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A METHOD FOR ESTIMATING THE HEAT OF
FORMATION AND FREE ENERGY OF FORMATION
OF INORGANIC COMPOUNDS

Berkeley, California

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AND FREE ENERGY OF FORMATION OF INORGANIC COMPOUNDS

Darrell E. Wilcox
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ABSTRACT

A general method of independently estimating the heat of formation ΔH_f° and free energy of formation ΔF_f° of inorganic compounds has been developed from the work of Linus Pauling in formulating an electronegativity scale. The result is a simple equation involving three parameters characteristic of each ion. Each valence state of an element may be assigned a value for each of the parameters. These parameters may be evaluated for any ion if at least three experimental heats of formation or free energies of formation are known.

The equation has been applied to the correlation of known ΔH_f° data for 34 monovalent and divalent cations and 32 anions, including the metallic halides, oxides, sulfides, and compounds such as the sulfates, carbonates, and tungstates. The average deviation obtained for 427 compounds was 1.98 kcal/M, and the maximum deviation was 8.73 kcal/M. Similar results were obtained in a correlation of ΔH_f° for a set of trivalent and tetravalent cations, and in the correlation of ΔF_f° of many of the same compounds.

An error of less than 15 kcal/M may generally be expected in estimating an unknown if one uses parameters evaluated from three or more experimental data.

INTRODUCTION

Thermochemical data are necessary for many calculations of theoretical significance in the predictions of chemical equilibria or bond stabilities. Many data for heat of formation have been given by early investigators who believed that the limiting quantity of work obtainable from a chemical reaction is equivalent to $-\Delta H$. Since formulation of the second law of thermodynamics and the realization that the free-energy change measures the maximum capacity for performing useful work, much effort has been directed toward the evaluation of the free energy of formation as well as the heat of formation of chemical compounds.

A number of methods for estimating these quantities are now available. None, however, is sufficiently general to permit accurate estimation of data for a wide range of compounds. By using Latimer's method for estimating entropy changes,¹ one can calculate free-energy data which are just as accurate as many experimental data for heat of formation justify. However, this method requires that the heat of formation of the compound be known.

The present work was directed toward the development of an accurate and simple method for estimating both heat of formation and free energy of formation. It was considered essential that the method be general enough to apply to many types of inorganic compounds, and that it permit the free energy of formation to be estimated independently of the heat of formation.

BACKGROUND AND THEORY

The work of Linus Pauling in developing a scale of electronegativities of the elements provided the theoretical origin of this research. Since the heat of formation was used to set up Pauling's scale, an equation resulted which could be used to estimate the heat of formation of simple gaseous compounds. This equation is only approximate and applies only to substances containing single bonds, but serves as a useful starting point in attempting to extend the method.

The wave function representing the single bond in a symmetrical molecule A-A can be written in the form²

$$a \phi_{A:A} + b \phi_{A^+A^-} + b \phi_{A^-A^+} \quad (1)$$

A similar expression may be written for the molecule B-B.

For the molecule A-B, involving a single bond between unlike atoms of similar character, the representative wave function would be like that in Eq. (1), but would be an average of those for the symmetrical molecules A-A and B-B. Pauling describes this as a normal covalent bond. For it he postulates a bond energy equivalent to the arithmetic mean of those for the molecules A-A and B-B. This postulate is not always valid, but has been shown empirically to be approximately correct for many compounds.

For the molecule A-B in which the atoms A and B are dissimilar, a more general wave function must be used to represent the bond:

$$a \phi_{A:B} + c \phi_{A^+B^-} + d \phi_{A^-B^+} \quad (2)$$

The best values of c/a and d/a are those that make the bond energy a maximum. The energy of an actual bond between unlike atoms is therefore greater than or equal to the energy of a normal covalent bond between these atoms. This additional bond energy is due to the ionic character of the unsymmetrical bond and is equivalent to the heat liberated in the reaction

Pauling examined data for gas-phase formation of simple non-metallic compounds. He found that the magnitude of the heat of formation increased with increasing differences in electronegativity, or electron-affinity, between the atoms A and B. He also observed that an approximate additivity relationship existed between the square root of the heat of formation and the contribution of each atom to the bond.

