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FORMATION OF INORGANIC COMPOUNDS

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UNIVERSITY OF CALIFORNIA

Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

A METHOD FOR ESTIMATING THE HEAT OF FORMATION
OF INORGANIC COMPOUNDS

Howard W. Anderson

(Master's Thesis)

January 1958

Printed for the U. S. Atomic Energy Commission

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A METHOD FOR ESTIMATING THE HEAT OF FORMATION
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Contents

Abstract	3
Introduction.	4
Background and Theory.	5
Results and Discussion	13
Conclusion	37
Acknowledgment	38
Nomenclature.	39
Appendix	40
I. Methods of Estimation: Heat of Formation.	40
II. Electronegativity Scales	42
III. Simplified Lattice Energy Equation.	44
IV. Data.	50
V. Solution by Iteration	52
Bibliography.	54

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ABSTRACT

In thermochemical calculations, it is frequently necessary to estimate the standard heat of formation of compounds for which experimental data are unavailable. Although there are several methods that may be used, none is completely reliable or general. It was the purpose of this research to develop a more reliable and/or more general method of estimation.

To do this several modifications were made to the work done by Linus Pauling in developing a scale of electronegativity. The result is a simple equation,

$$-\Delta H_f = v_{AB} (x_B - x_A)^2 + v_A Y_A + v_B Y_B,$$

where v_{AB} is the apparent number of single bonds,

v_A is the number of atoms A in the mole,

and v_B is the number of atoms B in the mole,

with a set of parameters x and Y . Each valence state of each element may be assigned a value x and a value Y . Where these parameters have not been determined, they may be calculated for any cation when experimental heats of formation of two compounds of the cation are known.

The equation applies primarily to metallic halides, although it may also be used (with reservation) for other anions, including carbonates, sulfates, and similar radicals. It is not restricted to binary compounds. The average deviation obtained for a set of the halides of twenty-two metals was 0.93 kcal/mole. An error of less than 10 kcal/mole may generally be expected in estimating an unknown using only two experimental data.

A METHOD FOR ESTIMATING THE HEAT OF FORMATION
OF INORGANIC COMPOUNDS

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I. INTRODUCTION

In the estimation of chemical equilibria or the stability of chemical bonds it is often necessary to estimate the free energy of formation of chemical compounds. One way of doing this is to consider separately the contributions of the heat of formation and the entropy of formation. These two quantities may be estimated individually when they are not tabulated.

Let us consider the heat of formation. It may be defined as the enthalpy change for the reaction



where A and B are elements. When both reactants and products are at an arbitrarily defined standard state, e.g., 25°C and 1 atm., the enthalpy change is the standard heat of formation at those conditions. Several methods for estimating this quantity are available. Some of them are discussed briefly in Appendix I. None of these methods is sufficient in itself as a general method with reliable accuracy. The purpose of this research was to develop a more general and/or more reliable method of estimation which would also be easy to apply. The work done by Linus Pauling in developing a scale of electronegativities of the elements was taken as the starting point of the project.

BACKGROUND AND THEORY

For a symmetric molecule, the wave function representing a single bond A-A may be written¹⁸

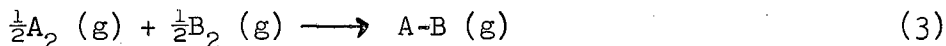
$$a \phi_{A:A} + d \phi_{A^+A^-} + d \phi_{A^-A^+}.$$

A similar function would represent a molecule B-B. If A and B are closely similar an average of their wave functions could be used to represent the single bond A-B. Pauling defined this bond as a normal covalent bond. That the wave functions are additive is the postulate of additivity of covalent bonds.

Consider now a bond between dissimilar molecules whose wave function is

$$a \phi (A-B) + b \phi (A^+B^-) + c \phi (A^-B^+). \quad (2)$$

The best values of b/a and c/a are those which minimize the total energy of the molecule, i.e., maximize the bond energy. Thus, if the postulate of additivity were always valid, the actual bond energy between dissimilar molecules would be greater than or equal to the normal covalent bond energy. This extra energy we call D. D is the heat liberated in the reaction



and the requirement that it be greater than or equal to zero is simply the specification of an exothermic reaction. D is not always greater than or equal to zero, since the postulate of additivity of covalent bonds does not hold universally. However, the result has been shown empirically to be approximately valid for many compounds.

Pauling examined D values for gas-phase heats of formation of simple nonmetallic compounds. He observed that the magnitude of D increased as the participating molecules became increasingly different with respect to the qualitative property of electronegativity, the power of electron attraction of an atom. On this scale, fluorine is considered most electronegative, the values decrease through oxygen, chlorine, bromine, iodine, hydrogen, etc. He also observed that the

square root of the D values approximately satisfied an additivity relationship for the contribution of each atom to the bond. From this he was able to set up a scale of electronegativity for these elements, assigning a constant value to each atom. Since the heat of formation was used to set up this scale, an equation resulted that could be used to roughly approximate the heat of formation of these simple gaseous compounds:

$$-\Delta H_f = \sum_{A-B} (x_B - x_A)^2 - 55.1 n_N - 24.2 n_O \quad (4)$$

where x is electronegativity (in $\text{kcal}^{\frac{1}{2}}$),

n is the number of atoms of nitrogen or oxygen in the molecule,

ΔH_f is the standard heat for formation (in kcal).

The summation is taken over the apparent number of single bonds. The corrections for nitrogen and oxygen are a result of their excessive stability in the standard state in comparison with the energy of single N-N or O-O bonds.

This scale can be extended to include metallic elements and liquid or solid compounds with these assumptions: (a) The energy of an element in its standard state does not differ from that of a covalent bond; (b) the van der Waals stabilization and other contributing factors have the same value for reactants and products; (c) unknown bond types are essentially single bonds; (d) the heat of formation of a compound in its standard state from elements in their standard states is given by Equation (4). Pauling did this for many elements. Haissinski later revised and extended his values.¹⁰ These are given in Table I. The heats of formation calculated from these values are only approximate since the electronegativity values are given to only two significant figures and are based on several questionable assumptions. Errors as large as 200 kcal obtain.

Although Pauling's equation was developed strictly empirically, Mulliken later gave some theoretical justification for its form.¹⁷ Using LCAO approximate molecular orbitals, he obtained the relation for monovalent species

$$-\Delta H_f = a V^2 - b V^4, \quad (5)$$

where a and b are positive constants,
and V is analogous to the electronegativity difference,
whereas empirically it is

$$-\Delta H_f = a (x_B - x_A)^2. \quad (4b)$$

Milliken's equation implies that the error in Equation (4b) should increase with increasing difference in electronegativity. He pointed out that the equation should not apply to highly polar molecules like H_2O or to heteropolar compounds like diatomic $NaCl$, since the assumptions of the derivation are not met.

Let us now consider methods of improving the accuracy of Equation (4). Pauling's use of correction factors for the standard states of nitrogen and oxygen suggests that this type of correction might also be employed for the other elements. It was decided to assign such a constant, designated Y , to each element. These constants may serve not only as corrections for deviations in the standard states of the elements but also as a convenient means for altering the standard state of any element. Standard states are somewhat arbitrary and there is some doubt that the standard states in general use are in all cases the best for use with Equation (4). Empirically determining these constants to provide the best fit to the available experimental data automatically takes care of any problems of this nature. It should also be pointed out that constants resulting from an empirical fitting process do not necessarily have physical significance, as do the correction factors for nitrogen and oxygen obtained by Pauling.

We note that the Pauling scale of electronegativity was determined initially as a unit for a small group of nonmetallic elements, and then extended one value at a time for the metallic elements. It should be possible as well as desirable to evaluate the whole set at once. A set of Y values could be determined simultaneously. That is, we take Eq. (4) as the form of our tentative relation. We use a complete set of Y values but do not assign values for x or Y ,

Table I

Electronegativity Scales

G is the scale of Gordy (Appendix II); P is the scale of Pauling by Haissinski;¹⁰ and M is from Equation (8). Units of x are $(\text{kcal}/4.8)^{\frac{1}{2}}$ or $(\text{electron volts})^{\frac{1}{2}}$.

Ion	G	H	M	Ion	G	H	M
H ⁺	2.17	2.1		Ni ⁺⁺		1.7	1.50
Li ⁺	.96	1.0	.97	Cu ⁺		1.8	1.38
Na ⁺	.90	.9	.92	Cu ⁺⁺		2.0	1.59
K ⁺	.82	.8	.78	Ag ⁺		1.8	1.36
Rb ⁺	.79	.8	.75	Zn ⁺⁺		1.5	1.64
Cs ⁺	.78	.7	.70	Cd ⁺⁺		1.5	1.56
Be ⁺⁺	1.38	1.5	1.64	Hg ⁺		1.8	1.87
Mg ⁺⁺	1.16	1.2	1.36	Hg ⁺⁺		1.9	1.77
Ca ⁺⁺	1.03	1.0	1.08	Al ³⁺	1.48	1.5	1.48
Sr ⁺⁺	.98	1.0	1.00	C ⁴⁺	2.52	2.5	2.47
Ba ⁺⁺	.93	.85	.91	Si ⁴⁺	1.82	1.8	1.72
Ti ⁴⁺	1.6	1.6	1.56	Sn ⁺⁺	1.61	1.65	1.31
Zr ⁴⁺	1.48	1.4	1.36	Sn ⁴⁺		1.8	1.56
V ³⁺	1.4	1.35	1.35	Pb ⁺⁺	1.56	1.6	1.33
V ⁴⁺	1.7	1.65	1.55	Pb ⁴⁺		1.8	1.61
Cr ⁺⁺	1.3	1.5	1.34	O ⁻²	3.47	3.5	3.02
Cr ³⁺	1.5	1.6	1.48	S ⁻²	2.58	2.5	2.46
Mn ⁺⁺	1.3	1.4	1.36	F ⁻	3.94	4.0	3.86
Fe ⁺⁺		1.65	1.42	Cl ⁻	3.00	3.0	2.98
Fe ³⁺		1.8	1.55	Br ⁻	2.68	2.8	2.74
Co ⁺⁺		1.7	1.47	I ⁻	2.36	2.6	2.44

and obtain
$$-\Delta H_f = v_{AB} (x_B - x_A)^2 + v_A Y_A + v_B Y_B, \quad (6)$$

where v_{AB} is the apparent number of single bonds,

v_A is the number of atoms of element A,

v_B is the number of atoms of element B.

