical change between electrolytes in solution into a form which enables constant values to be found for the affinities of these electrolytes (par. 229).

245 There are definite connexions between the affinities, and the composition, of acids (pars. 231–233). To trace definite connexions between composition and properties has always been the aim of chemistry. The study of composition has advanced further than the study of properties. The connexions between composition and properties have been quantitatively investigated only in a few cases. Great difficulties attend the elucidation of the connexions between the composition and the properties of bodies: some properties, such as weight, are purely *additive;* the weight of a body is the sum of the weights of its parts; other properties are purely *cumulative*, they are dependent on the mode of combination of the parts and are wholly independent of the nature and number of these parts; the volume occupied by gaseous molecules under standard conditions belongs to this category, the volume is independent of the nature and number of the atoms provided these are all chemically combined; but many properties, including most chemical properties, are *constitutive*, i.e. they depend not only on the number of the parts but also on their nature and relative arrangement; such properties as boiling point, crystalline form, and specific rotatory power, belong to the category of constitutive properties[1]. The affinities of acids and bases are dependent on the *constitutions* of these compounds. Each acid, and each base, has its own affinity-coefficient. If the change of constitution in the passage from one of two acids to the other were identical with the change of constitution in the passage from one of a second pair of acids to the other, the difference between the affinities of the first pair of acids

[1] Ostwald, *v.* especially *Königl. Sächsischen Gesellschaft der Wissenschaften* (math. phys. Classe) Bd. **26.** [1889] 237.

would, almost certainly, be identical with the difference between the affinities of the second pair of acids; but such a case probably never occurs.

The chemists who have studied the subject of affinity have belonged either to the school of Bergmann or to that of Berthollet. To Ostwald, more than to any other chemist, belongs the signal honour of finding the middle course, which, neglecting the work of neither of these great naturalists, leads to a well-founded and consistent method of measuring affinities, and points the way to the elucidation of the fundamental problem of chemistry. Bergmann taught that every body has a definite affinity, and in this he was doubtless right; he also taught that the contest of affinities always leads to the occurrence of chemical change in one direction only, in this he was certainly wrong. Berthollet was right in asserting that chemical change is quantitatively conditioned by the relative masses of the reacting bodies; but his view that the affinities between acids and bases are inversely proportional to the equivalent weights of these bodies is not in keeping with recent research. (Ostwald)

246 But we have not yet gained a complete theory of chemical change. Such a theory must shew us what chemical constitution means, and it must quantitatively generalise the relations of constitution to properties. In doing this, the theory must bring into one point of view the scattered partial hypotheses which at present are so numerous in chemistry. The theory must, for instance, connect the valencies of atoms with the other properties of atoms, and with the properties of molecules. To do this requires a conception of valency more exact and at the same time wider than we have at present, and a more thorough elucidation of the way in which the stabilities of molecules are connected with the valencies of their atoms.

While holding that it is better at present to limit discussions about atomic valencies to data obtained from the compositions and reactions of gaseous molecules, I am of opinion that much progress will not be made in our knowledge of the constitution of compounds, and the connexions between

constitution and properties, unless the chemical properties of bodies in solution, and of solid bodies, are carefully and exhaustively examined. The study of valency, and the study of affinity, overlap; yet I do not think that the study of either will be materially advanced by confusing one with the other[1]. The composition of the molecules of a certain gaseous compound is known, and the valency of each atom in the gaseous molecule is also known; but when the compound is dissolved in water, or when it is solidified, the interatomic relations may be, and in many cases most probably are, modified, so that the molecules are able to take part in chemical changes which could not be brought about by the gaseous molecules. The cause of the chemical reactions of the molecules, in both cases, we call affinity; the number of atoms with which any specified atom is directly associated in one of the gaseous molecules is called in this book the valency of that atom in that molecule. It may be that the electrical charges of the atoms are not fully neutralised in the gaseous molecules (whatever this may mean), but that the residual charges do not suffice to hold together a greater number of atoms than that constituting these molecules, and that on solution, or solidification, these residual charges are able loosely to bind together complex molecular aggregates the atoms in which are brought into such intra-molecular relations that new atomic arrangements result, and so new compounds are formed[2]. If something of this kind occurs, we should expect to find series of bodies ranging from mixtures to definite and stable compounds. Let two molecules, one composed of atoms *ab*, and the other of atoms *cd*, be brought together; the (hypothetical) residual electric charges may just suffice to form an aggregate *ab . cd*, wherein the properties of the constituent molecules, or radicles, *ab* and *cd*, are recognisable, although they are to some extent merged

[1] There is an interesting paper on *The thermal phenomena of neutralisation*, by Pickering in *C. S. Journal*, **51**. 593; the reasoning seems to me sometimes to be marred by confusing together valency and affinity.