From this he was able to formulate an electronegativity scale of the elements. Accordingly, the enthalpy of formation of a substance in its standard state was found to be approximated by the summation

$$-\Delta H_f^0 = \sum_{A-B} (x_A - x_B)^2 - 55.4 n_N - 26.0 n_O, \quad (4)$$

where x is the electronegativity in $(\text{kcal})^{1/2}$, n is the number of atoms of nitrogen or oxygen in the molecule, and ΔH_f^0 is the standard heat of formation in kilocalories. The summation is over the apparent number of single bonds in the molecule. The correction terms for nitrogen and oxygen are used because N_2 contains a triple bond that is much more stable than three single bonds, and O_2 a bond that is more stable than two single bonds. This extraordinary stability leads to positive heats of formation for many compounds.

Pauling proposed that the scale might be extended to include metallic elements and liquids or crystals if one assumes that (a) the energy of an element in its standard state does not differ from that of a normal covalent bond; (b) the van der Waals stabilization of the reactants and products in their standard states are equal, and accordingly the enthalpy of formation of a solid or liquid compound referred to the standard states is approximately equal to the enthalpy of formation of the gaseous compound from gaseous elements; (c) unknown bond types do not contain multiple bonds of significantly greater energy than the corresponding number of single bonds.

Haissinsky revised and extended Pauling's original electronegativity scale.³ Heats of formation calculated from this scale are only approximate, however, since the electronegativity values are given to only two significant figures. Errors as large as 200 kcal resulted.

Anderson and Bromley modified Pauling's equation for estimating the heat of formation and extended it to empirically correlate the monohalides and dihalides of 21 metals.⁴ Using correction factors for all of the elements similar to those of Pauling for nitrogen and oxygen, they obtained

$$-\Delta H_f^0 = n_{AB} (X_B - X_A)^2 + n_A Y_A + n_B Y_B, \quad (5)$$

where n_{AB} is the apparent number of single bonds, n_A and n_B are the number of atoms A and B in the molecule, and X and Y are empirically determined parameters for each valence state of each element. Values of X and Y were empirically evaluated for each element. The constant X shows a trend through the periodic table similar to that of Pauling's electronegativity. The constant Y serves both as a correction for deviations in the standard states of the elements and also as a means of altering the standard states where necessary.

The average deviation of calculated values from experimental data for the 85 halides included in the correlation was 0.93 kcal/M. An attempt to extend the equation to correlate the heat of formation of oxides, sulfides, and compounds such as carbonates, sulfates, acetates, and nitrates was made by considering the radicals as acting as entities in the equation rather than as a combination of elements. Considerably poorer agreement resulted, especially for the oxides. Errors as large as 84 kcal/M were found.

The objective of the present work was to improve the accuracy of the equation when applied to compounds such as the oxides, sulfates, and tungstates which form bonds unlike those of the halides. It is believed that for these compounds the postulate of additivity of covalent bonds is not accurate, and the argument must therefore be modified.

Pauling and Sherman performed a quantum-mechanical treatment of one-electron bonds which leads to the conclusion that the postulate of additivity, while approximately correct for certain compounds, is not valid for many others.⁵ A similar postulate was proposed involving the geometric mean of the bond energies of the molecules A-A and B-B (that is, the square root of their product) instead of the

arithmetic mean. This new postulate states that the energy, D , of a normal covalent bond between atoms A and B is equal to $[D(A-A) D(B-B)]^{1/2}$, and that in consequence the heat of formation is approximated by

$$-\Delta H_f^0 = D(A-B) - [D(A-A) D(B-B)]^{1/2}. \quad (6)$$

If the bond energies $D(A-A)$ and $D(B-B)$ do not differ greatly in value, there is only a small difference between their geometric and arithmetic means. Therefore, the arguments based on the earlier postulate are valid for compounds such as the halides. For compounds such as carbonates, sulfates, or the alkali hydrides, however, the new postulate leads to results much different from those given by the earlier one, since the bond energies of the metals are much less than those of the anion molecules.

The conclusion to be reached from this is that, in general, the postulate of the geometric mean leads to more satisfactory values for the energy of normal covalent bonds between unlike atoms than does the postulate of the arithmetic mean. However, application of the former is considerably more difficult because knowledge of individual bond energies is required. Therefore, the method of Anderson and Bromley was modified and extended to include an additional correction factor for each element or radical.