Although the equation is written for binary compounds, it is not restricted to them. It is readily adapted for more general compounds. For example, if a compound contains anion C in addition to anion B, we write

$$-\Delta H_f = v_{AB} (x_B - x_A)^2 + v_{AC} (x_C - x_A)^2 + v_A Y_A + v_B Y_B + v_C Y_C. \quad (6b)$$

Since all the data used in this study are for compounds of only one cationic and one anionic species, the binary form of the equation is used throughout. This does not affect the generality of the results.

To evaluate the set of x and Y , we may utilize the technique of least squares to fit the equation to the experimental data.

Let

$$\Delta = (-\Delta H_f)_{\text{exptl}} - (-\Delta H_f);$$

$$\frac{\partial}{\partial \xi} [\sum \Delta^2] = 0 = \sum \frac{\partial}{\partial \xi} \Delta^2 = 0,$$

$$\xi = x_{A_n}, x_{B_m}, Y_{A_n}, Y_{B_m}$$

The result is

$$\xi = x_{B_m} : \sum_{i=A_1}^{A_n} 2 \Delta v_{A_i B} (x_{B_m} - x_{A_i}) = 0, \quad (7a)$$

$$\xi = x_{A_n} : \sum_{j=B_1}^{B_m} -2 \Delta v_{A_n B_j} (x_{B_j} - x_{A_n}) = 0, \quad (7b)$$

$$\xi = Y_{B_m} : \sum_{i=A_1}^{A_n} \Delta v_{B_m} = 0, \quad (7c)$$

$$\xi = Y_{A_n} : \sum_{j=B_1}^{B_m} \Delta v_{A_n} = 0. \quad (7d)$$

There result $2(m + n)$ equations in $2(m + n)$ unknowns, variables inseparable, to be solved simultaneously.

An Alternate Approach

Another possibility for improving the accuracy of Equation (4) is to improve the precision of the electronegativity values. The Pauling (Haissinski) values were determined empirically by taking an average of values obtained for several compounds. Several other methods of estimating the electronegativity are available. The method of Mulliken was chosen because of its potential for high precision. Several others are discussed in Appendix II.

Mulliken developed his absolute scale of electronegativity from consideration of Equation (2) as follows:¹⁶ If A is identical with B, b equals c . For the case of A not identical to B, let us assume that the energy required to produce A^- and B^+ from A and B is the same as that for A^+ and B^- . This is reasonable if A is similar to B. Let us also assume that A^- and B^+ (and also A^+ and B^-) approach each other without deformation until r , the distance between the nuclei, is the same as that in the bond A-B. If the energy given off were the same for both forms, the net energies would be the same. According to quantum mechanics, both A and B should participate equally in the resulting bond if $I_A - E_B$ equals $I_B - E_A$. I and E are the first ionization potential and electron affinity respectively. When the equality holds we may expect c to equal b . This condition is the state of equal electronegativity on Pauling's scale. Alternatively, the equality becomes: $I_A + E_A$ equals $I_B + E_B$. Its use as a criterion of equal electronegativity is apparent. It is this sum that Mulliken used to establish his absolute scale of electronegativity for monovalent species.

Using a similar argument, Mulliken defined a second-stage electroaffinity as the sum of the second ionization potential and the second electron affinity divided by two. The question immediately arises as to which quantity to use for a divalent ion -- the first-stage value, the second-stage value, or some combination of the two.

He suggests that the true value might be a weighted mean of the two, the weighting being a function of the nature of the elements and of the bond formed.

Several combinations of I_n and E_n were compared with the scale of Pauling. Values for ΔH_f were calculated and compared with the experimental data. From these as well as practical considerations Equation (8) was chosen as our scale of x , referred to the Pauling scale in units of $(\text{kcal})^{\frac{1}{2}}$:

$$x = \frac{\frac{1}{K} \sum_{n=1}^K \frac{I_n}{n} + E_1}{27.1}, \quad (8)$$

where n is the charge of the ion,

K is the valence.

The difficulty of obtaining electron affinity estimates is minimized by elimination of all but first-stage values. Moreover, E_1 is approximately zero for most metals. The scale of x represented by this equation is compared with others in Table I.

It might be expected that the size of the atoms would affect the heat of formation to a greater degree than can be accounted for by its effect on the ionization potential and electron affinity. The heat cycle given in Fig. 1 suggests the use of the lattice energy for this

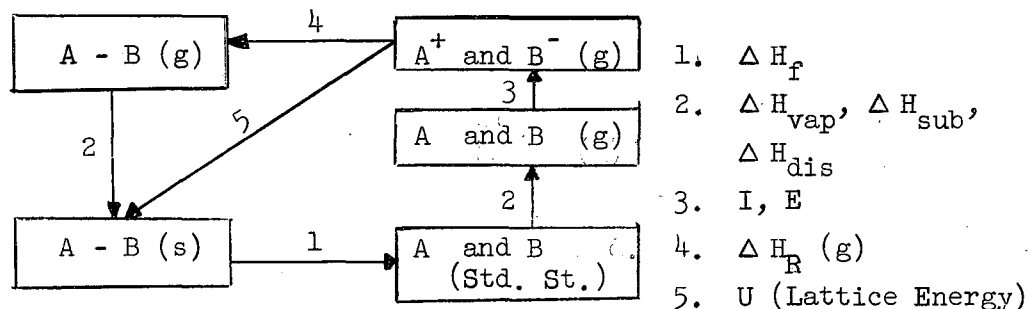


Fig. 1. Born-Haber cycle.

contribution; the lattice energy is a function of the size of the ions A and B. This is tantamount to assuming that the deviations of the

Pauling equation from the experimental values are proportional to the lattice energy. The fact that the lattice energy of the halides increases from iodine to fluorine and that the error in the Pauling equation increases from iodine to fluorine lends some credence to this postulate.

After assembling this alternate series of proposed corrections to Equation (4), we have a tentative equation for estimating the heat of formation of a compound:

$$-\Delta H_f = a \sum_{A-B} (x_B - x_A)^2 + n_A Y_A + n_B Y_B + d U, \quad (9)$$

where a and d are constants,

U is the lattice energy,

Y is an artificial constant, characteristic of each element.

Y is used in the same sense as in Equation (6). Yet undetermined are a , d , and the set of factors Y . A means of calculating U is also required. The development of a simplified equation for calculating the lattice energy is given in Appendix III. To evaluate a , d , and the Y factors we may utilize the technique of least squares.

$$\text{Let } \Delta = -\Delta H_f,$$

$$\Delta = \Delta_{\text{exp}} - \Delta.$$

we want $\sum \Delta^2$ to be a minimum.

$$\text{Let } \frac{\partial \sum \Delta^2}{\partial \xi} = 0 = \sum \Delta \frac{\partial \Delta}{\partial \xi} \quad (10)$$

$$\xi = a, d, Y_A, Y_B$$

$$\xi = a: \sum_{\Delta} \Delta \sum_v (x_B - x_A)^2 = 0 \quad (11a)$$

$$\xi = d: \sum_{\Delta} \Delta U = 0 \quad (11b)$$

$$\xi = Y_A: \sum_{\Delta} \Delta v_A = 0 \quad (11c)$$

$$\xi = Y_B: \sum_{\Delta} \Delta v_B = 0 \quad (11d)$$

For compounds including n elements there result $2+n$ equations in $2+n$ unknowns to be solved simultaneously. The equations are linear.

RESULTS AND DISCUSSION

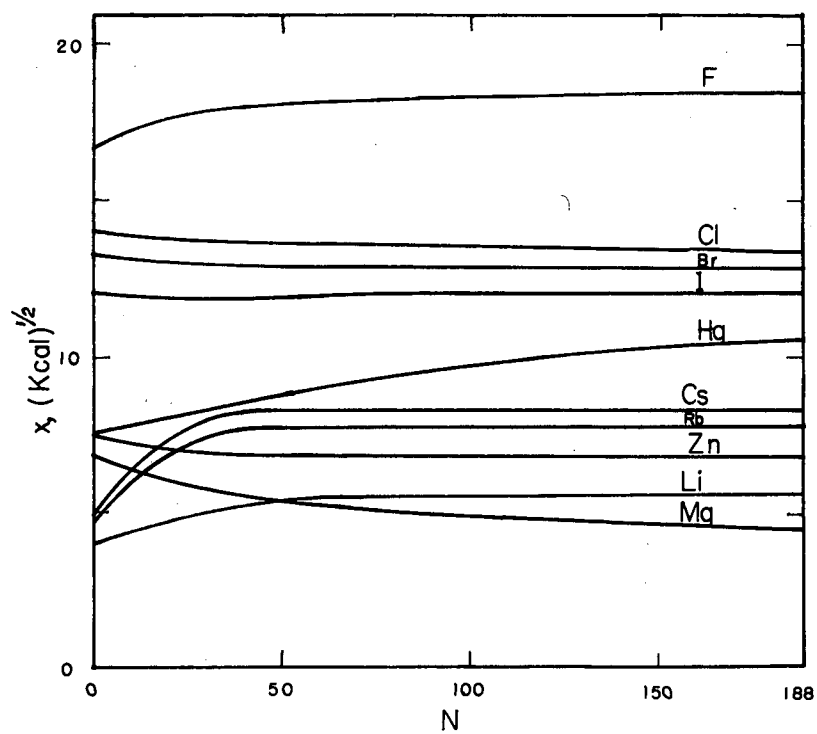
Solution of Equations (7)

This set of equations is nonlinear and implicit in x . The method of solution chosen was the use of an iterative procedure. The particular method selected is discussed in Appendix V.

Equations (7c) and (7d) are linear in Y and present no difficulty as far as the iterative solution is concerned. Equations (7a) and (7b), on the other hand, are cubic in x and pose a problem in root selection. Preliminary hand calculations indicated that for the cations one root was greater than the anion electronegativities, one was approximately equal to the average of the anion values, and one was less. The first root is contrary to the Pauling scale and the general theory. The second leads to a solution in which all the electronegativities are nearly the same. This is also contrary to the electronegativity concept. The third root is in agreement with the scale of Pauling and is thus the root of interest. A similar situation was found for the anion roots. Owing to the nature of the equations, these roots were evaluated by trial-and-error calculations.

