

THE HEATS OF FORMATION OF SIMPLE INORGANIC COMPOUNDS

By L. H. LONG, B.Sc., PH.D.(LONDON), PH.D.(CANTAB.), A.R.C.S., D.I.C.
(DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE, EXETER)

1. Introduction

THE contribution made to chemistry by an ever-increasing knowledge of heats of formation has, broadly speaking, been twofold. In the first place, heats of formation may be utilised directly to compute heats of reaction, and these, in conjunction with other thermodynamic data such as concentration, pressure, volume, temperature, and specific heats, used in turn to provide much useful data concerning chemical processes. Thus, given enough data, it is possible to predict not only the direction of a reaction, but, in the case of a reversible reaction, the position of equilibrium, its variation with temperature, and the output of mechanical or electrical work. Heats of formation have also on occasion found application in making intelligent qualitative predictions concerning the types of phase diagrams to be expected for multicomponent systems. It should be emphasised that it is only possible to obtain a knowledge of the thermodynamic *possibilities* of a reaction in this manner. Heats of formation tell us nothing concerning the *probabilities* or the *rates* of reactions, since they are concerned neither with the paths a reaction may take nor with the potential barriers encountered *en route*. This limitation can be overcome only by resorting to reaction kinetics, a subject outside the scope of the present Review.

The other major contribution concerns the energetic aspect of the structures of inorganic compounds, whether crystalline or molecular. True, heats of formation tell us nothing concerning the structures themselves, but they are nonetheless indispensable for obtaining crystal energies and bond energies.

The numerical data may therefore be said to be of great importance to the theoretical chemist as well as to the industrial chemist. Indeed, interest in heats of formation extends to other fields of science than chemistry, for they have been utilised in attempting to account for the composition of the earth and other planets,¹ as well as for elucidating the processes occurring in the upper atmosphere as a result of photodecomposition.²

In view of the advances made during the last quarter-century and more, an account of the various aspects of the present subject is timely. In such a wide subject it is not possible to be comprehensive, and emphasis will here be laid on those matters not conveniently summarised in text-books.

2. Historical

Oxides apart, it is rarely possible to measure the heats of formation of an inorganic compound directly and in a single step. Normally, the heats

¹ Urey, *Geochim. Cosmochim. Acta*, 1951, **1**, 209.

² See, e.g., Herzberg, *J. Roy. Astron. Soc. Canada*, 1951, **45**, 100.

liberated or absorbed in a number of different steps must be determined independently, and the required heat of formation calculated by algebraic summation of the values obtained.

This being the case, the dawn of thermochemistry may be said to have occurred with the enunciation of Hess's law in 1840³ (although it had been recognised some 60 years earlier by Lavoisier and de Laplace that the heat of decomposition of a compound is in magnitude equal and opposite to its heat of formation). Hess's law, now frequently termed the "law of constant heat summation", states that the heat liberated or absorbed in a chemical reaction is independent of the number and nature of the steps by which the reaction is effected. The law, which was originally based on a large number of calorimetric measurements, is thus seen to be a special case of the first law of thermodynamics (law of conservation of energy), which was first propounded a few years later, likewise on an empirical footing.

The latter half of the 19th century witnessed the measurements of the heats of reaction of thousands of chemical processes and the accumulation of a vast amount of thermochemical data. This must be accredited mainly to Thomsen and Berthelot,⁴ although others also contributed. Thomsen, who carried out most of his investigations between 1852 and 1886, included gas calorimetry in his studies, and evolved a so-called "universal burner", the precursor of the modern gas calorimeter. Berthelot commenced his thermochemical studies in 1864. To him is due the development of bomb calorimetry from 1880 onwards.⁵ True, a type of bomb had been used as early as 1846,⁶ but this worked at atmospheric pressure, whereas Berthelot utilised the advantages offered by working at high pressures (ultimately exceeding 20 atm.) and by other improvements in technique.

By modern standards, the accuracy of the work accomplished during this period was far from high. Errors of 1—2% were common, and still larger errors not infrequent. Both Thomsen and Berthelot were spurred on in their researches by the belief that in the heat of reaction they had found a measure for the "affinity" of a process, and that in consequence they had found in calorimetry a means of attacking the then-unsolved problem of chemical affinity. To see this development in its true perspective, it is necessary to recall that the whole question of chemical affinity was one which had largely preoccupied the minds of many scientists and philosophers for a very long time. For example, Boyle and a number of his contemporaries had considered it, while the concept can be traced as a hazy notion at least as far back as the 13th century! In independently equating affinity with the heat of reaction, therefore, Thomsen and Berthelot both believed that they had opened up the way to satisfying one of the main lines of chemical enquiry.

³ Hess, *Pogg. Annalen*, 1840, **50**, 385; 1841, **52**, 97.

⁴ Both experimenters summarised their work in book form. See: Thomsen, "Thermochemistry" (English translation by K. A. Burke, London, 1908 and 1920); Berthelot, "Thermochimie" (Paris, 1897).

⁵ Berthelot, *Compt. rend.*, 1880, **90**, 779; **91**, 188.

⁶ Andrews, *Phil. Mag.*, 1848, **32**, 321; *Pogg. Annalen*, 1848, **75**, 27.

One of the logical consequences of the Thomsen-Berthelot principle, however, is that only exothermic reactions can proceed. Quite apart from the subsequent discovery of reactions that are inescapably endothermic, a moment's reflection on the existence of numerous chemically reversible reactions—which cannot be exothermic in both directions—is sufficient to demonstrate the unsatisfactory nature of this viewpoint. Reversible reactions had been known for a long time, and the position is the more surprising when it is reflected that, before embarking on his thermochemical studies, Berthelot had himself made a study of the reaction between acetic acid and alcohol.

That the inconsistency was not immediately detected is in part due to the imperfect ideas then current concerning the nature of chemical equilibria (which were widely regarded as "static" systems, though a few such as A. W. Williamson thought otherwise), and in part due to the fact that neither Thomsen nor Berthelot adopted an essentially atomistic approach to chemistry. It is doubtful if the importance of the combined effect of these two chance factors has been fully appreciated, even by thermochemists themselves. Thus it was that Thomsen and Berthelot failed for a long time to recognise the untenability of their main hypothesis, even after 1879 when Guldberg and Waage put the "law of mass action" (which they had first enunciated clearly in 1867) on a "dynamic" footing by the introduction of velocity constants. Had Thomsen and Berthelot come to this recognition at an early date, they might well have turned their attention to other fields and the historical development of thermochemistry would have been quite different.

The actual cause of the relinquishing of this false position was the discovery of the second law of thermodynamics, one consequence of which was a redefinition of chemical affinity (in 1884 by van't Hoff⁷) as the maximum amount of external useful work which can be obtained from a chemical process at constant temperature and pressure. Before the end of the century, both Thomsen and Berthelot reluctantly accepted the new standpoint, from which the data they had amassed appeared to be relegated to a position of secondary importance. The true relationship between the heat of reaction and chemical affinity was finally clarified in 1906 by Nernst.⁸

3. Modern Developments

The first two decades of the present century witnessed only comparatively small additions to the thermochemical data compiled during the previous half-century. Nevertheless, two important developments occurred during this period. One of these was the determination of specific heats down to very low temperatures, on the one hand by direct measurement and on the other by applying statistical mechanics to observable spectroscopic data. Since these values could be used for the accurate experimental computation of entropies, it now became possible to determine affinities at a given temperature by means of the simple relation $\Delta G = \Delta H - T\Delta S$. Here

⁷ "Études de dynamique chimique" (Amsterdam, 1884).

⁸ *Nachr. K. Ges. Wiss. Göttingen*, 1906, 1.

ΔG , ΔH , and ΔS are the changes in free energy, heat content, and entropy respectively of the isothermal system undergoing the chemical change under consideration at temperature T . The true measure of the affinity is the decrease in free energy, which is only equal to the heat of reaction (decrease in heat content) at absolute zero. Heats of reaction and hence heats of formation thus took their rightful places as indispensable thermodynamic quantities, and this gave to calorimetry a new impetus that became increasingly apparent after 1920.

The other major development was a vast improvement in experimental technique and accuracy. Electrical calibration was introduced in 1903,⁹ and temperatures began to be measured by thermocouples and platinum resistance thermometers. Rotary stirring, the avoidance of heat losses by evaporation, and the more accurate estimation of heat corrections were among the other improvements. The experimental side was largely perfected in the hands of Dickinson,¹⁰ whose paper repays perusal. It may be noted that one important recommendation by Dickinson has unfortunately still not been adopted by instrument makers in this country, namely, the total avoidance of poor thermal conductors like ebonite in calorimeter construction. Such "thermal insulators" increase the time required to re-establish equilibrium and render the *accurate* computation of heat transferred impossible. Other names which must be mentioned in connection with advances in experimental technique are T. W. Richards, W. A. Roth, Swarts, Verkade, and Swietoslawski (microcalorimetry¹¹⁻¹⁴). The various types of calorimeters evolved have been critically discussed by White.¹⁵

The several advances mentioned rapidly led to the realisation of an accuracy of $\pm 0.1\%$ or better, and since about 1930, the National Bureau of Standards in Washington has been the source of a steady flow of data accurate to about $\pm 0.02\%$. As high an accuracy has been attained in other laboratories.¹⁶ To achieve this, very special attention has had to be paid to purity of material and purity of reaction. True, heats of reaction known with such accuracy are still almost entirely confined to processes involving combustible organic substances, but, the fundamental obstacles in technique having been overcome, there is no reason why a similar order of accuracy should not in time be achieved for many types of inorganic processes. Much research remains to be done. Since, however, for a reaction to be amenable to accurate calorimetric study it must follow a single path, involve only stoichiometric compounds, and go to completion rapidly,¹⁷ it is clear

⁹ Jaeger and von Steinwehr, *Verh. deut. phys. Ges.*, 1903, **5**, 50.

¹⁰ *Bull. U.S. Bur. Stand.*, 1915, **11**, 189.

¹¹ Swietoslawski and Dorabialska, *Compt. rend.*, 1927, **185**, 763.

¹² Swietoslawski, *J. Chim. physique*, 1930, **27**, 96.

¹³ Swietoslawski, Rybicka, and Solodkowska, *Bull. Acad. Polonaise (Cl. Math. Nat.)*, 1931, **A**, 322.

¹⁴ Swietoslawski and Bartoszewicz, *ibid.*, p. 336.

¹⁵ "The Modern Calorimeter" (New York, 1928).

¹⁶ See, e.g., Coops, Van Nes, Kentie, and Dienske, *Rec. Trav. chim.*, 1947, **66**, 113.

¹⁷ A calorimetric method for studying slow reactions has recently been developed by Buzzell and Sturtevant, *J. Amer. Chem. Soc.*, 1951, **73**, 2454.

from the outset that the accuracy realisable in inorganic chemistry will not be as uniformly high as in organic chemistry. Solid reactions are particularly unsuited to direct thermochemical measurement.

The increase in accuracy referred to came at a timely juncture for meeting the growing chemical and thermodynamical needs of the modern era, and these needs were themselves a stimulus to thermochemical research. In particular, the calculation of equilibrium constants for industrial processes demanded thermochemical data of a hitherto unprecedented order of accuracy. The bearing of thermochemical values on one such process and its historical significance have been briefly discussed recently by Parks,¹⁸ who has also pointed out that the sensitivity of equilibrium constants to inaccuracies in the thermochemical data makes a further tenfold reduction in calorimetric errors desirable.

The principle employed in calculating equilibrium constants is equally true in reverse, so that very accurate thermodynamic data have been obtained from the experimental study of equilibria over a temperature range. Likewise, the temperature-dependence of electrochemical potentials is able to provide very accurate figures for heats of reaction. These methods are of course restricted to cases providing suitable chemical equilibria or electrochemical processes respectively.

Finally, it must be mentioned that the determination of a number of heats of formation has been brought about to meet the requirements of certain academic studies, more particularly in connection with crystal energies of heteropolar compounds on the one hand and bond energies of homopolar compounds on the other. Here the accuracies demanded are not so high. Both lines of enquiry entail a knowledge of heats of atomisation of the elements concerned, and the former also involves ionisation energies and electron affinities.

4. Experimental Determination of Heats of Formation

Except in the case of certain oxides, it is only rarely possible to determine heats of formation of inorganic compounds by direct measurement. Consequently, indirect paths usually have to be employed, and the heats of formation computed by means of Hess's law. Thermochemical data of the most varied kind may be utilised.

The four principal methods of gaining thermochemical information have already been mentioned, and may be summarised thus: (i) Calorimetric measurement, from which heats of reactions and specific heats can be directly obtained; (ii) study of the temperature-dependence of equilibrium constants, from which ΔH can be calculated by means of van't Hoff's equation (reaction isochore); (iii) study of the temperature-dependence of e.m.f. data of electrochemical processes at strictly reversible electrodes, whereby ΔH can be calculated by means of the Gibbs-Helmholtz equation; (iv) infra-red spectroscopy, from which specific heats of gaseous substances may be computed.

¹⁸ *J. Chem. Educ.*, 1949, **26**, 262.

In addition, thermochemical data have been obtained by means of ultra-violet spectroscopy from convergences of spectral series (and predissociation data), reaction-kinetic studies, and electron-impact experiments. These methods are normally used to afford the heats of formation of free radicals, since they concern processes in which chemical bonds are ruptured. By exception, the heat of formation of a stable compound may be obtained by one of these methods. Thus, the heat of formation of ClO_2 can be calculated from a predissociation (attributed to the process $\text{ClO}_2 \rightarrow \text{Cl} + \text{O}_2$).¹⁹ Likewise, heats of formation of the halides and oxyhalides of sulphur, selenium, and tellurium have been obtained from spectroscopic data in the ultra-violet.²⁰ Again, ionisation energies and electron affinities have been utilised for calculating heats of formation, notably in the case of free ions, both simple and complex. The inter-relationship between heats of formation and certain other physical properties and the extent to which the former may be derived from the latter will be discussed in later sections.

Of the methods outlined above, method (i) calls for further comment as being that which has received by far the widest application. In organic chemistry the matter is considerably simplified by the fact that the majority of organic compounds are combustible, so that the determination of the heat of combustion in a bomb calorimeter—or in the case of very volatile substances in a gas calorimeter—is all that is required in order to be able to calculate the heat of formation. The only organic compounds which will not yield to this type of treatment are those poor in hydrogen that simultaneously contain an unusually high proportion of oxygen, nitrogen, or halogen. In inorganic chemistry, on the other hand, no such universal process is available, since inorganic substances, as a class, cannot be made to react with a single substance such as oxygen. Bomb calorimetry has consequently found only a very limited application in inorganic chemistry, but it has been employed for determining the heats of combustion of numerous elements, principally by Roth and his collaborators, and, more recently, of a number of metal alkyls.²¹ The difficulties confronting the experimenter are considerable and much greater than when organic compounds are being investigated. The bomb calorimeter has also been adapted on occasion for determining the heats of formation of sulphides, chlorides,^{21a} and intermetallic compounds, and one important modification has been the development of high-temperature bomb calorimeters for studying inorganic compounds.²² By way of example, the heats of formation of a number of metal phosphides have been determined in a bomb operating at 630° ;²³ and an evacuated bomb has been employed for determining the heat of formation of chromium trifluoride by double decomposition.²⁴ Occasionally it has proved possible to determine the heat of formation of an

¹⁹ Mayer, *Z. physikal. Chem.*, 1924, **113**, 220.