[2] This view, or a view resembling this, seems to be favoured by Armstrong (see *Proc. R. S.* **1886**. 268; also Pickering).

in those of the new body; or the residual charges may suffice to cause a rearrangement of the atoms with production of the new molecule *abcd*; or lastly an exchange of atoms may occur resulting in the formation of two new molecules *ac* and *bd*. In the first case two different substances would be obtained, according as we started with *ab* and *cd*, or with *ac* and *bd*; but in the second case the same body would be produced whether *ab* reacted with *cd* or *ac* with *bd*: which reaction should occur would depend on the affinities of the reacting bodies rather than on the valencies of the atoms[1].

247 A complete theory of chemical change must elucidate and accurately set forth the connexions between changes of properties, changes of constitution, and changes of energy.

In Book I. we learned that the primary object of thermal chemistry is to measure the changes of energy which accompany definite changes of composition. We found that definite quantities of energy change form in the passage from one isomeride to another (pars. 85—89). No discussion was attempted in these paragraphs of the relations between thermal changes and affinity, or between thermal changes and chemical equilibrium.

A word or two must now be said on this subject.

The heats of neutralisation of most acids in aqueous solution are independent of the nature of the base used, and the heats of neutralisation of very many bases are independent of the nature of the acid used; hence it follows that the heats of formation, in solution, of two similar salts of different metals differ by a constant quantity which is independent of the nature of the acidic radicles of the salts[2]; or it may be said that the heat of formation of a salt, in aqueous solution, is the sum of two constants, one of which belongs to the basic, and the other to the acidic, radicle. Arguing on these lines, Lothar Meyer[3] arrives at the con-

[1] See Atkinson's experiments (*C. S. Journal*, **1885**. 122), described in par. 102.

[2] This is a development of the statement of the thermoneutrality of salts first laid down by Hess in 1842; *Pogg. Ann.* **52**. 79. Among more recent papers on the subject, see Pickering, *C. S. Journal*, **51**. 593.

[3] *Zeitschr. für physikal. Chemie*, **1**. 134 (Translation in *Phil. Mag.*, June, 1887).

clusion, that the heat produced in the formation of a salt is a consequence of the change of state which the substances undergo, and that it is not conditioned by the mutual actions of the constituents, i.e. in ordinary chemical language, by the affinity of one constituent for the other. Although each acid and each base has a definite thermal constant which quantitatively conditions the thermal phenomena accompanying the formation of salts by that acid or base, and although each acid and base has also a definite affinity-constant which quantitatively conditions its salt-forming reactions, nevertheless, according to Meyer's view, the thermal constant does not measure the affinity-constant. Meyer regards each substance as having a definite quantity of available energy which is increased or diminished by every change of state; one of those changes in which the available energy is diminished takes place when an acid and a base react to produce a salt; but the degradation of energy which accompanies this change of composition is not the cause, but rather the consequence, of the mutual action of the acid and the base; the cause of the change we call affinity; it is dependent on the relations of the reacting bodies; but the degradation of the energy of each body is dependent only on the nature of that body and on the change of state which it undergoes, and is independent of the nature of the other body by the presence of which the change of state is rendered possible.

The conclusions drawn by Meyer may be too sweeping. The heats of formation of salts, even in aqueous solution, are the algebraical sums of many thermal changes which as yet we cannot disentangle. But, granting this, we have a large probability in favour of the statement that the heats of formation of many salts, when the physical conditions are kept as constant as possible, can be represented as the sum of two constants, one of which belongs to the basic radicle and one to the acidic radicle, of the salts. This statement enables us, I think, to say distinctly that the affinities of acids and bases are not measured by the quantities of heat produced in their reactions, unless indeed we use the term affinity as synonymous with potential energy of a body, and we assume that

the heat produced in a reaction of this body with another measures the total change of potential energy into kinetic energy.