The form of the third parameter to be employed must satisfy two important conditions: (a) to adequately characterize the elements (or radicals), it must be flexible enough to provide small contributions for compounds whose heats of formation follow closely those given by Eq. (5), yet give large contributions to the heat of formation of other compounds; (b) from practical considerations the constant must be simple to evaluate and easy to handle when included in the equation.

After several trials, the best form of the third parameter, designated W , was found to be

$$-\Delta H_f^O = n_{AB} (X_B - X_A)^2 + n_A Y_A + n_B Y_B + n_{AB} \left(\frac{W_B}{W_A} \right). \quad (7)$$

However, it should be pointed out that constants of this nature obtained by empirically fitting the experimental data do not necessarily have physical significance; as do the correction factors for nitrogen and oxygen employed by Pauling.

The Pauling scale of electronegativity was determined initially for a small group of nonmetallic elements, and then extended one value at a time for the metallic elements. The X , Y , and W parameters of this work were evaluated simultaneously for all the elements and radicals included in the correlation. Equation (7) was assumed to be the correct form for the heat of formation, and the least-squares method was applied to fit the equation to available experimental data. Details of the method and the set of equations used to evaluate the constants are given in Appendix I.

It is desirable to be able to estimate the standard free energy of formation independently of the heat of formation. This may be accomplished by an equation of the same form as that for the heat of formation:

$$-\Delta F_f^O = n_{AB} (X_B - X_A)^2 + n_A Y_A + n_B Y_B + n_{AB} \left(\frac{W_B}{W_A} \right). \quad (8)$$

The constants n_{AB} , n_A , and n_B retain their values from Eq. (7), but new values must be determined for the parameters X , Y , and W .

RESULTS AND DISCUSSION

Solution of Equations

The equations to be evaluated are nonlinear and implicit in X . An iterative procedure was chosen as the method of solution,⁶ as this is handled very efficiently by high-speed digital computers. The equations were programed for the IBM 7090 computer. Details of the procedure are discussed in Appendix I.

Preliminary hand calculations indicated that for the cations one root was greater than the anion roots, one was approximately equal to the average of the anion values, and one was less. The first and second are contrary to the Pauling electronegativity scale and lead to solutions in which very high corrections by the Y and W terms are required to fit the experimental data. The third root agrees with the electronegativity scale, and thus was used in the correlation. For the same reason, the largest value of the anion root was the value of interest.

A plot of several X values as functions of the iteration number in the ΔF_f^0 correlation is given in Fig. 1. Sets of Y and W values are plotted in Figs. 2 and 3. At first there appears to be a tendency toward convergence. However, the values continue to drift as the solution proceeds, and there is no indication that convergence on a unique set of values would be obtained in a finite number of iterations.

The erratic behavior observed in the value of W near the end of the iteration process occurred for other ions and also for values of X and Y in earlier programs. In all cases it dampened out with continued iteration, and the values reassumed their pre-oscillation values. It is believed that this indicates insensitivity to the set of values that is obtained as the least-squares solution. Thus the individual values constantly change, but the total deviation decreases toward a minimum.

Figure 4 is a plot of the total deviation from experimental data of values of $-\Delta F_f^0$ calculated from sets of X , Y and W at different iteration numbers. Agreement is continually improving and tending toward a minimum. The log of the slope of this curve is plotted in Fig. 5.

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Fig. 1. Iterative solution of Eqs.(A-1) for X .

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Fig. 2. Iterative solution of Eqs. (A-1) for Y .

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Fig. 3. Iterative solution of Eqs. (A-1) for W .

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Fig. 4. Total deviation vs N.

MU-27689

Fig. 5. Plot of $-d(\Sigma\Delta)/dN$ vs N . The slop is -4.05.

as a function of the log of the iteration number. The curve is a straight line of slope -4.05:

$$\frac{d(\Sigma\Delta)}{dN} = -b N^{-4.05}$$

Graphically, b is 6.62×10^9 . Integrating from $N = 800$ to infinity, we find $(\Sigma\Delta)_{N=\infty} - (\Sigma\Delta)_{N=800} = -7.8$ kcal.