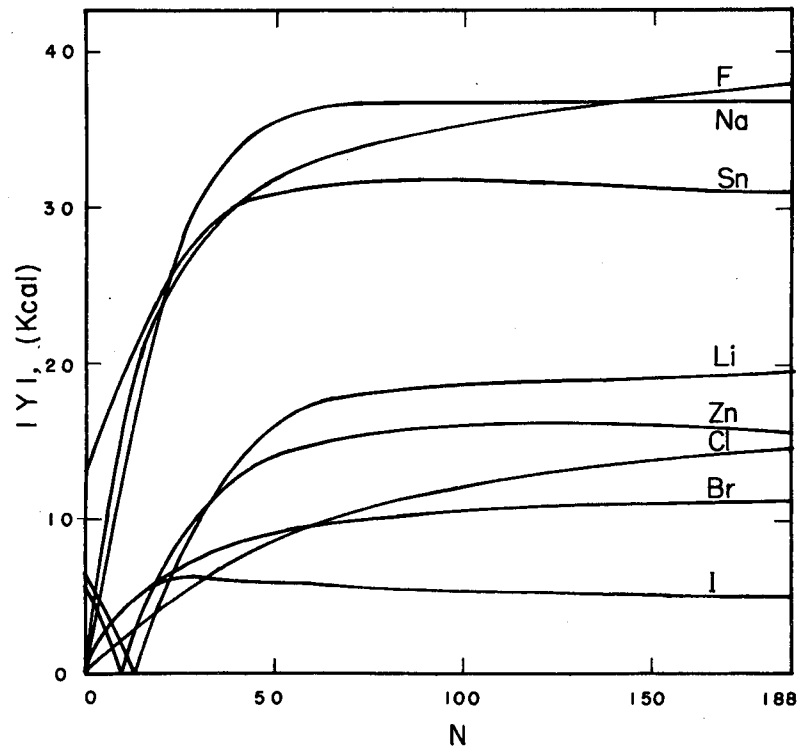
The calculations required for the iterative solution and the trial-and-error evaluation of roots are readily performed by high-speed digital computers. In this case the problem was programmed for the IBM 701. The experimental data used in the solution were the heats of formation of the halides of twenty-two metals. The halides were selected because they are chemically similar and should pose no great problem in radical behavior.

A plot of several x values as a function of the number of iteration is given in Fig. 2, and a set of Y values is plotted in Fig. 3. There is a tendency for the system to converge, although a few values seem particularly recalcitrant. The slopes of these curves are plotted in Figs. 4 and 5. Initially there appears to be a decided tendency toward convergence. However, as the solution continues, the rate of change of the x values seems to be heading toward a common value, as are the rates for Y . Although the rates



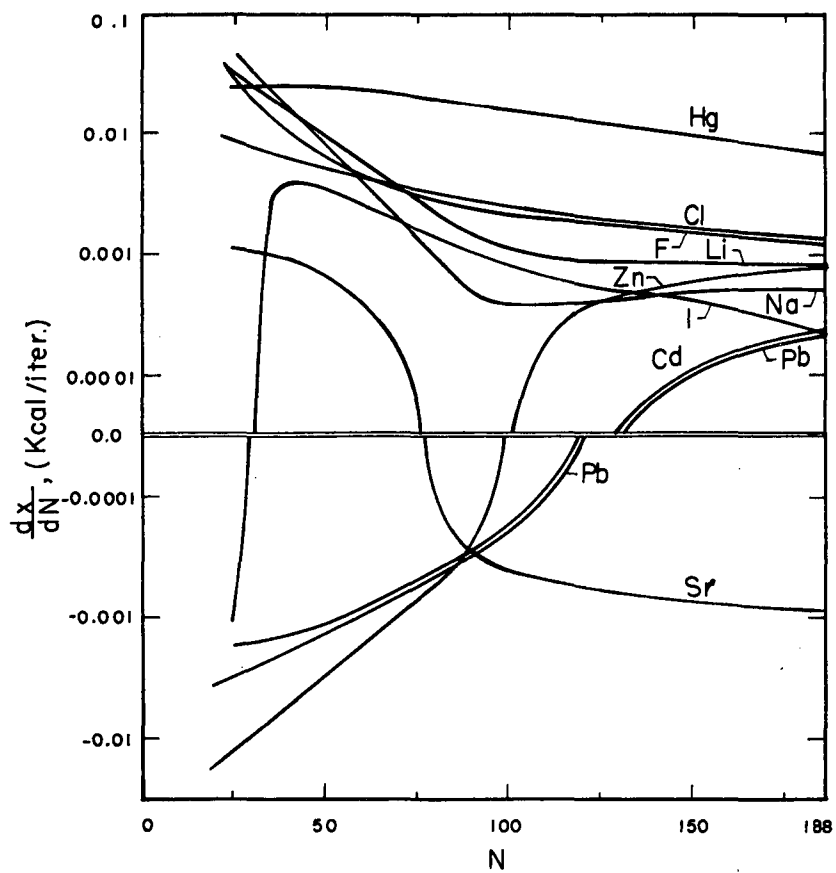
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Fig. 2. Iterative solution of Eq. (7); x vs. N .



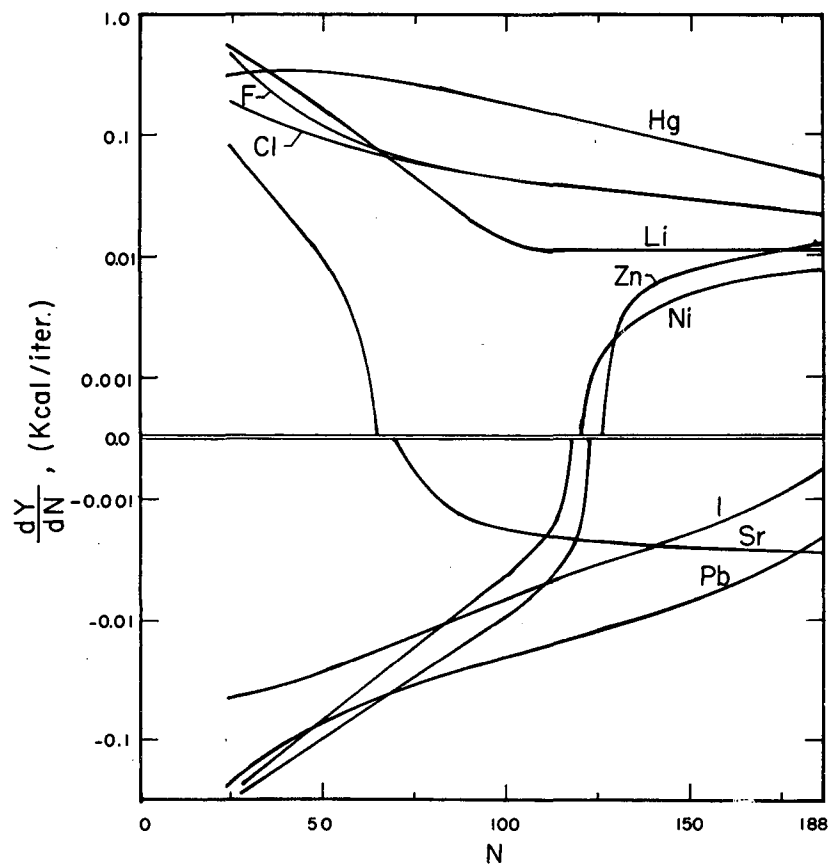
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Fig. 3. Iterative solution of Eq. (7); Y vs. N .



MU-14719

Fig. 4. Iterative solution of Eq. (7); dx/dN vs. N .



MU-14720

Fig. 5. Iterative solution of Eq. (7); dY/dN vs. N .

at the end of 188 cycles are generally small, there is no indication that convergence on a unique set of values would be obtained in any finite number of additional cycles. The system at 188 cycles may be thought of as a pseudo solution; it approximately satisfies the set of equations, yet unique values have not been found for x and Y.

Figure 6 is a plot of the total deviation from experiment of values of $-\Delta H_f$ calculated from sets of x and Y at different iteration numbers. It indicates that the agreement is continually improving and tending toward a minimum. The log of the slope of this curve is plotted in Fig. 7 as a function of the log of the iteration number. Within the accuracy of the data the curve is a straight line of slope minus 2.0. That is,

$$\frac{d \sum \delta}{d N} = b N^{-2} \quad (12)$$

Graphically, b is 1.60×10^3 .

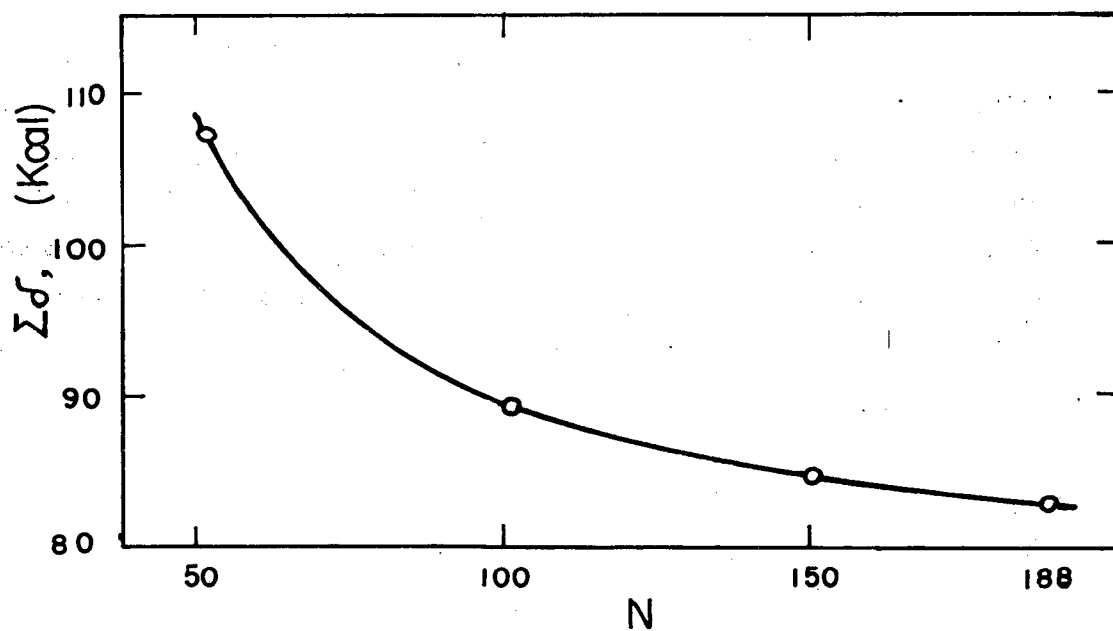
Integrating from $N = d$ to infinity, one obtains

$$\int_d^{\infty} \frac{d \sum \delta}{d N} d N = (\sum \delta)_{n=\infty} - (\sum \delta)_{n=d} = - \frac{1.60 \times 10^3}{d}$$