²⁰ Hussain and Samuel, *Current Sci.*, 1936, **4**, 734.

²¹ Long and Norrish, *Phil. Trans.*, 1949, *A*, **241**, 587.

^{21a} See, e.g., Siemonsen, *Z. Elektrochem.*, 1951, **55**, 327.

²² See, e.g., Biltz, Rohlfis, and von Vogel, *Z. anorg. Chem.*, 1934, **220**, 113.

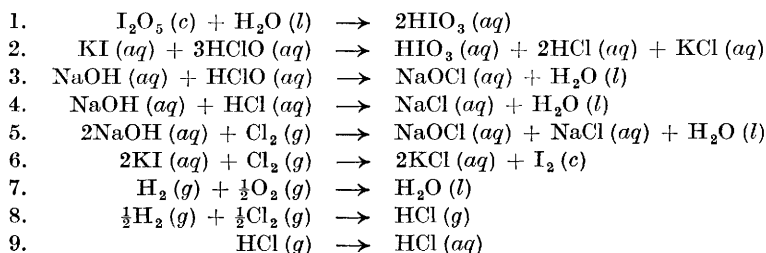
²³ Weibke and Schrag, *Z. Elektrochem.*, 1941, **47**, 222.

²⁴ von Wartenberg, *Z. anorg. Chem.*, 1942, **249**, 100.

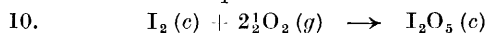
endothermic compound in a bomb calorimeter by direct measurement of the *heat of decomposition*, as in the case of copper nitride.^{24a}

Such instances are, however, comparatively rare, and other types of calorimeter have been used to provide most of the data required. The thermochemistry of inorganic substances is less concerned with heats of combustion than with heats of hydration, of solution, of dilution, of neutralisation, and of reaction of various kinds, including direct combination, decomposition, and double decomposition. Of particular importance are reactions in solution, which have provided probably more than half of the available thermochemical data relating to inorganic compounds.

The variety of reactions which may be drawn upon to determine the heat of formation of an inorganic compound may be conveniently illustrated by selecting an example. The heat of formation of iodine pentoxide, I_2O_5 , is determined by measuring its heat of solution in excess of water, with which it forms iodic acid. The calculation of the required value demands a knowledge of the heat of formation of iodic acid. This, in turn, can be calculated in a number of ways, one of them being from the reaction $KI + 3HClO \rightarrow HIO_3 + 2HCl + KCl$. The heat of formation of hypochlorous acid can be calculated from the heats of reaction of hypochlorous acid, hydrochloric acid, and gaseous chlorine respectively with aqueous sodium hydroxide, and the heat of reaction of chlorine with aqueous potassium iodide dispenses with the difference in the heats of formation of potassium iodide and potassium chloride. Also required to complete the calculation are the heat of formation of water from its elements and the heat of formation of aqueous hydrochloric acid, which is equal to the sum of the heat of formation of gaseous hydrogen chloride from its elements and the heat of solution of the gas in water. The processes involved may be summarised thus :



On adding and subtracting the appropriate multiples of these equations, one obtains the overall equation :



The overall heat of reaction, Q_{10} , namely, the heat of formation of iodine pentoxide, is related to the various heats of reaction in the following manner :

$$Q_{10} = 2Q_2 + 6Q_5 + 5Q_7 - Q_1 - 6Q_3 - 6Q_4 - Q_6 - 10Q_8 - 10Q_9$$

^{24a} Juza and Hahn, *Z. anorg. Chem.*, 1939, **241**, 172. In this instance a special microcalorimeter was developed for the purpose.

Even this is not quite the whole story, since small corrections for heats of dilution and mixing are also involved in the accurate computation of Q_{10} .

5. The Tabulation of Experimental Values

In harmony with the foregoing example, the heat of formation of a compound is defined as the heat liberated when one mole of the substance is formed from its component elements at constant pressure (1 atm.) and some specified temperature. Whereas the older European workers for the most part chose 18° as their working temperature, much of the more accurate recent work refers to 25°, a temperature better suited to the climate of Washington and some other parts of America. Although this temperature is less convenient for temperate latitudes and the transition to it is by no means complete, it seems highly probable that in the future—if only as an outcome of the disproportionately large amount of thermochemical research being carried out across the Atlantic—25° will be universally accepted as the “standard” working temperature to which the heats of reaction carried out at other temperatures must be recomputed.

In expressing heats of formation (and, indeed, heats of reaction generally) it is of course vital to define the *state* of every participant, whether solid, liquid, or gaseous. For example, the heat of formation of gaseous sulphur trioxide differs from that of liquid sulphur trioxide by an amount equal to the heat of vaporisation of this compound. Again, where more than one solid modification of a compound exists, or where an element exists in allotropic forms, the variety under consideration must be stated. It is usual in the case of elements to select the form most stable at 25° as the *standard state*, and to compute all heats of formation accordingly.

As thus defined, the heat of formation, Q (or, more precisely, Q_f), assumes a positive value for an exothermic compound and a negative value for an endothermic compound. This convention has always been accepted in England and other European countries. Unfortunately, a different convention has sprung up in America, where the heat liberated on the formation of an exothermic compound is regarded as a decrease in internal energy, so that the quantity quoted, ΔH , is negative for an exothermic compound and *vice versa*. Care must therefore be exercised regarding the correct sign when referring to different sources for thermochemical data. The unit of energy usually employed is the kilocalorie, which is now defined in such a way as to be independent of the heat capacity of water.²⁵

The most recent, internally consistent sets of tables of heats of formation (and other thermodynamic data) are due to Rossini and his collaborators.²⁶ In these tables, all the available information regarding heats of formation has been critically compiled with respect to 25°, and in some cases to absolute zero as well. Where only old, discordant values are available, some

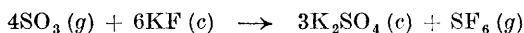
²⁵ See, e.g., Rossini, *Chem. Reviews*, 1936, **18**, 233.

²⁶ Rossini, Wagman, Evans, Levine, and Jaffe, “Selected values of chemical thermodynamic properties”, National Bureau of Standards, Circular No. 500, Washington, 1952. These tables began to appear in 1947 and are brought up to date from time to time.

arbitrariness of choice has doubtless been inevitable, and it is to be regretted that no indication is given as to whether any systematic corrections have been applied to the older data (*e.g.*, such as those recommended by Kharasch²⁷ for Thomsen's data). Except where otherwise stated, all the values quoted in the present paper are taken from these tables. Older compilations are due to Washburn,²⁸ Roth and Scheel,²⁹ and Bichowsky and Rossini.³⁰

The great advantage offered by tables of heats of formation is that the heats of all conceivable reactions between the substances listed—whether such reactions are realisable or merely hypothetical—can be simply calculated by algebraic treatment of the values tabulated. Manifestly, it is not necessary to measure the heat of every possible reaction in order to construct the tables in the first place, but merely those of a judicious selection embracing the maximum number of substances. In principle, the number of such reactions need only be of the same order as the number of substances to be included in the tables.

An illustration of the way in which the tabulated heats of formation may be employed to calculate heats of reaction may be furnished by considering the hypothetical reaction :



The heat of reaction is equivalent to the difference between the combined heat of formation of the reactants and that of the products. Since the heats of formation of gaseous sulphur trioxide, solid potassium fluoride, solid potassium sulphate, and gaseous sulphur hexafluoride are 94.45, 134.46, 342.66, and 262 kcal./mole respectively, it can be calculated that the foregoing reaction—if conditions could be found under which it could be made to proceed—would be exothermic to the extent of 105 kcal. at 25°. Hitherto sulphur hexafluoride has been prepared only by the use of elementary fluorine.

6. Heats of Formation and the Periodic Table

General Survey.—As is to be expected, the heats of formation of individual classes of compounds exhibit a periodicity similar in kind to that shown by many other properties of the same compounds. This periodic variation is most clearly seen in the case of binary compounds. If one element is kept the same and the other varied, a "saw-tooth" curve can be obtained not unlike that observed for, say, atomic volumes. The connection between the heat of formation and atomic number has been studied on an empirical basis by a number of investigators.³¹⁻³⁵ Because of certain

²⁷ *Bur. Stand. J. Res.*, 1929, **2**, 359.

²⁸ International Critical Tables, Vol. 5 (New York and London, 1929).

²⁹ Landolt-Börnstein's "Tabellen" (Berlin).

³⁰ "The Thermochemistry of the Chemical Substances" (New York, 1936).

³¹ Roth and Schwartz, *Z. physikal. Chem.*, 1928, **134**, 456.

³² Roth, *Naturwiss.*, 1931, **19**, 860.

³³ Lautić, *Bull. Soc. chim.*, 1938, **5**, 1321.

³⁴ Trombe, *Compt. rend.*, 1944, **218**, 457.

³⁵ Süe, *J. Chim. phys.*, 1945, **42**, 45.

striking regularities, it has even been claimed ³⁶ that a careful study of the heats of formation of simple compounds reveals the same regularity as that observed by Mendeléef for the atomic weights. According to this statement, the heat of formation of a compound of one element with a second invariant element approximates to the arithmetic mean of those of the compounds its neighbours—whether situated vertically or horizontally in the Periodic System—form with the same element (all the heats of formation being expressed per gram-atom of common element). This is, however, a gross overstatement. Although such a relationship can be shown to hold approximately in a large number of cases, it was subsequently shown by Roth and Becker ³⁷ that it broke down in several instances among the chlorides and oxides, and later by Kröger ³⁸ that it also failed when applied to the nitrides. Indeed, a close examination of the available values reveals numerous other exceptions and irregularities. One need only cite the hydrides, which as a class are most erratic, or the surprisingly low values for the alkali-metal oxides. Again, the maximum values within the individual groups or periods for one particular class of compounds fall not infrequently at points erratically situated within the respective groups or periods, as can be seen from a study of Tables 1 and 2.

These tables have been completed as far as the available data allow, but numerous gaps in present-day knowledge relating to heats of formation have made it impossible to complete all the columns. Where it is still possible that further measurements may reveal compounds with higher heats of formation, this has been indicated by a query in parentheses, while compounds for which experimental data are not available but whose heats of formation can be predicted with confidence to be supreme (*e.g.*, chromous bromide) are themselves inserted between parentheses. In point of fact, fluorine liberates the greatest heat when combining with lithium, chlorine when combining with potassium, bromine and iodine when combining with caesium, oxygen—as far as is known—with lanthanum, sulphur and selenium probably with lithium, nitrogen with zirconium, and carbon probably with tantalum. Also, except for Groups II and III, hydrogen liberates the greatest heat on combining with the lightest element in each group. The heats of formation of the relevant compounds are cited for comparison in Table 3. Except for TaC,³⁹ the figures are taken from Rossini *et al.*²⁶ Information regarding the tellurides, phosphides, arsenides, antimonides, silicides, and borides is either very incomplete or virtually non-existent.

Several points of considerable general interest emerge from Tables 1—3. Of the non-metals, oxygen is that which is able to liberate the greatest heat per gram-atom on combination, while fluorine liberates the most per gram-equivalent. The change in positions of the maxima in the individual groups and periods demonstrates the futility of trying to find some all-embracing relationship governing the whole of the Periodic System. Nor are the

³⁶ Berkenheim, *Z. physikal. Chem.*, 1928, **136**, 231.

³⁷ *Ibid.*, 1932, *A*, **159**, 1.

³⁸ *Z. anorg. Chem.*, 1934, **218**, 396.

³⁹ Brewer, Bromley, Gilles, and Lofgren, National Nuclear Energy Series, Div. IV, **19B**, Chem. and Met. of Misc. Materials, p. 40 (1950).

TABLE 1. *Binary compounds of F, Cl, Br, I, O, S, Se, N, and C with elements of the individual groups having the highest heats of formation per gram-atom of the former. (Only stoichiometric compounds are included)*

Combining element	Group: I	II	III	IV *	V *	VI *	VII	VIII
F . . .	LiF	CaF ₂	?	ZrF ₃ (?)	?	CrF ₂	MnF ₂	FeF ₂
Cl . . .	KCl	BaCl ₂	LaCl ₃	ZrCl ₂ (?)	?	CrCl ₂	MnCl ₂	FeCl ₂
Br . . .	CsBr	BaBr ₂	(LaBr ₃)	ZrBr ₂ (?)	?	(CrBr ₂)	MnBr ₂	FeBr ₂
I	CsI	BaI ₂	LaI ₃	ZrI ₂ (?)	?	CrI ₂	MnI ₂	FeI ₂
O	Li ₂ O	CaO	La ₂ O ₃ (?)	HfO ₂	Ta ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₃ O ₄
S	(Li ₂ S)	CaS	La ₂ S ₃ (?)	?	?	O ₃ S	F ₆ S	RuS ₂
Se . . .	Li ₂ Se (?)	BaSe	?	?	?	?	F ₆ Se	?
N	Li ₃ N	Be ₃ N ₂	LaN	ZrN	NbN	CrN	Mn ₄ N	Fe ₄ N
C	Li ₂ C ₂	?	?	ZrC (?)	?	O ₂ C	F ₄ C	Fe ₃ C

* In drawing up this table, Th, Pa, and U have not been included in Groups IV, V, and VI, respectively (cf. Tables 4 and 5).

TABLE 2. *Binary compounds of F, Cl, Br, I, O, S, Se, N, and C with elements of the individual periods having the highest heats of formation per gram-atom of the former. (Only stoichiometric compounds are included)*

Combining element	Period: 1st	2nd	3rd	4th	5th
F	LiF	NaF	CaF ₂	SrF ₂	BaF ₂
Cl	LiCl	NaCl	KCl	RbCl	CsCl
Br	LiBr	NaBr	KBr	RbBr	CsBr
I	LiI	NaI	KI	RbI	CsI
O	BeO	MgO	CaO	(Y ₂ O ₃) (?)	La ₂ O ₃
S	F ₆ S	Na ₂ S	CaS	SrS	BaS
Se	F ₆ Se	Na ₂ Se	K ₂ Se	SrSe (?)	BaSe (?)
N	Be ₃ N ₂	AlN	TiN	ZrN	HfN
C	F ₄ C	Cl ₄ C	?	?	TaC (?)

TABLE 3. *Heats of formation of binary compounds with the maximum values per gram-atom of H, F, Cl, Br, I, O, S, Se, N, and C*

Combining element	Compound with max. heat of formation	Heat of formation (kcal./g.-atom)	Combining element	Compound with max. heat of formation	Heat of formation (kcal./g.-atom)
H	HF (g)	64.2	O	$\frac{1}{3}$ La ₂ O ₃ (c) (?)	152.7
F	LiF (c)	146.3	S	Li ₂ S (c) (?)	—
Cl	KCl (c)	104.18	Se	Li ₂ Se (c) (?)	91.1
Br	CsBr (c)	94.3	N	ZrN (c)	82.2
I	CsI (c)	80.5	C	TaC (c)	63.8

maxima situated at the same positions for fluorine and oxygen. From Table 2 it is seen that fluorine forms the most stable compounds with the elements of groups I and II, while with oxygen the maxima have shifted to the right, namely, to groups II and III. With nitrogen and carbon the maxima move successively further to the right. This corresponds to a progressive decrease in the ionic character of the most stable compounds. The crystal structures with their differing energies also play a part in deciding where the maxima fall. This also applies to the vertical groups (Table 1), where the relative sizes of the cationic and anionic particles constitute a criterion for the lattice energy. Thus, chlorine finds the optimum energetic conditions when combining with potassium in group I and barium in group II, while fluorine, which has a smaller anion, finds them respectively with lithium and calcium with their smaller cations, the crystal types remaining unchanged. This accounts for the widespread immiscibility of the solid alkali halides and the observed reaction directions.⁴⁰ Another case in point is exhibited by the alkaline-earth metals, barium forming the most stable selenide and calcium the most stable oxide and sulphide.