If we adopt the general conception of chemical change between electrolytes in solution afforded by the hypothesis of electrolytic dissociation, we should picture to ourselves the ions of two electrolytes as giving up their electric charges and so combining to form a new compound; supposing, for simplicity, each ion to be an elementary atom, we should regard the valencies of the ions as determining the number of atoms which combine to form the molecule of the new compound; we should say that the cause of the union is to be found in the affinities of the ions, but what this affinity is we do not know; and we should look on the quantity of heat produced as to some extent measuring the energy degraded in the process. On this view, affinity is not identical with potential energy[1]. The stability of the new compound is determined by the condition that the entropy of the system shall be a maximum; but the measurement of the heat produced is not a complete determination of the change of entropy, for entropy is a quantity of heat divided by a temperature, and changes of entropy may be conditioned by changes other than thermal. (See par. 191.)

If we assert that the quantity of heat produced in a reaction measures the affinities of the interacting bodies, and the affinities quantitatively condition the direction, and the amount, of the chemical change, we must turn our backs on the results gained by Guldberg and Waage, Ostwald, and many other chemists, regarding the distribution of the interacting bodies in the changes which occur when acids and bases are mixed in equivalent quantities.

248 But surely there must be some connexion between the quantity of heat produced in a chemical change and the electromotive force of the arrangement.

[1] The kinetic theory of gases obliges us to regard the atoms of a molecule as in continual motion; the affinity of atoms cannot be looked on as altogether potential energy. (There is an interesting paper by Pringsheim in *Zeitschr. fur physikal. Chemie*, **3**. 145.)

In the course of his applications of the conception of the conservation of energy, Joule undertook a series of researches on the 'energetics' of the electric current[1]. The case of the passage of a current through a wire was considered, and the quantity of heat produced was found to be expressed by the equation

$$H = CE,$$

where H is the quantity of heat developed per second, and C and E are the current and the electromotive force respectively.

Since Joule had himself shewn that heat is changeable into work, the equation took the form

$$W = \mathcal{J}H = CE,$$

where $\mathcal{J}$ = the mechanical equivalent of heat.

The phenomena attending the production of heat during the passage of a current through an electrolyte were then examined by Joule, and it was shewn that the total quantity of heat could be separated into two parts. One part was expressible as the result of overcoming ordinary resistance, in accordance with his previous law, and the other part was due to chemical changes in the cell. He then determined the quantity of heat produced, during a given time, in a process of electrolysis by a current of given strength; then, by applying Ohm's law, and the law stated connecting heat with resistance and current, he found the heat which would have been produced had a wire with resistance equal to that of the electrolyte been substituted for the electrolyte. The difference between these two quantities of heat is, Joule said, 'equivalent to the heat which is due to the reverse chemical combination by combustion or other means' (*loc. cit.* (2) 3. 494).

The problem was further considered by Sir W. Thomson[2]. His reasoning was somewhat as follows.

[1] *Phil. Mag.* 20. 98; 22. 204; and *do.* (2) 3. 481. See also the article 'Electricity' in *Encycl. Brit.* Vol. 8. (9th Ed.) pp. 88-92.

[2] *Phil. Mag.* for December, 1851; see *Mathematical and Physical Papers*, 1. 472.

Let unit quantity of electricity pass through a cell of infinitely small resistance; then, by Joule's law, the work done by the current is equal to E, the electromotive force. But ϵ gram of one of the elements of the electrolyte has been electrolysed, in accordance with Faraday's law. Let θ be the quantity of heat developed by the combination of one gram of this element to reproduce the electrolyte, then, according to Thomson, since no work is expended in any other part of the circuit,

$$E = \mathcal{J}\epsilon\theta, \text{ and therefore } \theta = \frac{E}{\mathcal{J}\epsilon}.$$

To realise this equation in practice a great many corrections have to be applied.

This formula presents us with an electrical method for determining the heats of combination of various elements, or, we may say, the energy-changes attending the formation of various compounds. In Joule's papers, the values of the quantity θ were regarded as affording measures of 'the intensities of affinity' of different substances (*loc. cit.* 20. 99); but we have seen that this cannot now be held, except the term 'affinity' is used in a very vague sense.

Many investigations have been made into the accuracy of Thomson's law; but I cannot attempt to trace these here. Some results shew great discrepancies between the observed E. M. F.'s of cells and those calculated from thermal measurements of the chemical changes which are supposed to occur in the cells; but unless the exact chemical changes which occur are completely known, the discrepancies may be more fanciful than real[1].