Thus, the total deviation would be reduced only by 7.8 kcal after an infinite number of iterations. This is to be considered only as an approximation, but it does indicate the extent to which the correlation may be improved by continuing the iterative procedure. Further iteration is not warranted by so little improvement.

The results of the two heat-of-formation correlations are nearly identical to those above. In each case the plot of $\log \frac{d(\Sigma\Delta)}{dN}$ vs $\log N$ indicates that very little improvement would be realized if the iteration procedure were continued. The final values of the characteristic parameters are listed in Tables A-1 through A-4 of Appendix I, and these may be considered an approximate solution to the set of equations.

Evaluation of Solution

Separate correlations were developed for: (a) the heat of formation of 427 compounds of monovalent and divalent cations and anions, including halides, oxides, sulfides, and radicals such as the sulfates and tungstates; (b) the heat of formation of 184 compounds of trivalent and tetravalent cations with halide, oxide, sulfide, sulfate, and hydroxide ions; (c) the free energy of formation of 270 of the compounds above.

The experimental data and calculated values are compared in Tables I through III. Average deviations of calculated values from the experimental data of 1.98 kcal/M, 1.51 kcal/M, and 1.57 kcal/M, respectively, were obtained. The agreement is in general quite good and is comparable with the expected error in the experimental data of many compounds. That the agreement is not better for some of the

Table I. Solution of Eq. (7) for heat of formation. Experimental data are compared with calculated values of $-\Delta H_f^\circ$.

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental ^a	Calculated		Experimental	Calculated
NH ₄ Cl	75.38	74.49	LiOH	116.45	116.92
NH ₄ Br	64.61	64.32	LiNO ₂	96.6	89.22
NH ₄ I	48.30	50.35	LiReO ₄	253.4	252.56
NH ₄ NO ₃	87.3 ^b	87.59	LiH	21.666 ^d	20.87
(NH ₄) ₂ SO ₄	281.86	284.06	LiClO ₄	90.89 ^e	92.87
(NH ₄) ₂ SO ₃	212.0	211.79	LiHS	60.0 ^f	59.73
NH ₄ NO ₂	63.1 ^b	60.08	LiNH ₂	43.50	42.56
NH ₄ HSO ₄	244.83	245.92	Li ₂ O ₂	151.7	153.89
NH ₄ HCO ₃	203.7	203.39	NaF	136.3 ^g	131.88
NH ₄ ClO ₄	69.4 ^b	68.90	NaCl	98.232	96.08
NH ₄ ClO ₃	65±2 ^b	62.61	NaBr	86.03	85.39
LiF	146.3	145.08	NaI	68.84	70.88
LiCl	97.70	97.77	Na ₂ O	99.4	103.47
LiBr	83.72	84.91	Na ₂ S	89.2	91.94
LiI	64.79	68.15	Na ₂ CO ₃	270.3	268.68
Li ₂ O	142.4	142.69	NaNO ₃	111.54	110.19
Li ₂ S	106.5 ^c	106.46	Na ₂ SO ₄	330.9	329.80
Li ₂ CO ₃	290.54	290.86	NaC ₂ H ₃ O ₂	169.8	168.66
LiNO ₃	115.279	114.83	NaOH	101.99	101.58
Li ₂ SO ₄	342.83	342.91	NaCN	21.46	18.66

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
$\text{Na}_2\text{C}_2\text{O}_4$	314.3	313.44	KBr	93.73	94.59
NaCHO_2	155.3	153.48	KI	78.31	81.10
Na_2SO_3	260.6	258.	K_2O	86.4	91.14
NaNO_2	85.9	82.54	K_2S	100.	95.35
NaHSO_4	269.2	268.36	K_2CO_3	273.93	274.02
NaHCO_3	226.5	226.10	KNO_3	117.76	117.81
NaCNS	41.73	41.33	K_2SO_4	342.66	342.45
NaReO_4	249.4	252.08	$\text{KC}_2\text{H}_3\text{O}_2$	173.2	172.86
Na_2SiO_3	361. ^e	355.36	KOH	101.78	100.09
Na_2MoO_4	350.4 ^h	351.75	KCN	26.90	22.73
Na_2WO_4	379.6 ⁱ	381.57	$\text{K}_2\text{C}_2\text{O}_4$	320.8	320.30
NaH	13.487 ^d	17.96	KCHO_2	158.0	157.71
Na_2SeO_4	258.	259.50	K_2SO_3	266.9	269.72
NaClO_4	92.18	91.26	KNO_2	88.5	87.72
Na_2HPO_4	417.4	422.87	KHSO_4	276.8	275.86
NaHS	56.5	56.47	KHCO_3	229.3	230.96
NaClO_3	85.73	84.70	KCNS	48.62	49.53
NaNH_2	28.4	31.66	KReO_4	264.02	260.32
Na_2O_2	120.6	119.54	K_2MoO_4	357.3 ^j	360.29
KF	134.46	134.89	KH	13.819 ^d	17.24
KCl	104.18	104.30	KClO_4	103.6	101.45