It is to be observed in passing that electronegativities do not always prove to be the deciding factor in determining relative chemical reactivities. For example, the hydride, fluoride, oxide, and nitride of lithium have heats of formation which are respectively higher than those of the other alkali metals, so that chemical replacement with the latter would be effected by metallic lithium. On this basis, lithium might be said to be the most reactive alkali metal, notwithstanding the fact that it is the least electro-positive. Heats of formation have been discussed in connection with the electronegativity scale by Haïssinsky,⁴¹ who comments on the anomalous values. However, by confining attention essentially to the chlorides, bromides, and iodides, he succeeds by means of a semi-empirical relationship in drawing up a revised electronegativity scale embracing the whole of the Periodic System. Fluorides and oxides are observed to conform to the relationship in a far less satisfactory manner, while the order of the elements on the new scale is not invariably found to coincide with the order of their electrode potentials in solution. This is of course not surprising. Apart from its approximate character, the electronegativity scale is constructed from values for anhydrous compounds and is not concerned with solvent effects—notably heats of solvation—which will affect the observed potentials to varying extents.

The reason for the anomalous position of a number of fluorides is not far to seek. The increase in lattice energy on passing from the iodide of an element to its bromide is comparatively small, and the further increase observed on passing to the chloride is only of the same order. The step from the chloride to the fluoride, however, involves a jump in lattice energy about four times as big, with a correspondingly wide variation (in terms of kilocalories) from metal to metal, and it is this wider variation which is at

⁴⁰ Thomas and Wood, *J. Amer. Chem. Soc.*, 1935, **57**, 822; 1936, **58**, 1341.

⁴¹ *J. Phys. Radium*, 1946, **7**, 7.

least partly responsible for the seemingly erratic behaviour of the fluorides. The jumps in lattice energy referred to are listed for a number of elements by Süe.³⁵

Having dispensed with the possibility of finding any over-all regularity governing the whole of the Periodic System, it would be profitable to glance at the sort of regularities that are observed among certain types of compound in certain parts of the Periodic System. By confining attention to one group at a time, Roth and Schwartz³¹ have shown that, when plotted against the atomic number, the heats of formation of the chlorides or oxides frequently lie on smooth curves, the curves for the two sub-groups being distinct from one another. The types of curves obtained are reproduced here for compounds of the Group II elements, for which information regarding the heats of formation is relatively complete. In Fig. 1 the

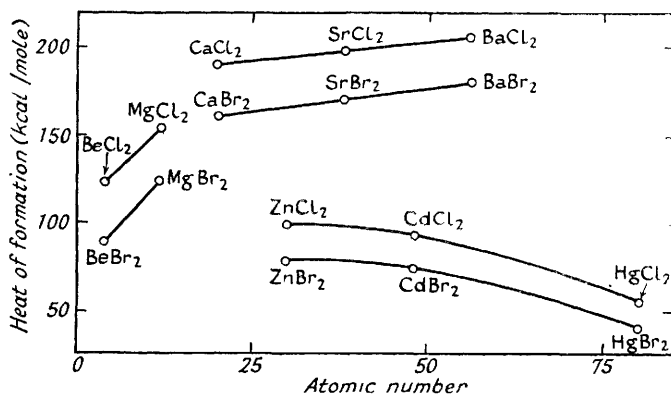


FIG. 1

Heats of formation of the chlorides and bromides of Group II elements plotted against their atomic numbers.

curves for the chlorides and bromides are shown, those for the fluorides and iodides (which are similar) having been omitted for the sake of clarity. It will be noted that the halides of the typical elements, beryllium and magnesium, do not lie on the same curves as those of the elements of either sub-group, although they lie nearer to the curves for the A sub-group. Indeed, by regarding the calcium halides as "anomalous", it is possible to draw smooth curves passing through the points for the respective halides of beryllium, magnesium, strontium, and barium. Such a procedure is, however, misleading. The uniformly "high" values for the calcium halides could then only be accounted for on the supposition that the heat of sublimation of calcium was anomalously low. In point of fact it is rather on the high side. Again, the construction of such a curve to include beryllium and magnesium is impossible in the case of the oxides. The curves for the oxides and sulphides are shown in Fig. 2, and those for the nitrides in Fig. 3. By exception, the nitrides of all five elements lie on a single curve.

By restricting attention to compounds in which the maximum group

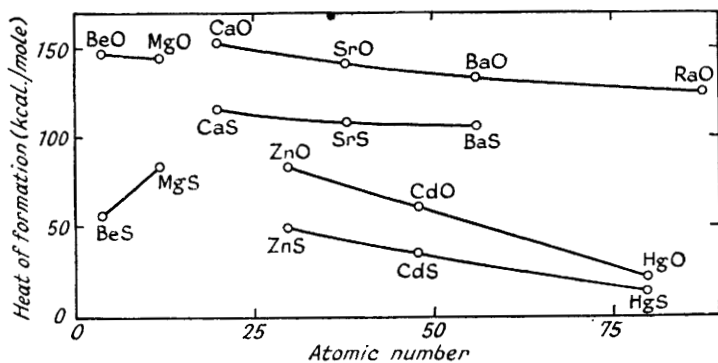


FIG. 2

Heats of formation of the oxides and sulphides of Group II elements plotted against their atomic numbers.

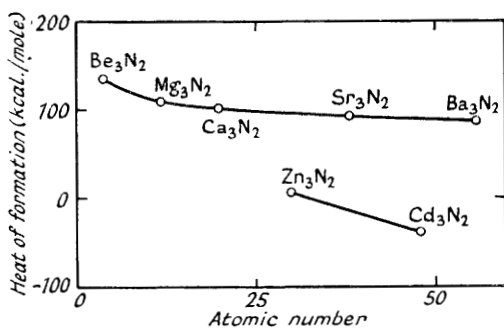


FIG. 3

Heats of formation of the nitrides of Group II elements plotted against their atomic numbers.

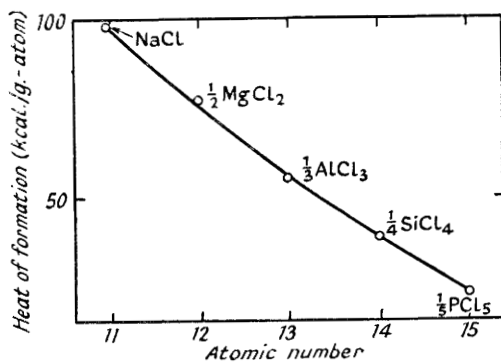


FIG. 4

Heats of formation of the chlorides (per g.-atom of chlorine) of second-period elements plotted against their atomic numbers.

valency is achieved and plotting heats of formation per gram-atom of common element, smooth curves are also frequently obtained for the horizontal periods. Thus the chlorides of the elements of the second period lie particularly well on a curve, notwithstanding the fact that silicon tetrachloride is exceptional in being a liquid at room temperature. The curve is reproduced in Fig. 4. The curves for the oxides have a different shape,

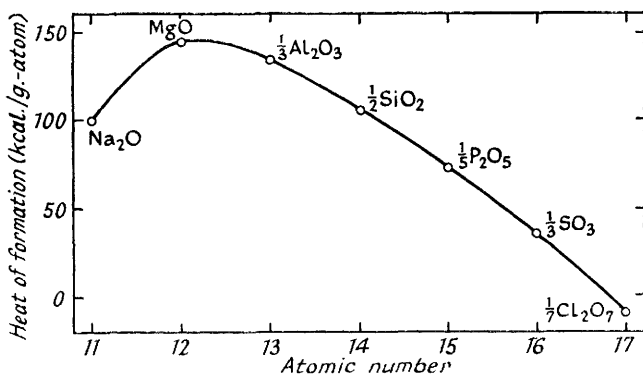


FIG. 5

Heats of formation of the oxides (per g.-atom of oxygen) of second-period elements plotted against their atomic numbers.

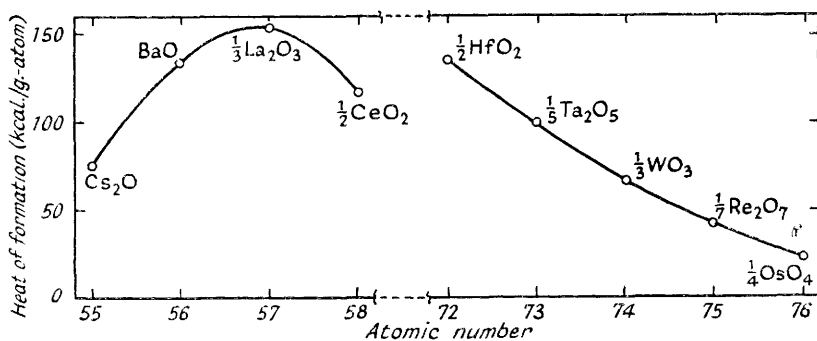


FIG. 6

Heats of formation of the oxides (per g.-atom of oxygen) of fifth-period elements plotted against their atomic numbers.

those for the second period and the fifth (excluding the rare earths) being given in Figs. 5 and 6, respectively.

It has recently been observed by Kapustinskii⁴² that if the heat of formation is plotted, not against the atomic number, but against the logarithm of the latter, the curves already referred to are frequently replaced by straight lines. This is perhaps best illustrated in the case of the chlorides

⁴² *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1948, 568, 581.

of Groups I—IV. The heats of formation are plotted against the atomic number in Fig. 7 and against the logarithm of the atomic number in Fig. 8. Some of the values for the heats of formation are seen not to lie exactly at the positions to be expected for them according to this treatment, the

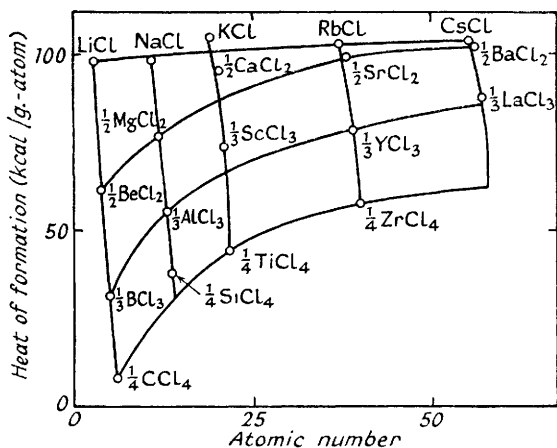


FIG. 7

Heats of formation of chlorides (per g.-atom of chlorine) of elements of the first four groups plotted against their atomic numbers.

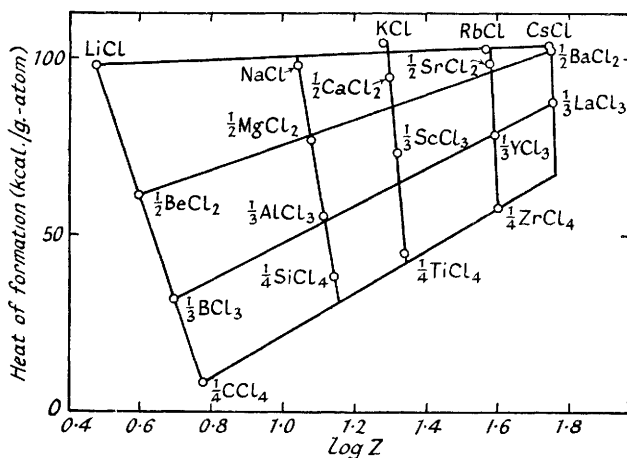


FIG. 8

Heats of formation of chlorides (per g.-atom of chlorine) of elements of the first four groups plotted against the logarithms of their atomic numbers.

“anomalous” position of calcium chloride referred to earlier being particularly apparent. The conformity of the fluorides to this linear rule is rather less impressive, and of the oxides and nitrides very much less so. In particular, some of the sub-groups fail to conform. Thus the heat of formation

of indium trichloride is anomalously high, and higher than that of the trichloride of either gallium or thallium: indeed, the anomalous positions of the compounds of trivalent indium are not confined to the halides, nor for that matter to the heats of formation.⁴³ Nevertheless, the logarithmic rule referred to may be of some service in predicting unknown heats of formation. Thus from the known heats of formation of gaseous silicon tetrafluoride (370 kcal./mole) and gaseous sulphur hexafluoride (262 kcal./mole), the heat of formation of phosphorus pentafluoride may in this way be predicted by interpolation to be 338 kcal./mole.

Hydrides.—It is now profitable to make a brief survey of the numerical values of the heats of formation of some of the more important classes of compound. The values for the hydrides of the various elements are set out in Table 4 in such a way as to facilitate comparison between the values for the various groups and periods. The arrangement chosen is based on the electronic structure of the free elements, so that the transition series from scandium to zinc, from yttrium to cadmium, and from lanthanum to mercury are separated out from the main groups. For the hydrides, this arrangement—in which boron and aluminium are situated above gallium—is fully appropriate and justifiable, though it is less so for the halides and oxides. In the case of elements which form more than one hydride, only the simplest or most stable has been included. Non-stoichiometric compounds have been omitted. In general, the heats of formation of the non-stoichiometric hydrides are low, but comparable with those of the stoichiometric hydrides of the transition elements where such exist.

The values given are all taken from Rossini *et al.*²⁶ (the figure for La_3H_8 , which is obviously an error, has been corrected here), except those for the hydrides of sodium, potassium, rubidium, and caesium.⁴⁴ To facilitate the calculation of atomic heats of formation (see later), the heat of atomisation (L_a) of each element is included for convenience and placed immediately after the symbol for the element concerned.

The distribution within the Periodic System of those elements which form stable hydrides is comparatively simple. In this connection, the recent discovery of BeH_2 ,⁴⁵ MgH_2 ,⁴⁶ ZnH_2 ,⁴⁷ CdH_2 ,⁴⁵ and HgH_2 ^{47a} is particularly interesting. It thus transpires that all the typical elements form stable hydrides. As is well known, the hydrides of the alkali and the alkaline-earth metals are essentially ionic in nature, while those of the elements of Group III—VII are covalent compounds. Where the transition elements form hydrides, those do not belong to either type, except that the hydrides of lanthanum, cerium, praseodymium, and neodymium are probably ionic in nature.

Viewed horizontally in periods, the hydrides show little regularity in

⁴³ Juza, *Die Chemie*, 1942, **55**, 45.

⁴⁴ Herold, *Compt. rend.*, 1949, **228**, 686.

⁴⁵ Barbaras, Dillard, Finholt, Wartik, Wilzbach, and Schlesinger, *J. Amer. Chem. Soc.*, 1951, **73**, 4585.

⁴⁶ Wiberg and Bauer, *Z. Naturforsch.*, 1950, **5b**, 396.

⁴⁷ Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199.