Concluding Remarks.

249 We have thus tried to gain some answers to the questions with which we started, What is the composition of compounds?

[1] Among the more important researches may be mentioned;—Braun, *Wied. Ann.* **16**, 561; **17**. 593; Wright, *Phil. Mag.* (5) **9**. 237, 331; **11**. 169, 261, 348; **13**. 265; **14**. 188; **16**. 25; a general account of his work to the end of 1880 is given by Wright in *Chem. News*, **42**. 249; see also *Proc. of the Physical Society*. In connexion with Wright's work, see Laurie's criticism, *Phil. Mag.*, August, 1886. See also *B. A.* '*Reports of the Electrolysis Committee*,' 1886-88.

What actions are compounds capable of performing? A complete answer to either question will be an answer to both, and that answer will include the whole of chemistry.

The atom of the chemical element has been the unit with which we have had to deal; the properties of compounds have been regarded as conditioned on the one hand by the nature, the number, and the arrangement, of the elementary atoms which together form the compound molecules, and on the other hand, by the greater or smaller quantities of available energy associated with these molecules. To determine the relations between the properties of various molecules, and the nature, number, and arrangement, of their constituent atoms was the first part of our task; to attempt an outline of a dynamical explanation of chemical operations between molecules was the object of the second part of the undertaking.

But inasmuch as the properties which chiefly concern us as chemists are the properties, not of individual substances, but rather of these considered as members of changing systems, it has been impossible to consider the questions arising in the first part without to a great extent making use of methods and conceptions more strictly belonging to the second part of our subject.

The facts connoted by the expression chemical statics were to some extent classified by the help of the hypothesis of valency, itself an outcome of the application of the molecular and atomic theory to chemical phenomena, and by the hypothesis regarding the relations between the atomic weights of the elements and the properties of these elements and their compounds which is known as the periodic law. The determination of physical constants, and more particularly the quantities of heat which are produced or disappear during chemical changes, the refraction-equivalents, the specific rotatory powers, and the relative volumes, of typical compounds and classes of compounds, helped somewhat towards a definite knowledge of the composition of these compounds.

The study of chemical kinetics, we found, was much advanced by the dynamical hypothesis of Guldberg and Waage, concerning mass-action and chemical affinity, which

in its primary form is nearly independent of any molecular theory of the structure of matter, but in its development and application by Ostwald forms a bridge connecting the investigation of the chemical properties of molecules with that of the actions of the forces which come into play during chemical operations. In the later outcome of the work on affinity, we found a general theory of chemical change between electrolytes in solution. Whether we accept this theory or not, we must admit that it has been prolific in work of first-class importance. It has advanced our conception of chemical change: it has given us definite measurements of the affinities of very many acids, and in these numbers it has presented us with quantitative connexions between the constitutions, and the reactions, of those acids.

We are getting nearer the goal towards which chemists have ever striven; we are learning to recognise and formulate definite connexions between properties and composition.

I have tried always to exhibit the hypotheses of chemistry as at once arising from facts, and serving as guides in the quest for facts It is especially necessary to do this, I think, in dealing with the questions concerning structural formulæ. If these formulæ are dissociated from the chemical facts which they symbolise they become intellectual tyrants; if each formula is considered simply as a summary of facts regarding the compound formulated, they are to be classed with the other 'brute beasts of the intellectual domain,' and cease to have much interest for one who believes that chemistry is a branch of science.

One great difficulty in using chemical hypotheses consists in determining the limits of the class of phenomena to which each hypothesis may be applied. Berzelius carried the hypothesis of dualism too far, and it was destroyed by the more elastic hypothesis of substitution; in our own day the hypothesis of valency has frequently been applied to phenomena with which it has little or nothing to do.

But each failure to explain all in terms of one hypothesis makes us more hopeful for the future, and convinces us that

we have to deal with a living and growing part of the study of nature. And nature is finer than our finest analysis.

Much work has yet to be done before a general theory of chemical change can be hoped for; a theory which shall represent every process of change as a function of the atomic weights of the elements, and the affinities of the reacting substances concerned in the operation. When such a theory is attained, will chemistry be complete? I hope not; for

'What's come to perfection perishes.'

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