Let d be 188; then one gets

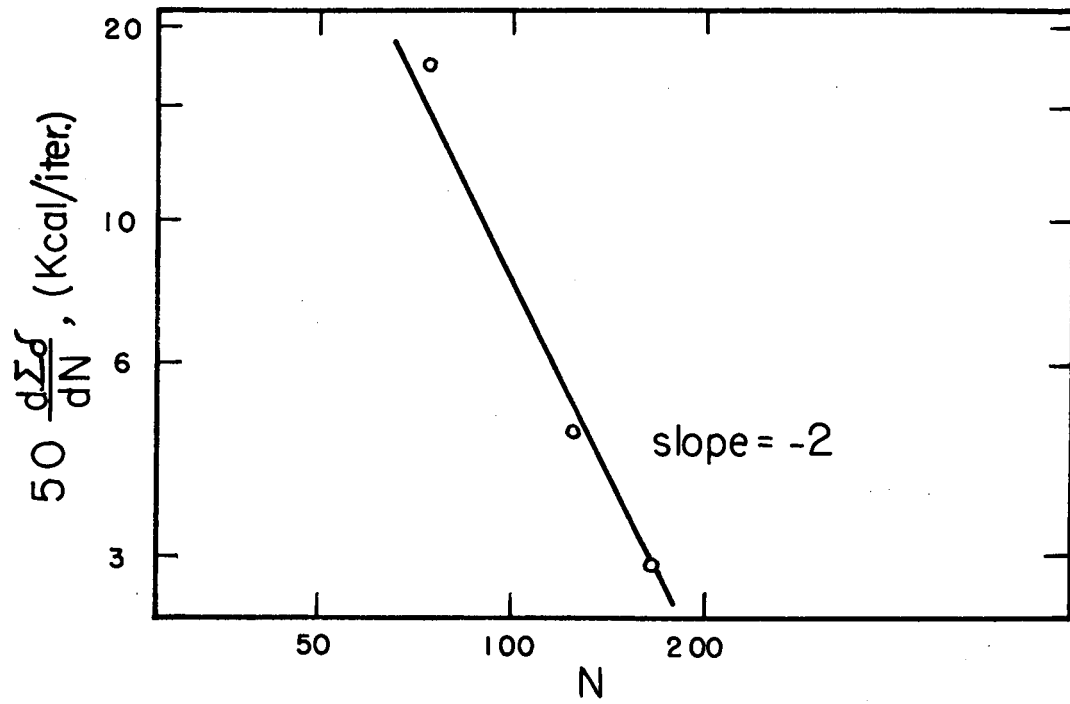
$$(\sum \delta)_{n=\infty} - (\sum \delta)_{n=188} = -8.5 \text{ kcal.}$$

Thus, if the slope of $\sum \delta$ vs N were to continue to decrease in accordance with Equation (12), $\sum \delta$ would be reduced by 8.5 kcal after an infinite number of iterations. Although this is to be considered only as an approximation, it is indicative of the extent to which correlation may be improved by continuing the iterative procedure. For the present purposes, this amount of gain in agreement with experiment does not warrant the time or the financial investment in computer time that is required to obtain it. The system at 188 iterations will be considered a "solution" and evaluated as such. It is given in Table II.



MU-14721

Fig. 6. Total deviation vs. N .



MU-14722

Fig. 7. $d\Sigma\delta/dN$ vs. N .

Table II

Iterative Solution of Equations (7)					
Values of x and Y for Iteration 188					
Ion	x	Y	Ion	x	Y
	(kcal ^{1/2})	(kcal)		(kcal ^{1/2})	(kcal)
Sn ⁺⁺	6.858	-30.91	Mg ⁺⁺	4.522	-36.60
Pb ⁺⁺	7.220	-18.30	Ca ⁺⁺	4.788	10.70
Zn ⁺⁺	6.858	-15.58	Sr ⁺⁺	4.618	13.70
Cd ⁺⁺	7.255	-10.16	Ba ⁺⁺	4.533	19.38
Hg ⁺	9.554	2.53	Li ⁺	5.595	19.61
Hg ⁺⁺	10.608	9.44	Na ⁺	6.718	36.81
Cu ⁺	10.107	6.68	K ⁺	7.553	54.00
Cu ⁺⁺	6.980	-60.47	Rb ⁺	7.794	55.90
Ag ⁺	9.134	-0.79	Cs ⁺	8.295	61.93
Ni ⁺⁺	6.480	-50.73	F ⁻	18.449	-37.97
Co ⁺⁺	6.620	-44.70	Cl ⁻	13.411	14.67
Fe ⁺⁺	6.534	-42.14	Br ⁻	12.840	11.31
Mn ⁺⁺	6.853	-3.35	I ⁻	12.076	5.22
Cr ⁺⁺	6.770	-17.14			

Evaluation of Solution

The experimental data and back-calculated heats are listed in Table III. The average and maximum deviations are compared with those obtained from Equation (4) in Table IV. The agreement with the experimental data is considerably better and comparable in order of magnitude with the expected error in the experimental values. Continuing the iterative procedure further can indeed result only in minor gains.

During the calculation of the average deviation it was observed that for chromium the deviation from experimental values was much larger than for any other element: the average error for three values of $-\Delta H_f$ was 3.90. A check of the experimental data revealed that they were in serious disagreement with the latest information;⁹ the error in the value for CrI_2 was 13.9, for CrCl_2 was 2.4 kcal. New x and Y values for chromium were calculated from the latest data using Equations (7b) and (7d). The average error was reduced to 1.45. This demonstrated that the present method might detect some large deviations in experimental determinations. These improved calculations were used in the preparation of Table IV.

Figure 8 is a periodic plot of the electronegativities of Pauling and those obtained from Equations (7). The plots are generally similar except for the alkali metals. The extent to which the least-squares values differ from those of Pauling is related to the magnitude of the Y values for the elements. For example, the deviation of the alkali metals relative to the Pauling scale is greatest for Cs and least for Li; the Y values are also greatest for Cs and decrease to the smallest for Li. Likewise for the alkaline earths -- Mg deviates more than Ba, Ba more than Sr, Sr more than Ca. The magnitudes of the Y values also follow this order. This correspondence is quite logical and needs no further explanation. Of more concern is an explanation for the fact that the equations found such large values of Y necessary to correlate the experimental values. It seems most unlikely that any combination of deviation of the standard states from the covalent state, unequal van der Waals forces for reactants and products, and deviations of the metal-halide bonds from the nature of single bonds could produce Y

Table III

Solutions of Equations (7) for Halides					
Comparison of experimental data and back-calculation for $-\Delta H_f^{29}$					
All data in kcal/mole.					
Compd.	Exptl.	Calc.	Compd.	Exptl.	Calc.
LiF	146.3	146.87	SrF ₂	290.3	-
LiCl	97.70	95.37	SrCl ₂	198.0	197.67
LiBr	83.72	83.41	SrBr ₂	171.1	171.52
LiI	64.79	66.84	SrI ₂	135.5	135.39
NaF	136.0	136.46	BaF ₂	286.9	-
NaCl	98.232	96.27	BaCl ₂	205.56	206.34
NaBr	86.030	85.60	BaBr ₂	180.4	180.0
NaI	68.84	70.74	BaI ₂	144.0	143.61
KF	134.46	134.75	CrF ₂	181.0	181.38
KCl	104.18	102.98	CrCl ₂	97.0	94.82
KBr	93.73	93.26	CrI ₂	40.3	42.11
KI	78.31	79.67	MnF ₂	189.0	189.66
RbF	131.28	131.46	MnCl ₂	115.3	112.00
RbCl	102.91	102.11	MnBr ₂	90.7	90.96
RbBr	93.03	92.67	MnI ₂	59.3	61.66
RbI	78.5	79.45	FeCl ₂	81.5	81.77
CsF	126.9	127.07	FeBr ₂	60.02	60.00
CsCl	103.5	102.77	FeI ₂	29.98	29.72
CsBr	94.3	93.89	CoF ₂	159.0	159.22
CsI	80.5	81.45	CoCl ₂	77.80	76.87
MgF ₂	263.5	-	CoBr ₂	55.50	55.30
MgCl ₂	153.40	150.75	CoI ₂	24.40	25.28
MgBr ₂	123.7	124.38	NiF ₂	159.5	159.86
MgI ₂	86.0	87.96	NiCl ₂	75.5	74.69
CaF ₂	290.3	-	NiBr ₂	54.2	52.79
CaCl ₂	190.0	188.74	NiI ₂	20.5	22.35
CaBr ₂	161.3	162.98	CuCl	32.2	32.26
CaI ₂	127.8	127.37	CuBr	25.1	25.45

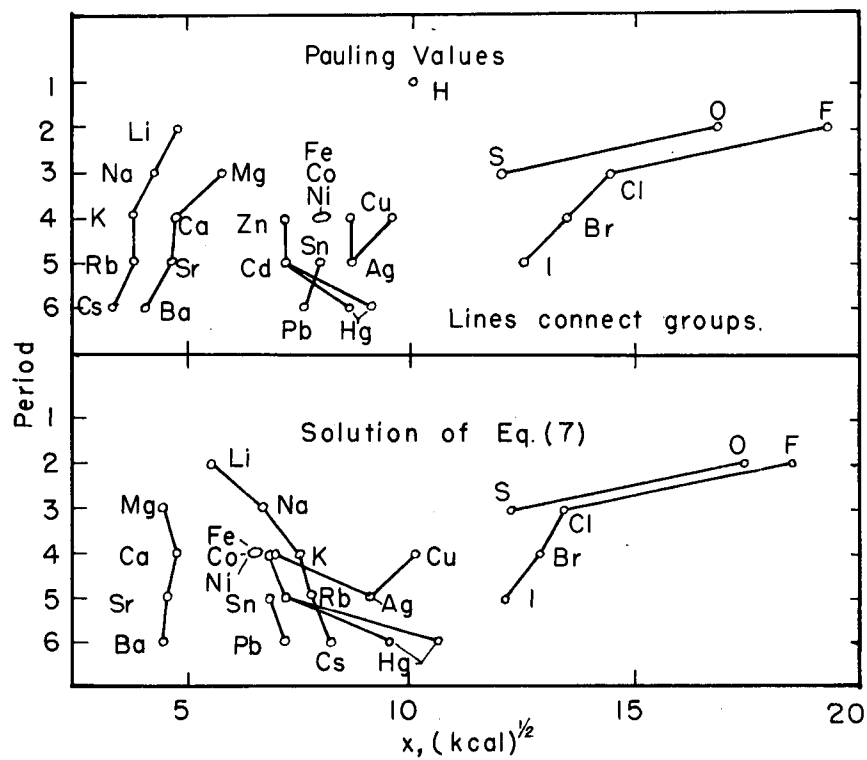
(continued)