^{47a} Wiberg and Henle, *Z. Naturforsch.*, 1951, **6b**, 461.

their heats of formation. Viewed vertically in groups, the tendency is for the first member in each group to form the hydride with the highest heat of formation. However, in Group III the heat of formation of the hydrides of boron fall far below that of lanthanum, and the Group II elements also fail to comply with this rule. True, the heats of formation of the hydrides of beryllium and magnesium are not known, but there can be no doubt from their rather low thermal stabilities that they will be smaller than the value for calcium hydride. In view of the high ionisation potentials of magnesium and beryllium, and of the latter in particular, these hydrides may not be truly ionic but highly polymerised covalent compounds containing chains of metal atoms linked by hydrogen bridges, thus resembling aluminium hydride rather than calcium hydride. The position with regard to the unstable hydrides of zinc, cadmium, and mercury also remains to be clarified.

Particularly noteworthy is the fact that the hydrides of the alkaline-earth metals have much higher heats of formation per gram-atom of hydrogen than the hydrides of the alkali metals. It may be remarked that the heats of formation of the latter compounds do not decrease systematically, the order being: LiH, KH, NaH, CsH, RbH. The cause of this is that, on passing down the group from one element to the next, the decrease in lattice energy is, purely accidentally, rather finely counterbalanced against the combined effects of the decreases in heat of atomisation and ionisation potential of the alkali metal, being sometimes slightly greater and sometimes slightly less.

Of the covalent hydrides, there is no doubt from the relative thermal stabilities that the heats of formation of the hydrides of the elements of Groups IV—VII decrease systematically on passing down each group, notwithstanding the fact that some of the values are lacking. The marked endothermicity of many of the hydrides (and, indeed, the low values for the heats of formation generally) is to be ascribed largely to the high heat of dissociation of hydrogen and its low electron affinity relative to other univalent non-metals. Probably all the hydrides of the Group III elements, with the exception of La_3H_8 , are endothermic, the covalent members constituting electron-deficient compounds of unusual interest.^{48, 49} The crystalline hydrides ThH_4 , UH_3 , and PuH_2 have comparatively high heats of formation and constitute a class of their own. (Conflicting statements appear in the literature concerning the formula of the last-named compound.)

Values for the higher hydrides have not been inserted in Table 4. The heats of formation of the paraffins increase with molecular weight, the increment per CH_2 group tending to a constant value.⁵⁰ Of the boranes, the heats of formation of two of the more stable members, B_5H_9 (*l*) and $\text{B}_{10}\text{H}_{14}$ (*c*), are -7.8 and -8 kcal./mole, respectively, so that there is scarcely room to doubt that all the members of this class are endothermic compounds. Hydrazine, N_2H_4 (*l*), is endothermic with -12 kcal./mole,

⁴⁸ Bell and Emeléus, *Quart. Reviews*, 1948, **2**, 132.

⁴⁹ Hodgkin, *Ann. Reports*, 1949, **46**, 64.

⁵⁰ Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 263.

TABLE 4. Heats of formation (in kcal./mole) of the principal hydrides and oxides of the various elements at 25°. The heats of atomisation of the elements (see Section 7) are given in parentheses after the symbols for the elements. The figures refer to the crystalline state unless otherwise indicated by a superscript *g* or *l* (gas or liquid, respectively)

		H (52.09) HH: 0.00 H ₂ O (<i>l</i>): 68.32; (<i>g</i>): 57.80												
Li (37.07) LiH 21.61 Li ₂ O 142.4	Be (76.63) BeH ₂ — BeO 146.0													
Na (25.98) NaH 13.94 Na ₂ O 99.4	Mg (35.9) MgH ₂ — MgO 143.70													
K (21.51) KH 14.11 K ₂ O 86.4	Ca (46.04) CaH ₂ 45.1 CaO 151.9													
Rb (20.51) RbH 12.98 Rb ₂ O 78.9	Sr (39.2) SrH ₂ 42.3 SrO 141.1													
Cs (18.83) CsH 13.48 Cs ₂ O 75.9	Ba (41.96) BaH ₂ 40.9 BaO 133.4													
Fr	Ra (31) RaO 125	Ac ThH ₄ 43 ThO ₂ 293.2	Pa U (125) UH ₃ 30.4 UO ₂ 302	Np Pu PuH ₂ 31.7 PuO ₂ 251	Am AmO ₂ 239.9	Co (85) Ce ₃ H ₂ 170 Ce ₂ O ₃ — CeO ₂ 233	Fr (87) Fr ₂ O ₂ 444.5 PrO ₂ 234.0	Nd (87) Nd ₂ O ₃ 442.0						
		Sc (93) Sc ₂ O ₃ —	Ti (112.6) {TiO 123.91 {TiO ₂ (rutile) 225.52	V (122.7) V ₂ O ₅ 373	Cr (94.0) CrO ₃ 138.4	Mn (68.34) {MnO (I) 92.0 {Mn ₂ O ₃ —	Fe (99.8) Fe ₂ O ₃ 196.5	Co (102.0) CoH ₂ 10.2 CoO 57.2						
		Y (103) Y ₂ O ₃ —	Zr (142.5) ZrO ₂ (III) 258.2	Nb (184.5) Nb ₂ O ₅ 463.2	Mo (155.5) MoO ₃ 180.33	Tc —	Ru (160) RuO ₂ 52.5	Rh (138) RhO 21.7						
		La ₂ O ₃ 458	Hf (170) HfO ₂ 271.5	Ta (185.6) Ta ₂ O ₅ 499.9	W (201.6) WO ₃ 200.84	Re (189) Re ₂ O ₇ 297.5	Os (174) OsO ₄ (II) 93.4	Ir (165) IrO ₂ 40.1						

H (52.09)
 HH (g) : 0.00
 H₂O (l) : 68.32 ; (g) : 57.80

Ni (101.61) NiH ₂ 6.2 NiO 58.4	Cu (81.52) CuH — {Cu ₂ O 39.84 CuO 37.1	Zn (31.19) ZnH ₂ — ZnO 83.17	B (97.2) B ₂ H ₆ — 7.5 B ₂ O ₃ 302.0	C (125.0) CH ₄ 17.89 CO ₂ 94.05	N (85.57) NH ₃ 11.04 {NH ₄ O ₃ — 20.0 N ₂ O ₅ 10.0	O (59.16) OH ₂ 68.32 OO 0.00	F (18.3) FH 64.2 F ₂ O — 5.5			
	Al (75.0) AlH ₃ — Al ₂ O ₃ (α cor.) 400.29	Si (88.04) SiH ₄ 14.8 SiO ₂ (α quartz) 210.26	Ge (84.0) GeH ₄ — GeO ₂ 129.2	As (60.64) AsH ₃ — 41.0 {As ₂ O ₃ (I) 156.97 As ₂ O ₃ (II) 218.6	S (53.25) SH ₂ 4.82 {SO — 19.02 SO ₂ 94.45	Se (48.37) SeH ₂ — 20.5 SeO — 9.48 {SeO ₂ —	Br (28.71) BrH 8.66 {Br ₂ O — BrO ₂ — 12.5			
Pd (93) Pd ₂ H 8.9 PdO 20.4	Ag (67.5) Ag — {Ag ₂ O 7.31 Ag ₂ O 3.15	Cd (26.97) CdH ₂ — CdO 60.86	In (58.2) In ₂ H ₃ — In ₂ O ₃ 222.5	Sb (60.8) SbH ₃ — {Sb ₂ O ₃ 234.4	Tc (47.6) TcH ₂ — 36.9 Tc ₂ O — 43.0 {TcO ₂ —	I (25.48) IH — 6.20 I ₂ O ₅ 42.34				
Pt (121.6) PtO —	Au (84.6) Au ₂ O — {Au ₂ O ₃ — 19.3	Hg (14.54) HgH ₂ — HgO (II) 21.68	Tl (43.34) Tl ₂ O ₃ —	Pb (46.34) PbH ₄ — PbO ₂ 66.12	Bi (49.7) BiH ₃ — {Bi ₂ O ₃ 137.9 Bi ₂ O ₅ —	Po	At			
Pm	Sm (87)	Eu (87)	Gd (87)	Dy (87)	Ho	Er	Tm	Yb (87)	Lu (87)	
Pm ₂ O ₃ —	Sm ₂ O ₃ 430	Eu ₂ O ₃ —	Gd ₂ O ₃ —	Tb ₂ O ₃ —	Dy ₂ O ₃ —	Ho ₂ O ₃ —	Er ₂ O ₃ —	Tm ₂ O ₃ —	Yb ₂ O ₃ —	Lu ₂ O ₃ —

TABLE 5. Heats of formation (in kcal./mole) of the principal fluorides and chlorides of the various elements at 25°. The heats of atomisation of the elements (see Section 7) are given in parentheses after the symbols for the elements. The figures refer to the crystalline state unless otherwise indicated by a superscript g or l (gas or liquid, respectively)

H (52.09) ^g HF 64.2 ^g HCl 22.06										
Li (37.07) LiF 146.3 LiCl 97.70	Be (76.63) BeF ₂ — BeCl ₂ 122.3									
Na _l (25.98) NaF 136.0 NaCl 98.23	Mg (35.9) MgF ₂ 263.5 MgCl ₂ 153.40									
K (21.51) KF 134.46 KCl 104.18	Ca (46.04) CaF ₂ 290.3 CaCl ₂ 190.0	Sc (93) ScF ₃ — ScCl ₃ 220.8	Ti (112.6) {TiF ₂ 198 TiF ₃ 370 TiCl ₂ 114 TiCl ₃ 179.3}	V (122.7) VF ₅ — VCl ₃ 108	Cr (94.0) CrF ₂ 181.0 CrCl ₂ 94.56	Mn (68.34) MnF ₂ (l) 189 MnCl ₂ 115.3	Fe (99.8) FeF ₂ 168 FeCl ₂ 81.5	Co (102.0) CoF ₂ 159 CoCl ₂ 77.8		
Rb (20.51) RbF 131.28 RbCl 102.91	Sr (39.2) SrF ₂ 290.3 SrCl ₂ 198.0	Y (103) YF ₃ — YCl ₃ 234.8	Zr (142.5) {ZrF ₂ 230 ZrF ₃ 445 ZrCl ₂ 145 ZrCl ₃ 230}	Nb (184.5) NbF ₅ — NbCl ₅ —	Mo (155.5) MoF ₆ — {MoCl ₄ 44 MoCl ₅ 90}	Tc Tc	Ru (160) RuF ₃ — RuCl ₃ 63	Rh (138) RhF ₃ — RhCl ₃ 36		
Cs (18.83) CsF 126.9 CsCl (II) 103.5	Ba (41.96) BaF ₂ 286.9 BaCl ₂ 205.56	La (88) LaF ₃ — LaCl ₃ (α) 263.6	Hf (170) HfF ₄ — HfCl ₄ —	Ta (185.6) TaF ₅ — TaCl ₅ —	W (201.6) WF ₆ 38 {WCl ₆ 98.7}	Re (189) ^g ReF ₆ 273 ReCl ₆ —	Os (174) OsF ₈ — OsCl ₂ —	Ir (165) ^l IrF ₃ 130 IrCl ₂ 42.8		
Fr	Ra (31) RaF ₂ — RaCl ₂ —	Ac Th ThF ₄ 477 ThCl ₄ 284.5	Pa U (125) {UF ₃ 357 UF ₆ 517 UCl ₃ 213.0 UCl ₄ 272.4}	Np NpF ₃ 360 NpCl ₃ 216	Pu PuF ₃ 375 PuCl ₃ 230.0	Am AmCl ₃ 251.3	Pr (87) PrF ₃ — PrCl ₃ 257.8	Nd (87) NdF ₃ — NdCl ₃ 254.3		

H (52.09)
 ρ HF 64.2
 ρ HCl 22.06

B (97.2) ρ BF ₃ 265.4 ρ BCl ₃ 94.5		C (125.0) ρ CF ₄ 231 ρ CCl ₄ 33.3		N (85.57) ρ NF ₃ 27.2 ρ NCl ₃ ~ - 55		O (59.16) ρ OF ₂ - 5.5 ρ OCl ₂ - 18.2		F (18.3) ρ FF 0.00 ρ FCI 11.6	
Al (75.0) AlF ₃ 311 AlCl ₃ 166.2		Si (88.04) ρ SiF ₄ 370 ρ SiCl ₄ 153.0		P (75.18) {PF ₃ - PF ₅ - PF ₆ , 262 P ₂ Cl ₄ , 81.0 PCl ₅ , 110.7		S (53.25) {SF ₆ - SF ₄ , 262 S ₂ Cl ₂ , 28		Cl (39.01) ρ ClF 11.6 ρ ClCl 0.00	
Ga (66.0) GaF ₃ - GaCl ₃ 125.4		Ge (84.0) GeF ₄ - ρ GeCl ₄ 130		As (60.64) {AsF ₃ 226.8 AsF ₅ - AsCl ₃ 80.2		Se (48.37) Se ρ SeF ₆ 246 ρ SeCl ₄ 9.7		Br (26.71) BrF - ρ BrCl - 3.51	
In (58.2) InF ₃ 230 InCl ₃ 128.4		Sn (72) SnF ₄ - ρ SnCl ₄ 130.3		Sb (60.8) {SbF ₃ 217.2 SbF ₅ - SbCl ₃ 91.34 SbCl ₅ 104.8		Te (47.6) Te ρ TeF ₆ 315 ρ TeCl ₄ -		I (25.48) IF ₇ - ρ ICl - 4.20	
Tl (43.34) TlF ₃ - TlCl ₃ 83.9		Pb (46.34) PbF ₄ 222.3 PbCl ₄ -		Bi (49.7) BiF ₃ - BiCl ₃ 90.61		Po		At	
Zn (31.19) ZnF ₂ 176 ZnCl ₂ 99.40		Cu (81.52) {CuF 60 CuF ₂ 126.9 CuCl 32.2 CuCl ₂ 49.2		Cd (67.8) {AgF 48.5 AgF ₃ 88.5 AgCl 30.36		Hg (14.54) HgF ₂ 95 HgCl ₂ 55.0		Pt (121.6) PtF ₄ - PtCl ₂ 35.5	
Ni (101.61) NiF ₂ 159.5 NiCl ₂ 75.5		Pd (93) PdF ₂ - PdCl ₂ 45.4		Ag (67.8) {AgF 48.5 AgF ₃ 88.5 AgCl 30.36		Au (84.6) {AuF 18 AuF ₃ - AuCl 8.4 AuCl ₃ 28.3		Pm PmF ₃ -	
Ni (101.61) NiF ₂ 159.5 NiCl ₂ 75.5		Pd (93) PdF ₂ - PdCl ₂ 45.4		Ag (67.8) {AgF 48.5 AgF ₃ 88.5 AgCl 30.36		Au (84.6) {AuF 18 AuF ₃ - AuCl 8.4 AuCl ₃ 28.3		Pm PmF ₃ -	
Pt (121.6) PtF ₄ - PtCl ₂ 35.5		Cu (81.52) {CuF 60 CuF ₂ 126.9 CuCl 32.2 CuCl ₂ 49.2		Cd (67.8) {AgF 48.5 AgF ₃ 88.5 AgCl 30.36		Hg (14.54) HgF ₂ 95 HgCl ₂ 55.0		Pm PmF ₃ -	
Sm (87) SmF ₃ -		Eu (87) EuF ₃ -		Gd (87) GdF ₃ -		Tb (87) TbF ₃ -		Dy (87) DyF ₃ -	
SmCl ₃ 249.8		EuCl ₃ 247.1		GdCl ₃ 245.		TbCl ₃ 241.6		DyCl ₃ 237.8	
Er (87) ErF ₃ -		Ho (87) HoF ₃ -		Er (87) ErF ₃ -		Tm (87) TmF ₃ -		Yb (87) YbF ₃ -	
ErCl ₃ 248.8		HoCl ₃ 243.8		ErCl ₃ 231.8		TmCl ₃ 229.5		YbCl ₃ 228.7	
Lu (87) LuF ₃ -		Lu (87) LuF ₃ -		Lu (87) LuF ₃ -		Lu (87) LuF ₃ -		Lu (87) LuF ₃ -	
LuCl ₃ 227.9		LuCl ₃ 227.9		LuCl ₃ 227.9		LuCl ₃ 227.9		LuCl ₃ 227.9	

which accounts for its explosive nature. Hydrogen peroxide, H_2O_2 (*l*), is not endothermic with respect to its elements (heat of formation 44.84 kcal./mole), but is endothermic with respect to water and oxygen, so is nevertheless capable of detonating.