Table III - continued

Compd.	Exptl.	Calc.
CuI	16.2	15.77
CuF ₂	126.9	126.67
CuCl ₂	49.2	51.58
CuBr ₂	33.2	30.82
CuI ₂	1.7	1.91
AgF	48.5	48.02
AgCl	30.362	32.17
AgBr	23.78	24.25
AgI	14.91	13.09
ZnCl ₂	99.40	99.63
ZnBr ₂	78.17	78.60
ZnI ₂	49.98	49.31
CdF ₂	164.9	164.50
CdCl ₂	93.00	94.95
CdBr ₂	75.15	74.83
CdI ₂	48.0	46.75
Hg ₂ Cl ₂	63.32	64.14
Hg ₂ Br ₂	49.42	49.27
Hg ₂ I ₂	28.91	28.22
HgCl ₂	55.0	54.48
HgBr ₂	40.5	42.02
HgI ₂	25.2	24.19
SnCl ₂	83.6	84.31
SnBr ₂	63.6	63.28
SnI ₂	34.4	33.99
PbF ₂	158.5	157.93
PbCl ₂	85.85	87.68
PbBr ₂	66.21	67.48
PbI ₂	41.85	39.30

Table IV

Comparison of Estimations with Experiment					
No. of compounds	Equation used for estimate	Types of compounds	Average deviation (kcal/mole)	Maximum deviation (kcal/mole)	Compound of maximum deviation
119	(4)	halides, oxides, and sulfides	35.6	261.5	Cs_2O
108	(9)	halides, oxides, and sulfides	13.7	74.85	Al_2O_3
81	(6)	halides	0.93	3.30	MnCl_2



MU-14723

Fig. 8. Periodic plot of electronegativity.

values of 50 kcal or even 30. More likely is an error in the fourth assumption required to extend Pauling's original x scale -- that the heat of formation of compounds in their standard states from elements in their standard states is given by Equation (4). As long as the agreement with experimental data is as good as that obtained for the halides, the magnitude of Y is of little significance, for the equation produces the desired result.

Extension of the x and Y Scale

Additional individual values can be readily calculated, as was done in correcting the chromium constants, if a set of values of x and Y is available. It would increase the range of applicability of the equations if the scale could be extended to include oxygen, sulfur, and also radicals like the carbonate and sulfate. That is, consider the radicals as acting as entities in the equations instead of a combination of elements. Such a calculation was made using carbonate, nitrate, sulfate, and acetate radicals. Constants for oxygen and sulfur were calculated at the same time. These calculations were again made on the IBM 701, using a modification of the original program to solve Equations (7a) and (7c) for each anion. The x and Y values are listed in Table V. The back-calculated heat values are compared with the experimental in Table VI. The agreement for the radicals and for sulfur is about the same and considerably worse than was obtained for the set of halides. That the agreement should not be as good was expected, since the x and Y values for the metallic elements were optimized for the halides, and it doesn't necessarily follow that they will also be optimum for other anions. Of particular concern is the extremely poor agreement obtained for the oxides. This was quite unexpected and cannot be left unexplained.

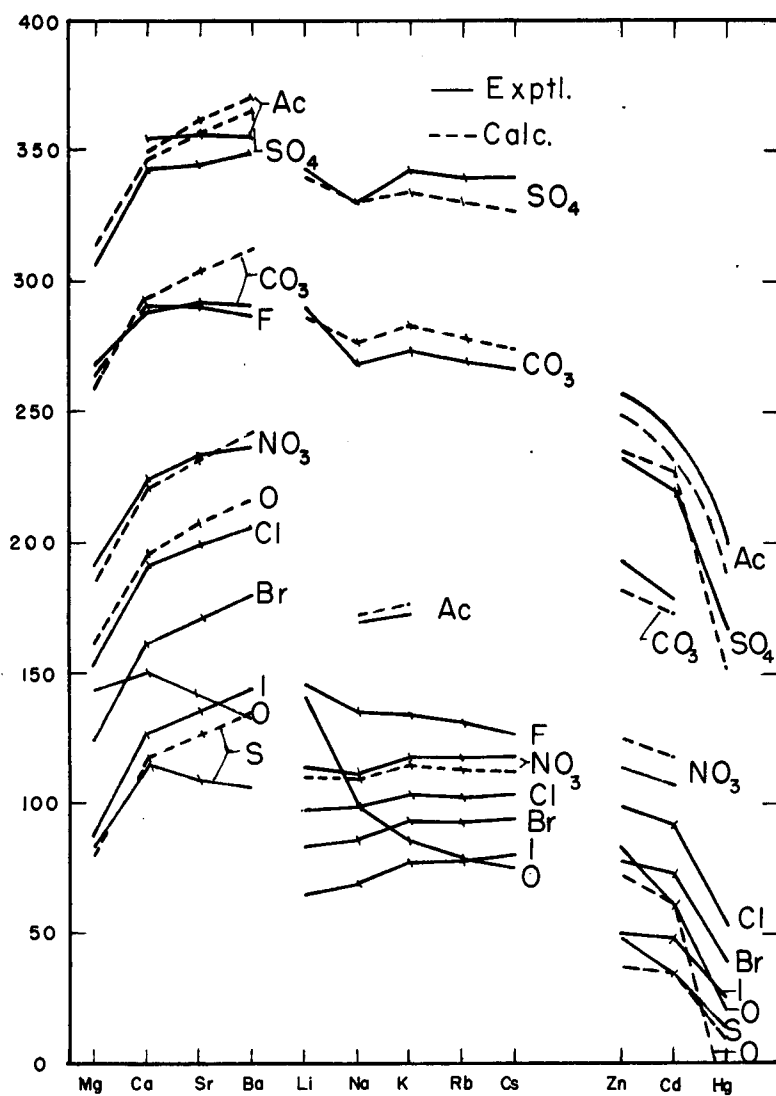
Figure 9 sheds understanding on this subject. The heats of formation determined experimentally and those from the back-calculation are plotted for the alkaline earth metals, the alkali metals, and the zinc-cadmium-mercury series. Where the calculated curves are not shown they are coincident with the experimental curves (except for the

Table V

Extension of Equation (6): x and Y Values		
Ion	x (kcal ^{$\frac{1}{2}$})	Y (kcal)
O ⁻⁻	17.374	-131.87
CO ₃ ⁻⁻	15.954	33.15
SO ₄ ⁻⁻	15.922	87.74
Acetate ⁻	14.658	72.69
NO ₃ ⁻	14.324	15.09
S ⁻⁻	12.260	-4.89

Table VI

Extension of Equation (6)				
Comparison of estimations with experiment				
No. of compounds	Anion	Average deviation (kcal/mole)	Maximum deviation (kcal/mole)	Compound of maximum deviation
18	O^{--}	24.80	83.89	BaO
22	SO_4^{--}	6.47	16.34	$BaSO_4$
17	NO_3^-	5.90	27.85	$Mn(NO_3)_2$
17	CO_3^{--}	8.73	22.11	$BaCO_3$
12	Acetate ⁻	7.18	14.68	$BaAc_2$
17	S^{--}	7.53	27.90	BaS



MU-14724

Fig. 9. Comparison of experimental and calculated $-\Delta H_f$ profiles.

alkaline earth fluorides and alkali metal oxides, which were not included in the calculations.) Looking at the curves for the alkaline earth elements we see that the calculated profiles are almost identical in shape. The profile was essentially fixed by the experimental data for the chlorides, bromides, and iodides when Equations (7) were solved as a set for the halides. This profile was faithfully reproduced when the solution for x and Y of the radicals, oxygen, and sulfur was made. We see that the experimental profile for the nitrate is in excellent agreement with this predetermined profile. The acetate, sulfate, carbonate, and sulfide profiles show rather similar disagreement with it. Oxygen violently misbehaves; the jump in $-\Delta H_f$ from magnesium to calcium is quite small; the oxides of calcium, strontium, and barium follow a trend just opposite that of the halides. Small wonder poor agreement was obtained here! The alkali metal oxides behave similarly, but they were not included in the solution and do not affect the results. The Group IIb elements also show a deviation in the profile of the oxide relative to the halides, though it is not as pronounced. The oxides of the remainder of the elements included in the solution seem less radical in behavior.

It seems then that as long as Equations (7) are confined to halide compounds acceptable results may be expected. It is apparent that the more general system, including oxygen, sulfur, and possibly radicals in addition to the halides, can hardly be treated adequately with these equations in their present form.

Application

Experimental values for at least two other halides of the element are required if one is to use Equation (6) to estimate the heat of formation of a halide of an element that was not included in the solution of Equations (7). Equations (7b) and (7d) are solved for x and Y when more than two data are used. The solution is facilitated by rearranging the equations:

$$Y_{A_n} = \frac{\sum_j \Delta - v_{B_j} Y_{B_j}}{\sum_j v_{A_n}} - \frac{\sum_j v_{AB_j} (x_{B_j} - x_{A_n})^2}{\sum_j v_{A_n}} \quad (13a)$$

$$\sum_j v_{AB_j}^2 (x_{B_j} - x_{A_n})^3 + \dots$$

$$(v_{A_n} Y_{A_n} v_{AB_j} + v_{B_j} Y_{B_j} v_{AB_j} - \Delta v_{AB_j}) (x_{B_j} - x_{A_n}) = 0; \quad (13b)$$

x and Y may be simply obtained for only two data by solving simultaneously Equation (10) for each datum. That is,

$$\text{For } x_A: (x_{B_1} - x_A)^2 - (x_{B_2} - x_A)^2 + v_{B_1} Y_{B_1} - v_{B_2} Y_{B_2} = 0; \quad (14a)$$

$$\text{for } Y_A: Y_A = \frac{-(x_{B_1} - x_A)^2 - v_{B_1} Y_{B_1}}{v_A} \quad (14b)$$

The desired heat of formation can then be calculated with these values and Equation (6).

In order to apply Equation (6) to the estimation of an unknown heat of formation, using only two or three data, we should know how sensitive the treatment is to the combination of data that is employed. In estimating a chloride, for example, we should know if our estimate will generally be as good when we use the data for the fluoride and iodide as when the data for the bromide and iodide are used. To get some feeling for this problem, several calculations of x and Y of an element were made for different combinations of the same data. The heats of formation were back-calculated from these for both the data used and for the heats that were not used. The deviation from experiment was then calculated for each. The results of these calculations for several elements are given in Table VII.

The values of x and Y for the different data combinations are generally quite similar. Those calculated from the bromide-iodide combination are the most erratic. This is logical because bromine and iodine differ only slightly in x or Y. It follows that the estimation of the heat of formation for the fluoride from this combination should be most unreliable, since a large change in electronegativity is involved. The calculations indicate that this is true. Estimates of the iodide from the fluoride-chloride combination show a

Table VII

Application of Equation (6)							
Deviation of estimates from experiment; x and Y for the halides were taken from Table II.							
Cation	Data used						
Sb ³⁺	F,Cl,Br,I	6.710	-83.32	-1.02	4.05	1.23	-4.28
	F,Cl	6.543	-94.16	---	---	-3.38	-9.66
	F,I	6.795	-76.32	---	7.65	5.13	---
	Br,I	7.913	-44.65	-42.72	1.31	---	---
H ⁺	F,Cl,Br,I	6.341	-44.19	.25	-1.60	.69	.66
	F,Cl	6.524	-40.04	---	---	-6.48	-2.73
	F,I	6.309	-45.21	---	-3.17	.09	---
	Br,I	6.370	-44.51	-.77	-2.33	---	---
Na ⁺	F,Cl,Br,I	6.718	36.81	.46	-1.96	-.43	1.90
	F,Cl	6.957	41.91	---	---	1.81	4.49
	F,I	6.605	33.69	---	-3.56	-2.15	---
	Br,I	5.198	16.32	17.94	.21	---	---
Be (aq) ⁺⁺	F,Cl,Br,I	6.754	54.11	.31	-1.33	-.20	.20
	F,Cl	6.836	57.61	---	---	1.32	2.96
	F,I	6.719	52.17	---	-2.34	-1.28	---
	Br,I	6.298	42.79	10.75	-.09	---	---

similar effect but of less severity. In general, then, estimates made by this technique will be most reliable when the data straddle the unknown or are similar to the unknown in regard to electronegativity. Estimates within 5 kcal of experimental may be expected when the method is used in this way.

These calculations also indicate that the method is applicable to aqueous compounds. The data for Be are for the heat of formation at infinite dilution. The agreement is actually better than for the other cations in the table. The average deviation when all four data are used is only 0.51 kcal.

Solution of Equations (11)

The experimental data chosen for use in solving these equations were the halides, oxides, and sulfides of 21 metals. By use of these data, the equations were solved and the heats of formation back-calculated from the solution. The solution is given in Table VIII. The agreement is compared with that of Equation (4) in Table IV. The agreement is considerably better, but remains intolerably poor. Close examination of the calculations indicates that the lattice-energy correction factor does not contribute more than a small percentage of the calculated value of $-\Delta H_f$ and that its contribution does not follow the error in Equation (4) with regularity, qualitatively or quantitatively. It was therefore discarded. The possibility exists that the poor agreement with experimental data was a result of the scale of electronegativity that was used. Examination of Table I reveals that the scale used agrees well in most cases with the generally accepted scale of Pauling. The back-calculations for the exceptions that agree poorly do not show any worse agreement with the data than those which agree well with the Pauling scale. In sum, this general approach did not yield a satisfactory result.

Extension of the Treatment

It has been shown that the method of estimation represented by Equation (6) yields acceptable results as long as it is restricted

Table VIII

Solution of Equations (11); a = 0.834, d = 0.01421.					
Element	Y (kcal)	Element	Y (kcal)	Element	Y (kcal)
Sn	-19.76	Al	50.40	Rb	-10.78
Pb	-25.29	Mg	53.31	Cs	-15.28
Zn	22.17	Ca	50.09	O	8.88
Cd	12.88	Sr	33.25	S	-27.45
Hg	2.07	Ba	23.59	F	-33.18
Mn	9.49	Li	17.09	Cl	-3.32
Ni	-10.03	Na	3.93	Br	3.18
Fe	-11.48	K	-4.27	I	6.98
Cr	11.08				

to halide compounds. When it was extended to include oxides, sulfides, and radicals, the results were quite erratic and not of acceptable accuracy. This suggests that a third parameter is required for adequate characterization of the elements. When included in the equation this parameter should have relatively little effect on the halide compounds and a large effect on oxygen, which seems to behave quite badly in the present treatment. From practical considerations the parameter must be included in the equation in such a form that it can be handled mathematically.

P. and R. Daudel improved the accuracy of Equation (4) by using a parameter d .³ This parameter is based on a theoretical argument of Pauling, (Ref. 17, p. 65). A value was assigned to each element. The numerical value was calculated from the electronegativity scale. Using this parameter they defined the electronegativity difference of a particular bond as

$$(x_B - d_B v_B f) - (x_A + d_A v_A f), \quad (15)$$

where v is the valence number,

f is the fraction of ionic character of the bond,

A and B are cation and anion respectively.

The term F was evaluated from an equation of Pauling:

$$f = 1 - \exp^{-c(x_B - x_A)^2}, \quad (16)$$

where c is $\frac{1}{4}$ on the Pauling scale.

This equation is not exact, but is indicative only of the ionic character of the bond. Since f and the electronegativity difference are interdependent, the final value of either must be obtained by an iterative procedure. Let us now attempt to simplify this operation. Equation (4) becomes

$$\frac{-\Delta H_f}{v_{AB}} = [(x_B - d_B v_B f) - (x_A + d_A v_A f)]^2. \quad (17)$$

Regrouping and expanding, we obtain

$$\frac{-\Delta H_f}{v_{AB}} = (x_B - x_A)^2 - 2(x_B - x_A)(d_B v_B f + d_A v_A f) + (d_B v_B f + d_A v_A f)^2. \quad (18)$$

The quantity $(d_B v_B f + d_A v_A f)$ is always much smaller than $(x_B - x_A)$ and therefore may be discarded. In the range of $(x_B - x_A)$ of interest (this range is quite small, being less than 4.0 on the Pauling scale), f may be approximated adequately by

$$f = s (x_B - x_A)^t, \quad (19)$$

where t is approximately 2. By suitably choosing s and t we can eliminate the necessity of solving for $(x_B - x_A)$ and of f by iterative procedures.

By substituting, we have

$$\frac{-\Delta H_f}{v_{AB}} = (x_B - x_A)^2 - 2s (d_B v_B + d_A v_A) (x_B - x_A)^{1+t} \quad (20)$$

$$\text{or } \frac{-\Delta H_f}{v_{AB}} = (x_B - x_A)^2 - 2s d_B v_B (x_B - x_A)^{1+t} - 2s d_A v_A (x_B - x_A)^{1+t},$$

where s , d , and v are always positive, and $1 + t$ is approximately 3.

We call to mind Equation (5) derived by Mulliken:

$$\frac{-\Delta H_f}{v_{AB}} = a V^2 - b V^4. \quad (5)$$

It seems that essentially what has been done in the treatment by the Daudels is to assign a different value of the constant b in Mulliken's equation to each element and to decrease the exponent slightly. It is possible that such a factor could be evaluated in addition to x and Y for each element. If $1 + t$ is taken to be 3 instead of the 4 in Equation (5), the least-squares equations are as high as sixth order in $(x_B - x_A)$. However, if an iterative procedure like the one of this work is applied, the highest-order equation that must be solved for x is five. This may be convenient to do if the roots behave in a predictable manner. Some calculations would have to be made to determine this. A solution would be, at least, messy.

Another type of third parameter which is flexible enough to provide only a small contribution for the halides yet a large one for any other element is provided by the inclusion in Equation (6) of a term

$$v_{ca} \left(\frac{W_c}{W_a} \right)^n,$$

where v_{ca} is the number of c - a bonds,

W_c is the cation parameter,

and W_a is the anion parameter.

The least-squares equations would involve terms of order n ($n-1$) in W_c and order $-n$ ($n+1$) in W_a . W_c is made the numerator for purely practical reasons; there will in general be a greater number of cations in an empirical analysis, and the numerator occurs in terms of lower order in the least-squares equation. If in addition n were to be determined empirically with W , x , and Y , the equation would become most awkward to handle. At present I can see no reason for n to be greater than unity. In that case W is readily handled empirically with x and Y . For the case of $n = 1$ it might be more convenient to invert the ratio so that a value of zero could be assigned to W_a for one or more of the halides; the contribution of this term to $-\Delta H_f$ for the halides was postulated small.

CONCLUSION

This research has resulted in a method for estimating the standard heat of formation at 25°C of a halide compound when experimental data are available for two other halides of the metallic ion. The estimation is best when the experimental data are for the halides immediately above and/or below the unknown in the electronegativity series. The estimates may be expected to be within 10 kcal of the actual value or better, depending on which experimental data are available. That is, the heat of formation of a fluoride is better estimated with data for the chloride and iodide than with data for the bromide and iodide. The experimental data for the halides of 22 metals were correlated with this technique, with an average deviation of 0.93 kcal/mole and a maximum deviation of 3.3 kcal/mole. This technique may similarly be applied to sulfates, carbonates, and other similar compounds, but with less assurance of accuracy.

Of secondary importance is the development of an approximate equation for estimating the lattice energy. This equation gives excellent agreement for the alkali metal halides and deviates an average of 18.8

kcal/equivalent for some fifty salts. As the equation is really an approximate Born equation, it gives best results for the same compounds as those for which the Born equation gives good results; agreement with experiment is poor for the nobel metals.