Halides.—Heats of formation of the fluorides and chlorides of the various elements are set out in a similar way in Table 5. In the case of elements of variable valency, for the sake of space and clarity never more than two halides of each class are shown. On the right-hand side of the Periodic System the valencies selected are that exhibited towards hydrogen and the normal group valency, namely, 3 and 5 for Group V, 2 and 6 for Group VI, and 1 and 7 for Group VII. For the transition elements, in addition to the group valency the valency 2 has been selected as being one of the more pronounced common valencies. Where neither valency is observed, the most stable halide or one for which the heat of formation happens to be known is cited. The valency 3 has been selected for the trans-uranic elements as well as for the rare earths. Except for CF_4 ,⁵¹ SCl_2 ,⁵² ClF ,⁵³ FeF_2 ,⁵² CuF ,⁵² ZnF_2 ,⁵² InF_3 ,⁵² CeF_4 ,⁵² AuF ,⁵² HgF_2 ,⁵² ThCl_4 ,^{53a} PuF_3 ,⁵⁴ and AmCl_3 ,^{54a} the values are all taken from Rossini *et al.*²⁶

The heats of formation of the fluorides have been the subject of a special discussion.⁵⁵ As is to be expected, the fluorides exhibit values which are everywhere the highest, while those of the iodides are everywhere the lowest. The general trend of the values is similar for the fluorides, chlorides, bromides, and iodides respectively, except that the fluorides of the first two groups are anomalous. In Group I (excluding Group IB) lithium fluoride has the highest and caesium fluoride the lowest heat of formation, while in Group II calcium fluoride has the highest value. This is essentially a question of lattice energy, and it is of interest that lithium and calcium have the least soluble fluorides in their respective groups. On the other hand, the chlorides—and likewise the bromides and iodides—show uninterrupted increases in their heats of formation on passing down Groups I and II. Among the transition elements, the same behaviour is observed for all the halides in Groups IIIA, IVA, and possibly VA. Elsewhere in the Periodic System, the general tendency is for the heats of formation to decrease on passing down the groups, but there are some irregularities. In particular, those of the halides of the second period are mostly higher than those of the first. Again, from indium onwards, the values for the elements of the fourth period mostly exceed those of the elements situated immediately above them. In particular, tellurium hexafluoride has a surprisingly high heat of formation, exceeding not only that for selenium hexafluoride, but even that for sulphur hexafluoride by a wide margin. It seems that fluorine is able to form extra

⁵¹ von Wartenberg, *Z. anorg. Chem.*, 1949, **258**, 356.

⁵² Brewer, Bromley, Gilles, and Lofgren, *op. cit.* (ref. 39), p. 76.

⁵³ Wicke, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Klasse*, 1946, 89.

^{53a} Eyring and Westrum, *J. Amer. Chem. Soc.*, 1950, **72**, 5555.

⁵⁴ Westrum and Eyring, National Nuclear Energy Series, Div. IV, **14B**, Transuranium Elements, Part II, p. 908.

^{54a} Lohr and Cunningham, *J. Amer. Chem. Soc.*, 1951, **73**, 2025.

⁵⁵ Wicke, *Naturwiss*, 1946, **33**, 132.

strong bonds with elements which have vacant orbitals available for bonding, which suggests that with tellurium the unfilled $4f$ orbitals may offer themselves as such in much the same way as the unfilled $3d$ orbitals do with silicon— TeF_6 and SiF_4 are hydrolysed by water, SeF_6 and CF_4 with their lower heats of formation are not. For the trichlorides of the rare earths, there is a remarkably steady drift in the values.

Where variable valency occurs, the heat of formation per gram-atom of halogen increases with decreasing valency. This is one of the conditions for stability (cf. Section 10).

The difference between the heats of formation of the fluoride and chloride varies considerably from element to element. It reaches a maximum at boron with 57 kcal. per gram-atom of halogen and drops to about 10 for univalent gold. The difference is also small for the silver and mercuric halides, which accounts for the especially good fluorinating powers of AgF and HgF_2 .

The heats of formation of the halides are greatest in the case of the purely ionic compounds, *i.e.*, for the alkali-metal halides. The values for the halides where the bonding is neither ionic nor covalent, but transitional in type, are particularly interesting, since these compounds frequently show features of unusual interest in their crystal structures.⁴⁹

Oxides and Sulphides.—To economise in space, the values for the heats of formation of the oxides have been inserted in Table 4. Where an element forms a number of oxides, the scheme adopted has been the same as in Table 5. Oxides such as VO , CrO and FeO , which in contrast to MnO are not stable as stoichiometric compounds at 25° , are not included. Except for MgO ,^{55a} Al_2O_3 ,^{55a} SiO_2 ,⁵⁶ P_2O_3 ,^{56a} TiO ,^{56b} TiO_2 ,^{56b} GeO_2 ,^{56c} BrO_2 ,^{56d} Sm_2O_3 ,³⁰ ThO_2 ,^{56e} and AmO_2 ,^{56f} the values have been taken from Rossini *et al.*²⁶ The heats of formation of the oxides are mostly known and are more complete than for any other class of compounds, but experimental values are still lacking for the oxides of scandium, yttrium, several rare earths, and platinum, although values have been predicted for Sc_2O_3 and Y_2O_3 .³⁷ However, especially in view of the opposite trends in the values for Groups IIA and IVA, overmuch confidence cannot be placed on such predictions.

The general trends in the values for the oxides within the groups resemble those for the fluorides. That this is less true when the Periodic System is viewed horizontally in periods is due to the different crystal structures of the oxides.⁵⁷ The decrease in values from lithium to caesium is again encountered in Group I, as is the maximum at calcium in Group II. For

^{55a} Holley and Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 5577.

⁵⁶ Humphrey and King, *ibid.*, 1952, **74**, 2041.

^{56a} Koerner and Daniels, *J. Chem. Phys.*, 1952, **20**, 113.

^{56b} Humphrey, *J. Amer. Chem. Soc.*, 1951, **73**, 1587.

^{56c} Jolly and Latimer, *ibid.*, 1952, **74**, 5757.

^{56d} Pflugmacher, Schwarz, and Rabben, *Z. anorg. Chem.*, 1951, **264**, 204.

^{56e} Huber, Holley, and Meierkord, *J. Amer. Chem. Soc.*, 1952, **74**, 3406.

^{56f} Eyring, Lohr, and Cunningham, *ibid.*, p. 1186.

⁵⁷ Wells, *Quart. Reviews*, 1948, **2**, 185.

the transition elements, the first few sub-groups again exhibit increasing values on descending the group, but this behaviour here extends as far as Group VIIA, at which the *d* sub-shells are exactly half-filled. Again, the second period from aluminium and the last few elements of the fourth period—in this case from tin onwards—contain oxides possessing higher heats of formation than the preceding periods, although chlorine constitutes an exception. Iodine is the only halogen to possess an exothermic oxide.

The heats of formation of the sulphides are lower than those of the oxides, exceptions being K_2S , Rb_2S , Cs_2S , and Ag_2S . The difference is very large for boron and aluminium. A few values which may be compared with those of the oxides are (in kcal./mole): BeS (*c*) 55.9, B_2S_3 (*c*) 57.0, CS_2 (*l*) — 21.0, Al_2S_3 (*c*) 121.6, K_2S (*c*) 100, CaS (*c*) 115.3, MnS (*I*) 48.8, As_2S_3 (*c*) 35, MoS_3 (*c*) 61.2, Ag_2S (*II*) 7.6, La_2S_3 (*c*) 306.8, HgS (*II*) 13.9.

Nitrides, Phosphides, and Carbides.—The comparatively low heats of formation of the nitrides are largely to be attributed to the very high stability of the nitrogen molecule. Many nitrides are endothermic and many elements form no stable nitrides at all. The most stable nitrides are formed by the elements of Groups II to V inclusive, those of the A sub-groups having heats of formation far higher than those of the B sub-groups. A comparative study of the nitrides of the first long period has been made.⁵⁸ Lithium is the only alkali metal to possess an exothermic nitride. The formulæ of the nitrides of many elements do not correspond to the normal group valencies. The figures²⁶ for a few typical nitrides are (in kcal./mole): Li_3N 47.2, Be_3N_2 135.7, BN 32.1, Ca_3N_2 103.2, TiN 80.47,⁵⁹ VN 41, CrN 29.8, Mn_5N_2 57.8, Fe_4N 2.55, Cu_3N — 17.8, Zn_3N_2 6.9, GaN 25, Ge_3N_4 14.8.

Information regarding the heats of formation of the phosphides is far less complete, even, than for the nitrides. It is, however, quite clear that the values are *higher* than for the corresponding nitrides, this being the opposite to the changes observed on passing from the fluorides to the chlorides and from the oxides to the sulphides. The following are some typical values²⁶ (in kcal./mole): Ca_3P_2 120.5, Fe_3P 40, CoP 35, Ni_3P 53, Cu_3P 36.4.

Carbon has a higher heat of atomisation than any other element in the first period, and this is partly responsible for the low values observed generally for the heats of formation of the carbides. Furthermore, very frequently the formulæ of the carbides do not correspond to the group valencies. The most stable carbides are formed by some of the transition elements. Many are highly refractory substances, and the negligible tendency for carbon to volatilise makes them stable at very high temperatures in spite of their low heats of formation. Knowledge concerning the heats of formation is very incomplete, but some of the values²⁶ are as follows (in kcal./mole): Li_2C_2 14.2, CaC_2 15.0, Al_4C_3 30.9, TiC 43.85,⁵⁹ Cr_3C_2 21.0, Mo_2C — 4.3, Mn_3C 1, Fe_3C — 5.0, Ni_3C — 11, Ag_2C_2 — 81.9. As is well known, the last of these compounds is explosive.

Apart from the silicides of magnesium and calcium (Mg_2Si 18.6, Ca_2Si 50,

⁵⁸ Juza, *Die Chemie*, 1945, **58**, 25.

⁵⁹ Humphrey, *J. Amer. Chem. Soc.*, 1951, **73**, 2261.

CaSi 36, CaSi₂ 36 kcal./mole²⁶), little is yet known concerning the heats of formation of silicides. Although many borides have been characterised and the crystal structures of a number determined,⁶⁰ apparently nothing is known about the heats of formation of any of them except that, as a class, the transition elements form the most stable borides. This constitutes one of the many gaps in our knowledge concerning heats of formation.

Intermetallic Compounds.—The heats of formation of alloys and intermetallic compounds are frequently comparatively low. However, it may at first sight appear surprising that the observed values are on occasion comparable in magnitude with those of other inorganic compounds. A study of the numerical data in connection with other physical properties has been undertaken by Sauerwald.⁶¹ The heats of formation of rather more than 100 intermetallic compounds are known, but this is only a tiny fraction of the realisable compounds. Some of the values²⁶ are tabulated in Table 6.

TABLE 6. *Heats of formation (in kcal./mole) of some intermetallic compounds at 25°*

Compound	Q_f	Compound	Q_f	Compound	Q_f
LiHg (c)	20.8	MgCe (c)	13	Ba ₃ Bi ₂ (c)	160
LiTl (c)	12.8	MgPr (c)	8.2	Al ₃ La (c)	36.1
Li ₄ Sn (c)	47.0	MgZn ₂ (c)	12.6	Al ₂ Ce (II)	39
LiSn (c)	16.8	MgCd (II)	9.2	AlCe ₃ (c)	22
Li ₄ Pb (c)	42	MgTl (c)	11	Al ₄ Pr (c)	52.1
LiPb (c)	14.6	Mg ₂ Sn (c)	17	AlFe (c)	12
Li ₃ Sb ₂ (c)	43.5	Mg ₃ Sb ₂ (c)	68.1	Al ₄ Co (c)	38
Li ₃ Bi (c)	55.2	Mg ₃ Bi ₂ (c)	36.5	Al ₃ Co ₂ (c)	70
NaK (l)	2.4	CaAl ₃ (c)	52	AlCo (c)	26
NaCd ₂ (c)	8.4	CaZn (c)	17.4	AlNi (c)	34
NaHg (c)	10.2	CaZn ₂ (c)	22	AlCu (c)	10.0
NaHg ₂ (c)	18.3	CaCd ₃ (c)	30	CeHg ₄ (c)	21.5
Na ₂ Sn (c)	14.4	CaTl (c)	35	FeSb (c)	- 2.4
NaSn (c)	12	Ca ₂ Sn (c)	75	CoSb (c)	10
Na ₂ Pb (c)	15.6	CaSn (c)	38	NiSn (c)	14.8
NaPb (c)	11.6	Ca ₂ Pb (c)	47	NiSb (c)	15.6
Na ₃ Sb (c)	47.2	CaPb (c)	25	Cu ₂ Zn ₃ (c)	16
Na ₃ Bi (c)	45.6	Ca ₃ Sb ₂ (c)	155	Cu ₃ Sn (c)	8
KHg (c)	11.6	Ca ₃ Bi ₂ (c)	112	Ag ₂ Zn ₃ (c)	9.5
KHg ₂ (c)	17.7	Ba ₃ Sn (c)	90	AuSb ₂ (III)	4.8
Mg ₂ Ca (c)	30.0	Ba ₂ Pb (c)	69	ZnSb (c)	36
Mg ₄ Al ₃ (c)	48.7	BaPb (c)	36	CdSb (c)	3.29
MgLa (c)	5.7	Ba ₃ Sb ₂ (c)	175	Hg ₅ Tl ₂ (c)	2.5

7. Heats of Formation and Crystal Energies

The crystal energy of an ionic lattice is the energy liberated on its formation from free ions at infinite distance. Subject to certain simplifying assumptions, this energy can be derived theoretically, as has long been realised.⁶²⁻⁶⁴ The derivation will not be repeated here, as it is given in

⁶⁰ Kiessling, *Acta Chem. Scand.*, 1950, **4**, 209; *J. Electrochem. Soc.*, 1951, **98**, 166, 518.

⁶¹ *Z. Metallk.*, 1943, **35**, 105.

⁶² Appell, *Acta Math.*, 1884, **4**, 313.

⁶³ Madelung, *Physikal. Z.*, 1918, **19**, 524.

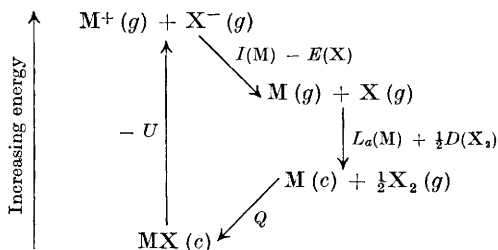
⁶⁴ Born, *Z. Physik*, 1921, **7**, 124.

numerous text-books. Suffice it to say that, with rigid ions the crystal energy, U_0 , is given by $U_0 = NAz^2e^2/r_0$ where N is Avogadro's number, A is a constant dependent on the crystal type⁶⁵ and known as the Madelung constant, z is an integer giving the multiple of the ionic charge with respect to that for which A has been derived for the respective crystal type, e is the electronic charge, and r_0 is the interionic distance. This energy arises from the Coulomb attractive forces, which are counterbalanced at equilibrium distance by repulsive forces. Since the ions are not rigid, the latter forces come into effect at larger distances, thus reducing the lattice energy. It can be shown that U_0 is reduced by a factor equal to $1/n$, where n is the exponent of the distance r in the expression reproducing the decrease of the repulsive forces with distance. Thus

$$U_0 = (1 - 1/n)NAz^2e^2/r_0 \quad . \quad . \quad . \quad (1)$$

The value of n can be determined for the crystal species from compressibility measurements. It varies from case to case according to the ionic species present, but lies between 5 and 12. The above expression has been further refined by Born and Mayer⁶⁶ to allow for van der Waals forces and zero-point energy.

Experimentally, the crystal energy is related to the heat of formation and other thermochemical quantities by the well-known Born-Haber cycle,^{67, 68} which for the special case of an alkali halide, MX, can be represented schematically in the following manner :



It is immediately apparent that

$$U = Q + L_a(M) + I(M) + \frac{1}{2}D(X_2) - E(X) \quad . \quad . \quad . \quad (2)$$

where $L_a(M)$ is the heat of atomisation of the metal, $I(M)$ its ionisation potential, $D(X_2)$ the dissociation energy of the halogen, and $E(X)$ its electron affinity [$\frac{1}{2}D(X_2)$ must be replaced by the heat of atomisation of the non-metal when the latter is not a diatomic gas at ordinary temperatures].

Some ionisation energies⁶⁹ are given in Table 7. The electron affinities⁶⁹ of hydrogen and the halogens are listed in Table 8. The accuracy of the figures is generally very high in the case of the ionisation energies derived from spectral series and, except for the electron affinity of fluorine, reasonably so for the remaining figures.

⁶⁵ Sherman, *Chem. Reviews*, 1932, **11**, 93.

⁶⁶ *Z. Physik*, 1932, **75**, 1.

⁶⁷ Born, *Verh. deut. physikal. Ges.*, 1919, **21**, 13.

⁶⁸ Haber, *ibid.*, p. 750.

⁶⁹ Herzberg, "Atomic Spectra and Atomic Structure" (2nd edn., New York, 1944).

TABLE 7. *Ionisation energies (in kcal./g.-atom) of hydrogen and some metals*

Element	Ionisation energy :			Element	Ionisation energy :		
	1st electron	2nd electron	3rd electron		1st electron	2nd electron	3rd electron
H . . .	313.4			Fe . . .	181.2	374.4	705
Li . . .	124.3			Co . . .	181.6	401	
Na . . .	118.4			Ni . . .	176.0	420	
Mg . . .	176.2	346.5		Cu . . .	178.0	466.6	
Al . . .	138.0	433.9	655.7	Zn . . .	217.5	414.0	
K . . .	100.1			Ag . . .	174.6		
Ca . . .	140.9	273.6		Cd . . .	207.3	389.7	
Mn . . .	171.3	358.5					

TABLE 8. *Electron affinities (in kcal./g.-atom) of hydrogen and the halogens*

Element	H	F	Cl	Br	I
Electron affinity	16.5	95.3*	85.8	80.5	72.4

* This figure must be regarded as highly uncertain. If the lower value (30—40 kcal./mole) for the energy of dissociation of the fluorine molecule should become finally established—and considerable evidence for it has accumulated latterly—application of the Born-Haber cycle to the alkali-metal fluoride lattices leads to an electron affinity for fluorine which is *lower* than that for chlorine. See also Johnston, *J. Chem. Phys.*, 1951, **19**, 1391.

The same is not always true of heats of atomisation, many of which in the face of sparse and discordant vapour-pressure data are little more than judicious guesses. Although a number of heats of atomisation, particularly for the more volatile elements, are known with fair precision, the values for nitrogen, fluorine, and many of the less volatile elements are still subject to considerable uncertainty. The values derived may only be considered reasonably reliable when the figures obtained by application of the second and third laws of thermodynamics respectively are in good agreement. Frequently, as, *e.g.*, in the case of tin,⁷¹ this is far from being the case. Values for most of the elements are listed by Rossini *et al.*²⁶ and by Brewer.⁷⁰ Their respective values differ appreciably in the cases of beryllium, boron, calcium, arsenic, niobium, antimony, tellurium, platinum, and thallium. More recent values are available for titanium,⁷¹ vanadium,^{71a} chromium,^{71b} iron,^{71c} cobalt,^{71c} germanium,^{71d} zirconium,^{71e} silver,⁷² tantalum,^{72a} and

⁷⁰ Brewer, National Nuclear Energy Series, Div. IV, **19B**, Chem. and Met. of Misc. Materials, p. 13 (1950).

⁷¹ Carpenter and Mair, *Proc. Phys. Soc.*, 1951, **64B**, 57.

^{71a} Edwards, Johnston, and Blackburn, *J. Amer. Chem. Soc.*, 1951, **73**, 4727.

^{71b} Speiser, Johnston, and Blackburn, *ibid.*, 1950, **72**, 4142.

^{71c} Edwards, Johnston, and Ditmars, *ibid.*, 1951, **73**, 4729.

^{71d} Searcy, *ibid.*, 1952, **74**, 4789.

^{71e} Skinner, Edwards, and Johnston, *ibid.*, 1951, **73**, 174.

⁷² Schadel and Birchenall, *J. Metals, Trans.*, 1950, **188**, 1134.

^{72a} Edwards, Johnston, and Blackburn, *J. Amer. Chem. Soc.*, 1951, **73**, 172.

gold,^{72b} and these (adjusted, where necessary, to 25°) have been included in Tables 4 and 5. Otherwise, except in the case of carbon, Rossini's values have been inserted uncritically in Tables 4 and 5, although this is not to be interpreted that they are favoured to Brewer's. The value for hafnium is due to Brewer. The figure these authors quote for carbon is based on calculations assuming an accommodation coefficient of approximately unity for this element and conflicts with much other evidence reviewed elsewhere.⁷³ Recently, Goldfinger and his co-workers⁷⁴ have found that the accommodation coefficient of carbon is of the order 10^{-3} to 10^{-4} , and obtain a much lower experimental value (~ 146 kcal./g.-atom) for the heat of atomisation. Electron-impact studies on CO⁷⁵ have yielded the figure ~ 136 , and those on CH₄⁷⁶ and CH₃·CN⁷⁶ ~ 120 – 125 with an upper limit of 140. Electron-impact work on other molecules^{76a-c} is in general harmony with these results. There is therefore no difficulty in accepting the upper limit of 135 kcal./g.-atom for the heat of atomisation of carbon as fixed by the photodissociation of CO.⁷⁷ Accordingly, it seems that the most probable value is 125.0 kcal./g.-atom obtained from a predissociation observed in the CO spectrum,⁷⁸ and this figure has been entered in Tables 4 and 5, though any value between 125 and 135 kcal./g.-atom could be harmonised with the evidence.

There are thus two principal methods of determining the lattice energies of purely ionic compounds. For any crystal type, the lattice energy obviously decreases as the ionic radii increase. From a study of the inter-relationship between heats of formation and crystal energies, it was early realised⁷⁹ that salts of cations with 18 electrons in their outer shells possess higher lattice energies than those of cations with the rare-gas electronic structure. The difference is due to the higher polarisabilities of the former, which have the effect of increasing the heats of formation.⁸⁰ Departure from strict heteropolarity is in this way revealed for a number of halides of the heavy metals.⁸¹

This method has been utilised by Sherman⁶⁵ for a wide range of compounds including not only halides, but also oxides, sulphides, and selenides. For typically ionic compounds such as the alkali halides, the theoretical value of U_0 may be used for calculating the electron affinity of the halogen by means of equation (2), and consistent values are obtained thereby. Thus the electron affinity of fluorine—*i.e.*, the heat of formation of the

^{72b} Hall, *J. Amer. Chem. Soc.*, 1951, **73**, 757.

⁷³ Long, *Proc. Roy. Soc.*, 1949, *A*, **198**, 62.

⁷⁴ Doechaerd, Goldfinger, and Waelbroeck, *J. Chem. Phys.*, 1952, **20**, 757.

⁷⁵ Hagstrum, *Rev. Mod. Physics*, 1951, **23**, 185.

⁷⁶ McDowell and Warren, *Discuss. Faraday Soc.*, 1951, **10**, 53.

^{76a} Branson and Smith, *J. Chem. Phys.*, 1952, **20**, 1047.

^{76b} Field, *ibid.*, 1951, **19**, 793.

^{76c} McDowell and Warren, *Trans. Faraday Soc.*, 1952, **48**, 1084.

⁷⁷ Faltings, Groth, and Harteck, *Z. physikal. Chem.*, 1938, *B*, **41**, 15.

⁷⁸ Herzberg, *J. Phys. Chem.*, 1942, **10**, 306.

⁷⁹ Grimm, *Z. physikal. Chem.*, 1922, **102**, 113, 141, 504.

⁸⁰ Born and Heisenberg, *Z. Physik*, 1924, **23**, 388.

⁸¹ Rabinowitsch and Thilo, *Z. physikal. Chem.*, 1930, *B*, **6**, 284.

fluoride ion from a fluorine atom plus an electron—as calculated from the lattice energies of LiF, NaF, KF, RbF, and CsF is constant to within about 2 kcal. This method being applied to the oxides of the alkaline-earth metals, the heat of formation of the oxide ion from an oxygen atom and two electrons can be likewise calculated. The values are, however, not consistent, and show a steady drift from BaO to MgO amounting to about 20 kcal. This may in part be attributable to the heat of formation of the oxide ion varying somewhat according to its surroundings, but the effect is doubtless also brought about by departure of these oxides from strict heteropolarity. Thus X-ray studies of MgO have revealed that the ions in this compound, in contrast to those in NaCl, for example, are not truly discrete, which is not difficult to understand in view of the fact that the heat of formation of the oxide ion is strongly negative, whereas for a halide ion it is positive.

Sherman then proceeds to use the mean values thus obtained for the halide and oxide ions to calculate the lattice energies of numerous other halides and oxides by means of equation (2). Some of these experimental values are reproduced uncorrected in Table 9 along with the theoretical values calculated for strict heteropolarity by means of equation (1).

TABLE 9. *Comparison of crystal energies (in kcal./mole) derived experimentally by means of the Born-Haber cycle with the theoretical values for strict heteropolarity (after Sherman⁶⁵)*

Compound	Structure type	$U_{\text{exp.}}$	$U_{\text{calc.}}$	Difference
MgF ₂ . . .	Rutile	688.8	696.8	— 8.0
CaF ₂ . . .	Fluorite	617.2	617.7	— 0.5
MnF ₂ . . .	Rutile	645.0	656.3	— 11.3
NiF ₂ . . .	Rutile	733.5	697.1	+ 36.4
CdF ₂ . . .	Fluorite	661.9	628.7	+ 33.2
CuCl . . .	Sphalerite	228.1	206.1	+ 22.0
SrCl ₂ . . .	Fluorite	494.0	493.6	+ 0.4
AgI . . .		201.9	175.9	+ 26.0
CdI ₂ . . .	Lead iodide	563.1	477.0	+ 86.1
Li ₂ O . . .	Antifluorite	693	695	— 2
MnO . . .	Rock-salt	959	912	+ 47
NiO . . .	Rock-salt	966	968	— 2
Cu ₂ O . . .	Cuprite	786	682	+ 104
ZnO . . .	Wurtzite	970	977	— 7
Ag ₂ O . . .	Cuprite	715	585	+ 130
CdO . . .	Rock-salt	911	867	+ 44
PbO ₂ . . .	Rutile	2832	2620	+ 212

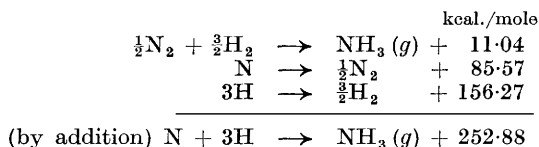
Although the utilisation of more recent thermochemical and crystallographical data would change some of the individual values somewhat, the general trend is unmistakable. Agreement is excellent for many compounds such as CaF₂, SrCl₂, or Li₂O, suggesting (but not proving) that they are truly ionic. For others, such as CuCl, AgI, CdI₂, Ag₂O, and PbO₂, ($U_{\text{exp.}} - U_{\text{calc.}}$) is strongly positive, implying considerable departure from strict heteropolarity. Heats of formation are thus not only serviceable for deriving lattice energies, important quantities not in the ordinary way

directly measurable, but also for deriving information concerning the state of bonding in crystals.

8. Heats of Formation and Bond Energies

Apart from the special cases of molecules of elements and of certain other diatomic molecules suitable for spectroscopic, electron-impact, kinetic, or equilibrium studies, the evaluation of bond energies cannot be made without a knowledge of heats of formation. In this section we are concerned with compounds which are essentially covalent in nature, the molecules of which are therefore more appropriately regarded as built up from free atoms than from ions, since the forces holding them together are decidedly not those of Coulomb attraction. Consequently the energy which is of fundamental importance here is the *atomic heat of formation*. The atomic heats of formation of molecules are simply calculated from the experimental heats of formation of the *gaseous* compounds by the addition of the appropriate heats of atomisation of the elements concerned (cf. Tables 4 and 5). It was early realised that the energy of a molecule obtained in this way could be divided up either among the atoms participating⁸² or among the chemical bonds present.⁸³ The values obtained by either method are, with certain restrictions, approximately additive. Although both are equally justifiable empirically, it is the latter method which has received by far the greater attention. The energy which is assigned to a particular bond is known as the "bond energy".

An illustration of the way in which bond energies are calculated is provided for the case of the N-H bond in ammonia :



The figure 252.88 kcal. represents the heat liberated on the formation of three N-H bonds, so that the (average) N-H bond energy is stated to be 84.3 kcal. Where a compound is liquid or solid at ordinary temperatures the heat of formation includes van der Waals forces, and these must be allowed for by subtracting the heat of volatilisation. Some bond energies calculated in this way are listed in Table 10.

For molecules containing more than one kind of bond, a certain arbitrariness in partitioning the energy is unavoidable. The usual method is to assume the strict validity of the postulate of additivity in bond energies and insert values for bond energies obtained from other molecules. By way of example, the N-N bond energy in hydrazine may be calculated by assuming that the N-H bond energy is the same as in ammonia. Since, however, it can be demonstrated that bond energies vary from compound to compound, this procedure is inaccurate. Thus a variation of 2 kcal.

⁸² Swietoslawski, *Bull. Soc. chim.*, 1921, **29**, 496.