ACKNOWLEDGMENT

The author is grateful to the following who contributed significantly to this work:

Professor L. A. Bromley, for his consistent good humor and guidance;

The National Science Foundation, which provided the fellowship which made these studies possible;

The Radiation Laboratory, for providing electronic computer time and assistance;

The thesis committee, for their critical examination of the manuscript.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
a,b,c,...	Numerical constants	
A	Designates a cation	
B	Designates an anion	
D	Extra-ionic energy of a bond	
E	Electron affinity	kcal/atom
f	Fraction of ionic character of a bond	
I	Ionization potential	kcal/atom
N	Iteration number	
U	Lattice energy	kcal/mole
W	Synthetic parameter	
x	Electronegativity	(kcal/mole) ^{1/2}
Y	Synthetic parameter	kcal/atom
δ	$(-\Delta H_f)_{\text{exp}} - (-\Delta H_f)_{\text{calc}}$	kcal/mole
ΔH_f	Standard heat of formation at 25°C, 1 atm.	kcal/mole
ΔH_{dis}	Heat of dissociation	kcal/mole
ΔH_r	Heat of reaction	kcal/mole
ΔH_{sub}	Heat of sublimation	kcal/mole
ΔH_{vap}	Heat of vaporization	kcal/mole
$v_{\text{A-B}}$	Apparent number of single bonds A-B in compound A_nB_m	
$v_{\text{A}}, v_{\text{B}}$	Number of atoms of A or B per molecule.	

APPENDIX

I. METHODS OF ESTIMATION: HEAT OF FORMATION

Kapustinskii¹¹ and others^{25,28} propose methods of estimation based on the variation of the heat of formation with atomic number. Kapustinskii found that a plot of the heat of formation per gram equivalent vs the log of the atomic number resulted in a straight line or lines for compounds of identical type along periods or groups in the periodic table. These plots sometimes show a discontinuity. Kapustinskii¹² correlated these deviations, using the ratio of the univalent radius to the crystal radius for both the anion and cation. A discontinuity occurs when these ratios are equal. Although the data are correlated quite well by these log plots, Kubaschewski¹⁴ points out that appreciable deviations do occur and that the method should be used in connection with other estimations.

Fomin⁴ suggests this equation

$$\frac{Q_{Ax'_n} - Q_{Ax''_n}}{Q_{Ax'''_n} - Q_{Ax''''_n}} = \frac{Q_{Bx'_n} - Q_{Bx''_n}}{Q_{Bx'''_n} - Q_{Bx''''_n}},$$

where Q is the heat of formation of compound, Ax_n or Bx_n .

A and B are atoms of metals,

x' , x'' , x''' , refer to halogens in order of increasing atomic weight.

This equation may be used when the heats of formation of five compounds are known. It is not limited to halogens. Fomin later modified the equation, but the principle remained the same.⁵

A. Gosselin adopted a unit bond energy.⁸ He expressed all other bonds as multiples of this unit in calculating heats of formation.

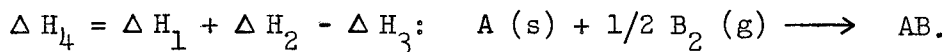
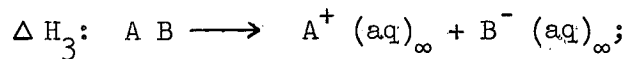
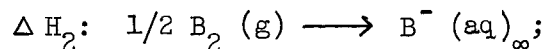
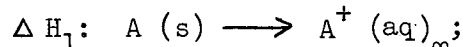
Cartledge obtained a correlation of heats of formation² by plotting $\log (-\Delta H/z)$ vs ϕ . Here ϕ , the ionic potential, is defined as z/r_u , where z is the charge of the cation and r_u is the univalent radius according to the method of Zachariasen with coordination number of 6. A plot is made for each anion. The average deviation for the plots was about 1%. There were some deviations of from 5 to 10 kcal.

The curves can also be applied to the heats and free energies of formation of aqueous ions. Cartledge investigated Groups I, II, and IV, for anions of the halogens, oxygen, sulfur, nitrogen, nitrate, carbonate, phosphate, arsenate, and anhydrous sulfate.

Brewer, et al. used an indirect method of estimating heats of formation.¹ The Born-Haber cycle permits the subdivision of the heat of formation into its components: energies of sublimation, ionization, dissociation, lattice energy, and electron affinity. By variously estimating the unknown component energies, using plots based on periodic (or other systematic) variation of the properties, they estimated the sum or heat of formation. This technique was applied primarily to halide compounds.

Still another method relates the heat of formation to the volume change in reaction. In this case, the heat of formation is plotted vs the volume change in reaction. There is considerable scatter if the data for all compounds are put on a single plot. A better technique is to treat each group of similar compounds as a unit.

When the heat of solution may be estimated, and data are available on the heat of formation of the ions (at infinite dilution) in aqueous solution of the participating atoms, the heat of formation may be calculated by use of these equations:



Values of the heat of formation of ions in solution for many elements are available in the literature. Heats of solution are generally small, but there are also numerous large values. It is here that this method runs into difficulty, for the available data are rather limited.

Some of these methods as well as others are discussed more fully in¹⁴ and ¹.

II. ELECTRONEGATIVITY SCALES

Sanderson²⁰ proposed a relationship between the stability ratio and the Pauling electronegativity. His equation takes the form²¹

$$x^{\frac{1}{2}} = 0.21 \text{ SR} + 0.77,$$

where SR is the stability ratio. This ratio is defined as the relative average electronic density of an atom. The values were calculated as the ratio of the average electronic density of an atom to that of a hypothetical iso-electronic inert atom. The value for the inert atom was interpolated from values for the actual inert elements. The electronic density in electrons per cubic angstrom is

$$\text{ED} = x / 4.19 r^3,$$

where z is the electronic number,

r is the nonpolar covalent radius.

Values of ED, SR, and r are given for about 50 elements. The agreement of the values with those of Pauling is quite good on the whole. The valence effect on the electronegativity might be introduced in this equation by modifying the z factor in the electron density calculation for the atoms.

Gordy obtained an absolute scale of electronegativity by considering the electronegativity as being equal to the potential resulting from the unscreened nuclear charge of the bonded atom effective on a bonding electron.⁶ The electron was considered to be a distance from the nucleus equal to the covalent radius. His result, referred to the scale of Pauling:

$$x = 0.31 (n + 1 \pm c / r) + 0.50,$$

where n is the number of electrons in the valence shells
(or valence),

c is the formal charge on the nucleus,

r is the single-bond covalent radius.

The results agree well with values obtained by Haissinsky¹⁰ who used the empirical method of Pauling. The equation broke down for silver,

copper, gold, and the transition elements. This was due in part to lack of knowledge of the screening factors.

Gordy and Thomas reviewed the various methods of estimating the electronegativity and assigned values to all of the elements.⁷ They mention that the values calculated with the method of Mulliken are in approximate agreement for the Groups I and II elements, but that they correlate poorly for the other groups. This was noted by Skinner and Pritchard,²⁴ who had previously evaluated and extended the work of Mulliken. They point out that the major drawback of this method is the requirement of electron affinity values. These are not known accurately for more than a few elements. Others must be estimated.

III. SIMPLIFIED LATTICE-ENERGY EQUATION

The common equation for crystal energy is

$$U = \frac{N e^2 A z_a z_c}{R_0} \left(1 - \frac{1}{n}\right), \quad (A-1)$$

where N and e^2 are universal constants, Avogadro's number and the specific charge, respectively; z_a and z_c are the anion and cation charge numbers; n , the Born exponent, may vary commonly from about 6 to 12, depending on the nature of the crystal. Some authors choose to use a value of 9 as an approximation to the experimental values. We follow Pauling, who assigned values to several ion types, and used averages of these for a specific crystal. His values are:

<u>Ion type</u>	<u>n</u>
He	5
Ne	7
Ar, Cu	9
Kr, Ag	10
Xe, Au	12

The quantity R_0 , the smallest anion-cation distance of approach, may be approximated as the sum of the crystal radii. Accurate evaluation of A , the Madelung constant, involves equations whose complexity is prohibitive for this study.²³ We will use the approximation proposed by Templeton,²⁷

$$A = \frac{\alpha \sum \bar{z}^2}{2}, \quad (A-2)$$

$\bar{z}$ is the ion charge number,

α is the Madelung constant per valence bond.

Empirically we have²⁶

$$\alpha = 1.890 - \frac{1.00}{m}, \quad (A-3)$$

where m is the harmonic mean coordination number of the crystal.

To maintain the simplicity of our empirical equation, we would like to express m in terms of other variables already employed.

Figure 10 is a plot of coordination numbers of various oxides as a function of the ratio of the crystal radii of the participating ions. Also included in this plot is the minimum radius ratio for stability of various crystal lattices estimated from geometrical considerations. The line through the data represents a sort of average coordination number. The straight line shown might be expected to give values accurate to ± 1 for the coordination number for the oxides and halides of the alkali and alkaline earth metals. Similar accuracy might be expected for many other crystals. An error of 1 gives the following maximum error in the term $(1.89 - 1/m)$:

m	$1.890 - 1/m$	max	% error
10	1.790	-0.0111	-0.62
8	1.765	-0.018	-1.02
6	1.723	-0.033	-1.92
4	1.640	-0.083	-5.06

This error should be tolerable. We therefore calculate m with the function

$$m = 2.15 + 7.50 R_a/R_c. \quad (A-4)$$

Substituting Equations (A-2), (A-3), and (A-4) in Equation (A-1), we obtain

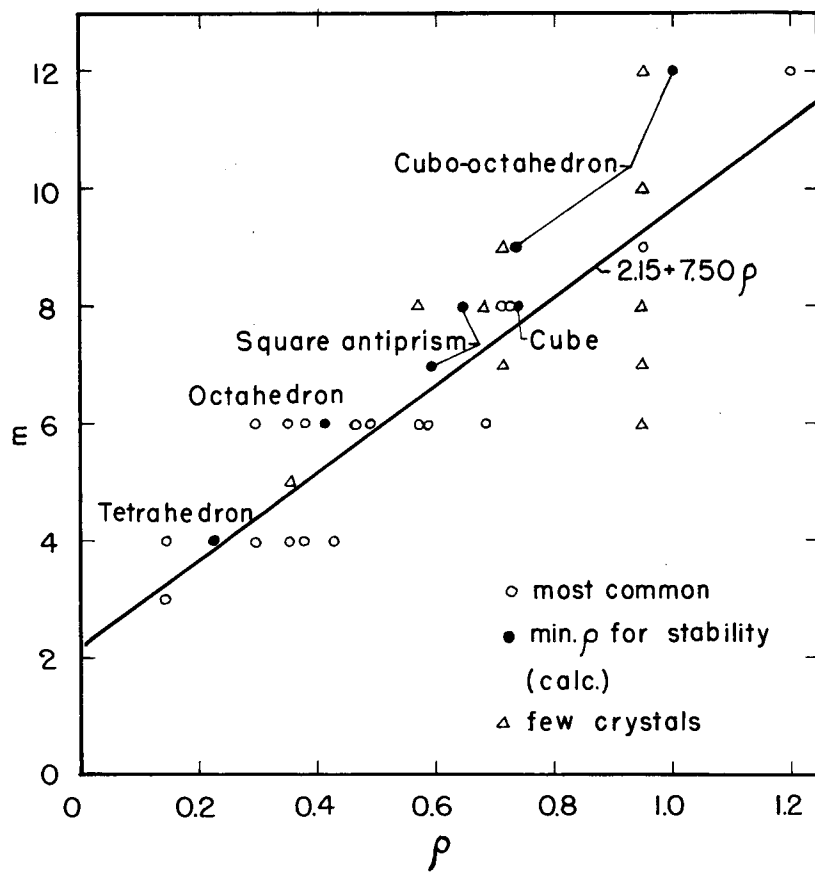
$$U = \frac{N e^2 \sum z_a^2 z_c}{(2 R_a + R_c)} \left(1.89 - \frac{1}{2.15 + 7.50 R_a/R_c} \right) \left(1 - \frac{1}{n} \right) \quad (A-5)$$

Several lattice energies calculated with Equation (A-5) are compared to those calculated by Sherman²³ using Equation (A-1) in Table IX.