⁸³ Fajans, *Z. Physik*, 1920, **1**, 101; *Ber.*, 1920, **53**, 643.

in the N-H bond energy would lead to an error of 8 kcal. in the N-N bond energy in the example cited. In compounds containing multiple bonds, the departure from strict additivity of bond energies is likely to be particularly large. A well-known example is that provided by conjugated hydrocarbons.

TABLE 10. *Net bond energies and bond lengths for some volatile binary inorganic compounds*

Bond	Compound	Net energy (kcal.)	Length (Å)	Bond	Compound	Net energy (kcal.)	Length (Å)
F-H	HF	148.5	0.92	As-Cl	AsCl ₃	73.1	2.16
Cl-H	HCl	103.2	1.32	Sb-Cl	SbCl ₃	74.3	2.37
Cl-F	ClF	72.9	1.63	Bi-Cl	BiCl ₃	67.1	2.48
Br-H	HBr	87.5	1.41	C-H	CH ₄	87.8	1.09
Br-Cl	BrCl	52.2	2.14	C-F	CF ₄	121.3	1.36
I-H	HI	71.4	1.60	C-Cl	CCl ₄	66.6	1.76
I-F	IF ₅	76.3*	1.75	C-O	CO ₂	168.7	1.16
I-Cl	ICl	50.4	2.32	C-S	CS ₂	102.0	1.55
I-Br	IBr	42.4	2.48	C-Se	CSe ₂	87.9	
O-H	H ₂ O	110.6	0.96	Si-H	SiH ₄	77.8	1.46
O-F	F ₂ O	56.1	1.41	Si-F	SiF ₄	146.8	1.54
O-Cl	Cl ₂ O	44.5	1.68	Si-Cl	SiCl ₄	87.4	2.02
S-H	H ₂ S	81.1	1.33	Si-Br	SiBr ₄	70.3	2.15
S-F	SF ₆	84.8	1.58	Ge-Cl	GeCl ₄	79.1	2.08
S=O	SO ₃	108.4	1.43	Sn-Cl	SnCl ₄	77.5	2.30
Se-H	H ₂ Se	66.0	1.50	B-F	BF ₃	153.1	1.29
Se-F	SeF ₆	81.3	1.68	B-Cl	BCl ₃	92.9	1.74
Se-Cl	SeCl ₂	58.0	2.00	B-Br	BBr ₃	74.0	1.87
Te-H	H ₂ Te	57.4	1.69	Hg-F	HgF ₂	79.0	
Te-F	TeF ₆	92.7	1.82	Hg-Cl	HgCl ₂	54.5	2.3
N-H	NH ₃	84.3	1.01	Hg-Br	HgBr ₂	44.8	2.4
N-F	NF ₃	69.8	1.37	Hg-I	HgI ₂	35.1	2.6
P-H	PH ₃	73.4	1.46	Ir-F	IrF ₆	80.0	
P-Cl	PCl ₃	78.5	2.02	Os=O	OsO ₄	122.6	1.66
P-Br	PBr ₃	63.7	2.2	Re-F	ReF ₆	109.3	
As-H	AsH ₃	58.6	1.56	Tl-Cl	TlCl ₄	99.7	2.2
As-F	AsF ₃	125.2	1.72	U-F	UF ₆	137.3	~2.0

* Heat of formation of IF₅ from Woolf, *J.*, 1951, 231.

Two points need specific mention. The first—which will be dealt with in greater detail in Section 11—is that the values listed in Table 10 are net quantities and are not suitable for directly relating them to other bond properties,⁸⁴ since they do not represent the absolute or intrinsic energies of the respective bonds. The reason for this is that the internal energy of an atom in combination is not identical with that of the free atom (as is tacitly assumed in deriving bond energies thermochemically), but is increased by an amount equivalent to the respective “valency-state energy”. The second point is, that with multivalent elements the energy required to rupture one bond of a molecule is not equivalent to the average bond energy for the respective molecule; *e.g.*, the energy required to dissociate one

⁸⁴ Cottrell and Sutton, *Quart. Reviews*, 1948, **2**, 260.

N-H bond in ammonia, $D(\text{NH}_2\text{-H})$, is 104 ± 2 kcal./mole,⁸⁵ whereas the net N-H bond energy is 84.3 kcal. The difference is in part caused by the valency-state energy of nitrogen, which is considerable, and in part by the "energy of reorganisation"⁸⁶ of the NH_2 radical. The subject of dissociation energies has been reviewed elsewhere.⁸⁷

9. Heats of Formation and Other Physical Properties

From the foregoing it is clear that heats of formation are composite quantities related to other energetic terms, namely, crystal energies, heats of dissociation and atomisation, ionisation potentials, electron affinities, bond energies, and valency-state energies. Consequently, such regularities as have been observed in the trends of the heats of formation must be reflections of like regularities in the trends of the other energetic terms involved. It follows also that any attempt to derive a means for calculating heats of formation empirically is likely to become involved,⁸⁸ and that simple relationships with other physical properties are not in general to be expected. Nevertheless, where such physical properties are themselves connected with the factors governing heats of formation, relationships may be discoverable. Two which have been the object of considerable study in this connection are molecular volumes (including the closely connected coefficients of expansion) and vibrational frequencies, and it would be profitable to glance at the outcome of these investigations.

Although it was early recognised^{89, 90} that there is a connection between the heat liberated and the contraction undergone by a compound on formation from its component elements, serious attempts to interrelate them on a quantitative basis were only undertaken during the second and the third decade of the present century. For condensed (solid or liquid) compounds, Bousfield⁹¹ observed that the heat of formation, Q , approximately obeyed a relationship of the type $Q = H_1 + H_2 + k \delta v$, where H_1 and H_2 are heat components characteristic of the elements or radicals participating in the compound, k is a constant, and δv is the molecular contraction on formation.

Collins⁹² likewise started from the thesis that the contribution to both the molecular volume and the heat of formation is specific for each element, and attempted to demonstrate from a large number of compounds that, for an element, the contribution to the heat of formation is proportional to the product of its atomic weight and volume contraction with respect to the element in the solid state.

Another linear relationship obtained by Balandin⁹³ has the form $C = k - Q/Q_0$. Here C is the "contraction constant" (namely, the volume of the compound divided by that of the uncombined elements),

⁸⁵ Szwarc, *Proc. Roy. Soc.*, 1949, *A*, **198**, 267.

⁸⁶ Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103.

⁸⁷ Szwarc, *Chem. Reviews*, 1950, **47**, 75; *Quart. Reviews*, 1951, **5**, 22.

⁸⁸ See, e.g., Fehrlé, *Physikal. Z.*, 1918, **19**, 281; 1919, **20**, 330.

⁸⁹ Muller-Erzbach, *Ber.*, 1881, **14**, 217.

⁹⁰ Richards, *Z. physikal. Chem.*, 1902, **40**, 169, 597.

⁹¹ *Proc. Roy. Soc.*, 1913, *A*, **88**, 147.

⁹² *Chem. News*, 1922, **125**, 81, 97.

⁹³ Balandin, *Z. physikal. Chem.*, 1925, **116**, 123.

k an empirical constant of the order of unity, and Q_0 an empirical energy dimension related to the heat of atomisation of the anionic component (both k and Q_0 are affected by the valency of the cation). For a large number of halides, hydroxides, and sulphates the normal deviation was observed to be of the order of 1%, but for some others (e.g., silver compounds) was about ten times as much.

Possibly a more satisfactory relationship is that due to Beck,⁹⁴ $kQ = RT(\log v_r - \log v_p)$, where k is an empirical constant (equal to 1.31 for the alkali halides) and v_r and v_p are the total volumes of the reactants and products respectively. Another relationship,⁹⁵ namely, $Q = 1.33z \times 10^5(\delta v)^{1/3}$ (z being the valency of the cation), has been tested only for the halides of the alkali and alkaline-earth metals. It receives qualitative confirmation in the work of Thomas and Wood,⁴⁰ who find that the reactions between alkali halides invariably proceed in such a direction that the average of the cube edges of the stable pair assumes the least possible value.

In addition to the foregoing, evidence has recently been put forward suggesting that a quantitative relation exists between the heat of formation and the *ionic potential* of the cationic component, that is to say, the ratio of the charge on the cation to its crystal radius.^{95a}

The different mathematical expressions for the relationship, and the fact that each contains one or more empirical constants or has limited applicability, suggests that the last word has not yet been said concerning the connection between contraction and heats of formation. That there is a connection is indisputable, since large contractions are associated with high heats of formation and *vice versa*. From general considerations this is not surprising, since for ionic compounds high lattice energies, and for covalent compounds high bond energies, are to be associated with small internuclear distances. Another related property which might similarly be expected to be connected with the heat of formation is the coefficient of thermal expansion, and, indeed, for the alkali halides at least,⁹⁶ the one is observed to be inversely proportional to the other.

On turning to consider the relationship between heats of formation and infra-red frequencies of crystalline compounds, one again finds a number of relationships. Possibly the most satisfying is that due to Lewis,⁹⁷ *viz.*, $Q = Nh(\sum \nu_{\text{resultants}} - \sum \nu_{\text{reactants}})$. Here N is Avogadro's number, h is Planck's constant, and the ν values are the frequencies of the chemical species concerned. Lewis's equation is a logical extension of the pioneer work of Lindemann⁹⁸ and Haber,⁹⁹ which in turn followed on the still earlier studies of Stark and Nernst on specific heats. The importance of the expression has perhaps not been generally recognised, and it would merit re-examination in the light of modern knowledge. One interesting side-light on its applicability is the fact that Lewis was able therefrom to deduce

⁹⁴ *Z. anorg. Chem.*, 1926, **156**, 288; 1927, **161**, 76; 1928, **174**, 31; 1929, **182**, 332.

⁹⁵ Balce, *Univ. Philippines Nat. and Appl. Sci. Bull.*, 1934, **4**, 119.

^{95a} Cartledge, *J. Phys. Colloid Chem.*, 1951, **55**, 248.

⁹⁶ Henglein, *Z. Elektrochem.*, 1925, **31**, 424.

⁹⁷ *J.*, 1917, **111**, 1086.

⁹⁸ *Verh. deut. physikal. Ges.*, 1911, **13**, 1107.

⁹⁹ *Ibid.*, p. 1117.

the energy required to rupture the carbon-carbon link in cyanogen, that is, the dimension of $D(\text{NC-CN})$. The value he obtained (115.2 kcal./mole) agrees quite well with that which now appears to be correct,^{73, 76c, 99-101} but not with other highly discordant values proposed in the interim.

An alternative expression due to Henry^{102, 103} assumes the form $Q = 3NMhc/\lambda_0J$, where M is the molecular weight, c the velocity of light, J the mechanical equivalent of heat, and λ_0 the average extinction wavelength of the compound in the infra-red. Since this takes no account of the frequencies of the elements concerned, this expression is probably less reliable. The same is true of the expression of the form $Q = k - k'(\nu_1 - \nu_2)$ deduced by Balandin,¹⁰⁴ in which ν_1 and ν_2 are the frequencies of the two residual rays ("Reststrahlen") of the compound in the infra-red. An additional disadvantage here is that the constants k and k' must be determined empirically for a few known compounds, but the relationship is also found to hold for certain gaseous compounds, even though the assumptions involved are not wholly valid for the latter.

A relation linking the ultra-violet radiation frequency to the heat of formation has also been derived.¹⁰⁵

10. Variable Valency and Stability

The question of stability in relation to valency is one of such great interest in inorganic chemistry that this Review could scarcely be regarded as complete without reference to it. Grimm and Herzfeld¹⁰⁶ have devised a method for estimating the heats of formation of ionic compounds in which the metal shows an unusual valency. The method makes use of known heats of formation and the Born-Haber cycle (see Section 7), and it is immaterial whether the compounds are preparable or merely hypothetical.

The Born-Haber cycle is equally valid for the real compound Na^+Cl^- and the hypothetical compound Ne^+Cl^- :

$$Q(\text{NaCl}) = U(\text{NaCl}) - L_a(\text{Na}) - I(\text{Na}) - \frac{1}{2}D(\text{Cl}_2) + E(\text{Cl})$$

$$Q(\text{NeCl}) = U(\text{NeCl}) - L_a(\text{Ne}) - I(\text{Ne}) - \frac{1}{2}D(\text{Cl}_2) + E(\text{Cl})$$

If it is now assumed that NeCl would have approximately the same lattice energy as NaCl , then, by subtraction,

$$Q(\text{NeCl}) \approx Q(\text{NaCl}) - L_a(\text{Ne}) + L_a(\text{Na}) - I(\text{Ne}) + I(\text{Na})$$

Since all the terms on the right-hand side of the equation are known, $Q(\text{NeCl})$ can be estimated. In like manner, $Q(\text{MgCl})$ can be deduced. In point of fact, the Ne^+ ion with its small nuclear charge would probably be slightly larger than the Na^+ ion, and the Mg^+ ion with an odd electron in the M shell certainly would be. The lattice energies of NeCl and MgCl would accordingly be reduced below that of NaCl , so that the estimates obtained in this

^{99a} Stevenson, *J. Chem. Phys.*, 1950, **18**, 1347.

¹⁰⁰ Brewer, Templeton, and Jenkins, *J. Amer. Chem. Soc.*, 1951, **73**, 1462.

¹⁰¹ Szwarc and Taylor, *Trans. Faraday Soc.*, 1951, **47**, 1293.

¹⁰² *Mem. Real Acad. Ciencias Barcelona*, 1921, **17**, No. 7.

¹⁰³ *Compt. rend.*, 1924, **178**, 2248.

¹⁰⁴ *Z. Physik*, 1924, **26**, 145.

¹⁰⁵ Bernoulli, *Helv. Chim. Acta*, 1920, **2**, 720.

¹⁰⁶ *Z. Physik*, 1923, **19**, 141.

way may be regarded as upper limits. Energies of transformation due to possible changes in lattice type would be negligible in comparison with the large differences observed.

For multivalent cations, the total ionisation energy must be included in the calculation. Figures for the total ionisation energies of the first four elements of the second short period are listed in Table 11, and values calculated in the foregoing manner for the heats of formation of the various fluorine compounds in Table 12. (The value for AlF_4 has been calculated for a molecular model with the same bond energy as SiF_4 .) The line in Table 12 separates the unstable endothermic compounds from the exothermic, and corresponds to a particularly high jump in ionisation energy in Table 11.