A simplified equation for the lattice energy has also been developed by Kapustinskii.¹³ He chose to neglect the factor $(1 - 1/n)$ in Equation (A-1), choosing n equal to 6 in his derivation.

His equation:

$$U = \frac{287.2 \sum n \eta_1 \eta_2}{t_a + t_c} \left(1 - \frac{0.345}{t_c + t_a} \right), \quad (A-6)$$



MU-14725

Fig. 10. Coordination of various cations with oxygen.¹⁸

Table IX

Comparison of Lattice-Energy Calculations									
Exp -- Experimental data ²³									
B ---- Calculated with Born Equation ²³									
E ---- Calculated with Equation (A-5)									
K ---- Calculated with Equation (A-6)									
All data in kcal.									
Cmpd	Exp	B	E	K	Cmpd	Exp	B	E	K
MgO		940	950	931	Al ₂ O ₃	3618	3708	3780	3710
CaO		842	853	822	Cr ₂ O ₃	3627	3655	3678	3530
SrO		791	728	782	Na ₂ S	524	516	538	540
BaO		747	770	731	Cu ₂ S	683	612	539	540
MgS		778	784	795	MnS	841	788	802	800
CaS		722	721	712	ZnS	852	816	776	770
SrS		687	633	683	CdS	802	770	730	717
BaS		656	651	641	HgS	842	774	711	690
Li ₂ O	693	695	706	714	PbS	732	705	746	725
Cu ₂ O	786	682	647	622	AgF	223	208	199	190
Ag ₂ O	715	585	587	563	MgF ₂	689	697	729	710
MnO	959	912	978	939	CaF ₂	617	618	652	625
FeO	964	944	993	955	SrF ₂	580	588	554	595
NiO	966	968	1029	990	BaF ₂	547	557	587	555
ZnO	970	977	937	900	MnF ₂	645	656	749	715
CdO	911	867	867	827	CuF ₂	693	690	698	667
SnO ₂	2813	2734	2893	2735	NiF ₂	734	697	790	755
PbO ₂	2832	2620	2768	2600	CdF ₂	662	629	662	630

(continued)

Table IX - continued

Cmpd	Exp	B	E	K	Cmpd	Exp	B	E	K
PbF ₂	590	581	619	639	KBr	157.8		158.4	157
CuCl	228	206	184	181	KI	149.0		149.6	148
AgCl	207	187	170	166	RbF	181.8		184.4	177.7
SrCl ₂	494	494	479	517	RbCl	158.9		159.4	156.3
CuBr	224	198	175	175	RbBr	152.5		153.3	150.6
AgBr	204	181	163	160	RbI	144.2		145.2	142.8
CuI	221	188	163	164	CsF	172.8		175.3	167.0
AgI	202	176	153	151	CsCl	148.9		152.6	147.9
CdI ₂	563	477	494	490	CsBr	143.5		146.8	142.8
PbI ₂	497	461	503	495	CsI	136.1		139.4	135.8
NaF	215.0		217.3	212	LiF	240.1		240.3	241
NaCl	181.3		181.3	182	LiCl	193.3		197.2	204
NaBr	171.7		173.2	174	LiBr	183.1		187.8	194
NaI	160.8		162.7	164	LiI	170.7		175.3	182
KF	190.4		192.4	186					
KCl	164.4		165.1	163					

where η_1, η_2 are ionic charges,
 t_a, t_c are ionic radii for $n = 6$,
 Σn is the number of ions in a mole.

Table IX indicates that the lattice-energy values calculated with Kapustinskii's simplified equation agree closely with the values calculated with Equation (A-5).

Table X compares the average deviation of the three equations from the experimental determinations.

Table X

Comparison of Lattice-Energy Calculations. Average error for 58 compounds of Table IX.		
Born Equation	12.0	kcal/equivalent ^a
Equation (A-5)	18.8	kcal/equivalent
Equation (A-6)	20.6	kcal/equivalent

^a The deviation for the alkali metal halides is small and was assumed zero for comparison.

IV. DATA

Ionization potentials have been determined spectroscopically for all the common elements in most of the valence states ordinarily encountered. A fairly complete set of consistent values is given in Bureau of Standards Circular 500. The data are listed as heats of formation of the gaseous ion with respect to the standard state. The ionization potential is simply the difference between these values and the heat of formation of the monatomic gas. These data were used throughout.

Electron affinities have not been determined to as great an accuracy as the ionization potentials because the methods of spectroscopy have not been applicable.¹⁹ They are commonly calculated by using the Born-Haber cycle. The values of electron affinity for the halogens, oxygen, and sulfur listed in Circular 500 were used. The values for the metals were assumed to be zero, since most of them are known to be small. Electron affinities other than the first stage are negative for all elements and were not required.

Values of crystal radii have been reported by various authors.¹⁸ Pauling's work was chosen for several reasons: (a) his work has partial theoretical justification from the Schrödinger wave mechanics; (b) the data are more complete; (c) an equation is given to permit calculation of the effect of different valence states of the same atom. Some of Pauling's data are listed in Table XI. The effect of charge is given by the equation

$$R_z = R_1 a^{-2/(n-1)},$$

where z is the charge of the ion,

R_z is the crystal radius for charge z ,

R_1 is the univalent radius,

n is the Born exponent.

Heats of formation and free energies of formation were also obtained from the Bureau of Standards Circular 500 in order to assume a consistent set of values.

Table XI

Crystal Radius ¹⁸					
Ion	Valence	Radius (Å)	Ion	Valence	Radius (Å)
F	-1	1.36	Sr	2	1.13
Cl	-1	1.81	Ba	2	1.35
Br	-1	1.95	Zn	2	0.74
I	-1	2.16	Cd	2	0.97
O	-2	1.40	Hg	2	1.10
S	-2	1.84	Fe	2	0.59
Li	1	0.60	Co	2	0.55
Na	1	0.95	Ni	2	0.50
K	1	1.33	Cu	1	0.96
Rb	1	1.48	Ag	1	1.26
Cs	1	1.69	Sn	4	0.71
Be	2	0.31	Pb	4	0.84
Mg	2	0.65	Al	3	0.50
Ca	2	0.99			

V. SOLUTION OF ITERATION²²

Consider the set of simultaneous equations

$$\begin{aligned} f_1(x, y, \dots, \xi) &= 0, \\ f_2(x, y, \dots, \xi) &= 0, \\ &\vdots \\ f_\xi(x, y, \dots, \xi) &= 0. \end{aligned} \tag{A-7}$$

Express them in the form

$$\begin{aligned} x &= F_1(x, y, \dots, \xi), \\ y &= F_2(x, y, \dots, \xi), \\ &\vdots \\ \xi &= F_\xi(x, y, \dots, \xi). \end{aligned} \tag{A-8}$$

Let an approximate solution be

$$(x_0, y_0, \dots, \xi_0).$$

Then the solution by iteration proceeds as follows:

$$\begin{aligned} x_1 &= F_1(x_0, y_0, \dots, \xi_0), \\ y_1 &= F_2(x_1, y_0, \dots, \xi_0) \\ &\vdots \\ \xi_1 &= F_\xi(x_1, y_1, \dots, \xi_0) \\ x_2 &= F_1(x_1, y_1, \dots, \xi_1) \\ &\vdots \end{aligned} \tag{A-9}$$

It can be shown that the necessary condition for convergence is expressed by the inequalities that must apply at all points at or near $(x_n, y_n, \dots, \xi_n)$:

$$\begin{aligned} \frac{\partial F_1}{\partial x} + \frac{\partial F_1}{\partial y} + \dots + \frac{\partial F_1}{\partial \xi} &< 1, \\ \vdots \\ \frac{\partial F_\xi}{\partial x} + \frac{\partial F_\xi}{\partial y} + \dots + \frac{\partial F_\xi}{\partial \xi} &< 1. \end{aligned} \tag{A-10}$$

We may apply the above equations to the case of simultaneous linear equations, e.g.,

$$\begin{aligned} a_1 x + b_1 y + \dots + n_1 \xi &= 0, \\ a_2 x + b_2 y + \dots + n_2 \xi &= 0, \\ \vdots \\ a_n x + b_n y + \dots + n_n \xi &= 0. \end{aligned}$$

The necessary condition for convergence becomes simply that the coefficient of the unknown for which a particular equation is solved must be greater than the sum of the magnitudes of all the other coefficients of that equation. This must be true for all equations. The greater the ratio of the largest coefficient to the sum of the magnitudes of the remaining coefficients, the greater is the rate of convergence. When the ratio is close to unity, the rate of convergence is diminished.

Let us now consider the convergence of Equations (7), which are nonlinear. In order to apply the criteria of convergence, Equations (A-10), we must express Equations (7) in the form of Equations (A-8). Because the equations are in the form of a summation, we are unable to do this in all cases. Therefore, we cannot test the equations for convergence in this manner but must determine convergence by attempting the solution and examining the results.

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