TABLE 11. *Total ionisation energy (in kcal./g.-atom)*

Ne ⁺ 497	Na ⁺ 118	Mg ⁺ 176	Al ⁺ 138
	Na ⁺⁺ 1209	Mg ⁺⁺ 523	Al ⁺⁺ 572
		Mg ⁺⁺⁺ 2370	Al ⁺⁺⁺ 1228
			Al ⁺⁺⁺⁺ 3993

TABLE 12. *Heats of formation of fluorides (in kcal./mole)*

NeF < - 217	NaF 136	MgF < 68	AlF < 67
	NaF ₂ < - 413	MgF ₂ 263	AlF ₂ < 175
		MgF ₃ < - 792	AlF ₃ 311
			AlF ₄ ~ - 1323

The question now arises whether any of the subhalides will be stable. Since the reaction $2\text{MgF} \rightarrow \text{MgF}_2 + \text{Mg}$ will, according to the data in Table 12, liberate a large amount of energy, MgF will not be stable—or, at the most, will be metastable—and tend to disproportionate spontaneously; *i.e.*, the criterion of stability is that the heat of formation (or, more strictly, the free energy of formation) of MgF exceeds one-half that of MgF_2 . Likewise, AlF will not be stable in the solid state, since its heat of formation is less than one-third that of AlF_3 . This is not to say that molecules such as AlF will not exist in the vapour phase. Indeed, the heat of formation of gaseous AlF has been estimated from equilibrium data to be 49 kcal./mole.¹⁰⁷ Since the latent heats of fusion and vaporisation of AlF have respectively been estimated to be 5 and 38 kcal./mole,¹⁰⁸ the discrepancy with the value obtained by Grimm and Herzfeld's very approximate method is only of the order of 25 kcal./mole. Whereas this procedure clearly indicates that the subhalides of magnesium will be unstable in the solid state, yet for the subhalides of the alkaline-earth metals it yields values for the heats of formation high enough to suggest that, in view of the inaccuracies involved, these compounds may be on the verge of stability. Experience teaches that this is indeed the case. Values for the heats of formation of the alkaline-earth subhalides have been estimated by Hush,¹⁰⁹ and for those of the subhalides of aluminium by Irmann.^{109a}

¹⁰⁷ Gross, Campbell, Kent, and Levi, *Discuss. Faraday Soc.*, 1948, **4**, 206.

¹⁰⁸ Brewer, *op. cit.*, (ref. 39), p. 193.

¹⁰⁹ *J. Proc. Roy. Soc. N.S.W.*, 1949, **82**, 229.

^{109a} *Helv. Chim. Acta*, 1950, **33**, 1449.

From a comparison of the figures cited for sodium and magnesium in Tables 11 and 12, it will be apparent that if the jump in the ionisation energy on passing from one valency to another is too high, then the higher valency (here 2) corresponds to an unstable compound: if, on the other hand, it is too low, then the compound corresponding to the lower valency (here 1) becomes metastable or totally unstable and liable to disproportionate. Intermediate magnitudes in ionisation energy appear with many of the transition elements, so that these elements commonly form whole series of stable compounds in which successive steps in valency are realised. As an example, the heats of formation of the solid halides of molybdenum²⁶ (those of the fluorides are unfortunately not known) are given in Table 13.

TABLE 13. *Heats of formation of the molybdenum halides*

Chlorides	Q_f (kcal./mole)	Bromides	Q_f (kcal./mole)	Iodides	Q_f (kcal./mole)
MoCl ₂	44	MoBr ₂	29	MoI ₂	12
MoCl ₃	65	MoBr ₃	41	MoI ₃	15
MoCl ₄	79	MoBr ₄	45	MoI ₄	18
MoCl ₅	90.8	MoBr ₅	51	MoI ₅	18
MoCl ₆	90	—	—	—	—

The figures for each column of halides lie almost on smooth curves. Van Arkel¹¹⁰ has recently discussed the various possible types of curves that may in theory be obtained for the halides of an element of variable valency. The iodides and bromides frequently give curves belonging to type *C* (see Fig. 9), in which a maximum is observed rendering the highest halides unstable. The increment in the heats of formation on passing from the bromide to the chloride (or from the chloride to the fluoride) varies according to simple theory in proportion to the square of the valency, so that the chlorides of higher valency are further stabilised with respect to those of lower valency, and a curve of type *B* (Fig. 9) may be realised for the chlorides, whereupon the highest chlorides are stable. (A glance at the values in Table 13 will show that the increments for the molybdenum halides are qualitatively but not quantitatively in agreement with the simple theory.) If now, on passing to the fluorides, the further enhancement of stability of the compounds of higher valency is such as to make the curve for the fluorides convex towards the valency axis (type *A*, Fig. 9), then the lower fluorides become metastable, since they liberate heat on disproportionation. This explains in principle why frequently the maximum valency is realised only in the case of the fluorides. Thus VF₅ exists, but the highest chloride of vanadium is VCl₄ and the highest bromide VBr₃. For molybdenum (Table 13), the hexachloride and pentaiodide are on the verge of stability, while the hexabromide and hexaiodide apparently do not exist and would at least be thermochemically unstable with respect to the pentahalides. That a higher compound may have a smaller heat of formation than a lower compound need not imply that the former is incapable of

¹¹⁰ *Research*, 1949, **2**, 307.

existence if it can be prepared indirectly. Thus rhenium heptasulphide, Re_2S_7 , decomposes into ReS_2 and sulphur with the liberation of heat so that it cannot be prepared from the elements ; but it can be prepared indirectly, and is metastable at ordinary temperatures.¹¹¹

Where a change in valency of a non-metal is involved, the picture is rather different, in that now bonding pairs of electrons have to be unpaired, and the valency increases by steps of two. The promotion involved at each step involves absorption of energy, the atom thereby becoming excited to a new valency state (see next section). An increase in valency usually decreases the bond length and increases the stretching force constant of the bonds. It may further be inferred that the bond polarity decreases. These factors are to be associated with an increase in the absolute or intrinsic energy of each bond. Nevertheless, when the above-mentioned promotional energy is taken into account, the net (or thermochemical) bond energy is usually decreased.

The chlorides of iodine may serve as an example. The heat of formation of gaseous ICl from gaseous I_2 and Cl_2 is 3.24 kcal./mole, from which the bond energy may be estimated to be 50.3 kcal. from the dissociation energies of iodine and chlorine. The trichloride, ICl_3 , is stable as a solid, but the vapour breaks down into $\text{ICl} + \text{Cl}_2$, from which it appears that the net $\text{I}-\text{Cl}$ bond energy in ICl_3 is depressed considerably below that in ICl . For the reaction $\text{ICl}_3(g) \rightarrow \text{ICl}(g) + \text{Cl}_2(g)$ to be exothermic, the net bond energy in ICl_3 must be less than 36.1 kcal. Thus, if both compounds are to be stable in the vapour phase, the depression in the net bond energy must not exceed a certain *upper limit* : nor must it fall below a certain *lower limit*, or the lower compound will become unstable. It can be shown that if the net bond energy exceeded 38.3 kcal., the reaction $3\text{ICl}(g) \rightarrow \text{ICl}_3(g) + 1\frac{1}{2}\text{I}_2(g)$ would become exothermic. The margin tends therefore to be narrow, especially where compounds with small heats of formation are being dealt with. In the case of the fluorides of iodine the depression in the net bond energy is too small for IF to exist. Indeed, IF_3 is likewise unstable with respect to IF_5 , this and IF_7 being the only known fluorides. Fluorine is the only halogen to form bonds with iodine strong enough to provide enough energy for raising the latter to the quinque- and septa-valent states.

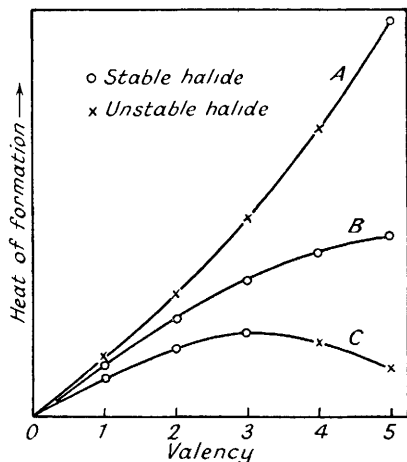


FIG. 9

Hypothetical curves illustrating the trends in the heats of formation of the stable and unstable halides of an element exhibiting all valencies from 1 to 5.

¹¹¹ Biltz and Weibke, *Z. anorg. Chem.*, 1931, **203**, 3.

The question of critical bond energies has been discussed recently from a rather different aspect.¹¹² A discussion of the conditions under which disproportionation may occur among inorganic compounds will not be entered into here, as the matter has been reviewed in detail elsewhere.¹¹³

11. Heats of Formation and Modern Chemical Theories

It is not the present purpose to review the various attempts to gain a theoretical understanding of the energetic structure of inorganic compounds since the earliest application of the quantum theory to this problem.^{114, 115} It will suffice to make some general observations.

The wave function of each electron in a molecule—whether involved in chemical bonding or not—is to be associated with a particular energy. In theory, the difference in the sum of the energies for the free atoms which make up the molecule and those of the molecule itself will provide an estimate of the atomic heat of formation. The mathematical difficulties in solving the Schrödinger wave equations for any except the simplest molecules have, however, compelled the introduction of certain approximations.

The valency-bond method and molecular-orbital method are two alternative ways of approaching this intricate problem. Whereas the former has proved itself to be reliable in certain simple cases of molecules with single bonds, the latter has proved the more adaptable for systems with π electrons, and has received the greater attention. The interested reader is referred to Coulson's excellent review on this subject.¹¹⁶ Both methods have their limitations. Whereas the original valency-bond method is unsuited for molecules in which delocalisation of bonding electrons is important, yet for molecules containing only σ bonds, the molecular-orbital approach tends to over-estimate the probability of both electrons of such a bond being found simultaneously round one atom, especially at large internuclear distances, this arising through the inadequate recognition of repulsive factors operative.

In emphasising these facts, Lennard-Jones and his collaborators have in the past four years made an important advance. Many of the weaknesses in the approximate treatment of earlier theories have been partly overcome by replacing molecular orbitals by equivalent orbitals, in which the respective pairs of electrons are assumed to interact according to the ordinary laws governing electrostatic forces. In this way, due account is taken of the Coulomb forces operating between the electrons without losing sight of their exchange energy. The various methods have been compared in a recent summary,^{117, 118} where reference to detailed treatment of specific molecules by the new procedure will be found. In this procedure, it is of importance

¹¹² Ormont, *Acta Physicochim. U.R.S.S.*, 1946, **21**, 409.

¹¹³ Wilson and Bremner, *Quart. Reviews*, 1948, **2**, 1.

¹¹⁴ Born, *Naturwiss.*, 1924, **12**, 1199.

¹¹⁵ Wilsdon, *Phil. Mag.*, 1925, **49**, 354, 900.

¹¹⁶ *Quart. Reviews*, 1947, **1**, 144.

¹¹⁷ Lennard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9.

¹¹⁸ Lennard-Jones and Hall, *ibid.*, p. 18.

to note that part of the total energy of a molecule becomes associated with the bonds and part with the atoms themselves.

Qualitatively, at least, this is in accord both with expectation and with experimental evidence provided by dissociation energies and bond properties (here come into consideration more particularly force constants¹¹⁹ and bond lengths^{120, 121}). Since the difference in the sums of the energies of the individual electrons in the molecule and in the free atoms respectively provides a measure of the energy of formation of a molecule, changes in the wave functions of the non-bonding electrons as well as those of the bonding electrons must be considered in the complete picture; *i.e.*, the energy of the bonds alone, as provided by the wave functions, cannot in general be equated with the atomic heat of formation of the molecule in question. A term must be included to take account of change in internal energy of the atoms themselves in bringing each to the appropriate valency state in which it finds itself in the compound. This will cover the energy required to promote one or more electrons to higher orbitals when the ground state of the atom has an insufficiency of unpaired electrons, and also hybridisation effects, which may affect non-bonding as well as bonding electrons. According to this viewpoint, the usual equation $Q_a = \sum E_n$, where Q_a is the atomic heat of formation and E_n the net or thermochemical bond energy, is replaced by $Q_a = \sum E_i - \sum V$, where E_i is the gross or intrinsic bond energy and V represents the valency-state energy. In the improved picture, therefore, the interatomic energy is enhanced at the expense of intra-atomic energy. Logically, it is the E_i values and not the E_n values which are to be related to other bond properties. (The energies listed in Table 10 are E_n values.) The derivation of E_i values from heats of formation requires a knowledge of valency-state energies.

Clearly, the calculation of resonance energy from atomic heats of formation by equating it to the deviation in the sum of the E_n values as derived from other molecules is a very risky procedure, since it takes no account of the variation in E_i values (as reflected in other bond properties) or in valency-state energies brought about by such effects as conjugation. Indeed, no conclusions regarding resonance can logically be drawn from heats of formation, nor do the latter enable a decision to be made between alternative structures,¹²² as has frequently been supposed. Other objections to certain common assumptions regarding resonance have been referred to elsewhere.¹²³⁻¹²⁵

It is only in recent years that attempts have been made to derive valency-state energies from experimental data, and, so far, estimates are available only for quadrivalent carbon,^{126, 127} the alkali metals (in their

¹¹⁹ Linnett, *Quart. Reviews*, 1947, **1**, 73.

¹²⁰ Wells, *J.*, 1949, 55.

¹²¹ Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

¹²² Samuel, *J. Chem. Phys.*, 1944, **12**, 180.

¹²³ Hückel, "Structural Chemistry of Inorganic Compounds", Vol. I (English translation by L. H. Long, Elsevier, Amsterdam, 1950), translator's note, pp. 434 ff.

¹²⁴ Longuet-Higgins, *Nature*, 1950, **165**, 908.

¹²⁵ Gillespie, *J.*, 1952, 1002.

¹²⁶ Long and Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.

¹²⁷ Long, *Experientia*, 1951, **7**, 195.

diatomic molecules),¹²⁸ oxygen,¹²⁹ nitrogen,¹³⁰ and bivalent carbon.¹³⁰ Earlier theoretical attempts to calculate valency-state energies were not wholly successful in view of the inadequate nature of the theories involved, and they sometimes provided values which, experimentally, are now known to be unacceptable. The observational data utilised in the experimental estimations are dissociation energies in conjunction with other bond properties for polyatomic molecules, and extrapolation of spectroscopically observed vibrational levels for diatomic molecules. Because of the approximating assumptions involved, neither method is very accurate, and it is doubtful if valency-state energies can be estimated with an accuracy better than $\pm 10\%$ (if as good) at present. However, the values derived by different methods exhibit reasonable agreement. In the case of quadrivalent carbon, for example, six different procedures¹²⁷ have yielded the values 58.6 (lower limit), 70.2 (upper limit), 66, 57, 65, and 67 kcal. for the valency-state energy. Clearly, what is needed is a reliable and accurate method for deriving valency-state energies along theoretical lines, and in this connection a step forward has recently been made by Moffitt.¹³¹

Given the valency-state energies, it will be possible to calculate intrinsic bond energies from atomic heats of formation, just as the reverse procedure is also possible. Like valency states, intrinsic bond energies are not directly observable, but it is to be expected that they are related to other bond properties. Thus attempts, such as those of Cook¹³² and Walsh,¹³³ to interrelate bond energies with stretching force constants, bond lengths, bond polarities, and ionisation potentials, all of which can be directly observed or calculated, may ultimately develop into a reliable method of assessing intrinsic bond energies. At all events, the near future should witness an increasing interest in determining the individual contributions of valency-state energies and intrinsic bond energies to atomic heats of formation.

¹²⁸ Pauling, *Proc. Roy. Soc.*, 1949, *A*, **196**, 343.

¹²⁹ *Idem*, *Proc. Nat. Acad. Sci.*, 1949, **35**, 229.

¹³⁰ Pauling and Sheehan, *ibid.*, p 359.

¹³¹ *Proc. Roy. Soc.*, 1950, *A*, **202**, 634.

¹³² *J. Phys. Colloid Chem.*, 1947, **51**, 407.

¹³³ *Discuss. Faraday Soc.*, 1947, **2**, 18; *J.*, 1948, 398; *Quart. Reviews*, 1948, **2**, 73.