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
KHS	63.2	64.18	RbNH ₂	26.2	24.81
KClO ₃	93.50	94.61	Rb ₂ O ₂	102.2	102.76
KNH ₂	28.3	30.56	CsF	130.3	133.88
K ₂ O ₂	118.	112.57	CsCl	106.9	105.61
RbF	131.78±2	134.31	CsBr	97.7	96.32
RbCl	103.41	102.99	CsI	83.9	83.29
RbBr	93.53	93.13	Cs ₂ O	79.3	75.73
RbI	79.0	79.51	Cs ₂ S	87.9	88.84
Rb ₂ O	79.9	78.57	Cs ₂ CO ₃	274.2	270.61
Rb ₂ S	84.2	85.65	CsNO ₃	121.51	119.16
Rb ₂ CO ₃	270.6	270.06	Cs ₂ SO ₄	346.18	343.63
RbNO ₃	117.54	117.41	CsOH	100.6	95.61
Rb ₂ SO ₄	341.5	341.05	CsHSO ₄	277.4	277.06
RbOH	99.4	96.20	CsHCO ₃	231.8	230.49
RbHSO ₄	274.2	275.22	CsReO ₄	260.6	261.43
RbHCO ₃	229.0	229.36	CsHS	66.3	65.35
RbCNS	50.4 ^k	47.93	CsNH ₂	28.8	25.57
RbReO ₄	257.4	258.43	Cs ₂ O ₂	99.6	100.86
RbClO ₄	104.37	102.01	BeF ₂	242±6 ^l	249.68
RbHS	62.9	63.18	BeCl ₂	122.3	121.51
RbClO ₃	94.3	94.73	BeBr ₂	88.4	89.45
			BeI ₂	50.6	49.36

Table I (Continued).

$-\Delta H_f^\circ$ (kcal/gM)			$-\Delta H_f^\circ$ (kcal/gM)		
Compound	Experimental	Calculated	Compound	Experimental	Calculated
BeO	143.1 ^l	142.10	MgH ₂	17.7 ^p	118.88
BeS	55.9	62.17	Mg(ClO ₄) ₂	140.6	138.25
BeSO ₄	286.0	282.00	MgO ₂	148.9	147.39
Be(OH) ₂	216.8	211.52	CaF ₂	290.2 ^l	290.43
BeMoO ₄	316.3 ^m	315.68	CaCl ₂	190.0	190.83
BeWO ₄	342.9 ^m	340.05	CaBr ₂	161.3	164.16
BeSeO ₄	213.24 ⁿ	213.88	CaI ₂	127.8	129.67
MgF ₂	268.0 ^l	266.67	CaO	151.79 ^l	150.82
MgCl ₂	153.2 ^l	152.38	CaS	115.3 ^o	107.40
MgBr ₂	123.7	122.93	CaCO ₃	288.45	291.26
MgI ₂	86.0	85.56	Ca(NO ₃) ₂	224.0	225.61
MgO	143.77 ^l	143.77	CaSO ₄	342.42	340.09
MgS	83.0 ^o	81.49	Ca(C ₂ H ₃ O ₂) ₂	355.0	352.61
MgCO ₃	266.0	266.57	Ca(OH) ₂	235.8	237.90
Mg(NO ₃) ₂	188.72	189.91	Ca(CN) ₂	44.2	46.78
MgSO ₄	305.5	307.38	Ca(CHO ₂) ₂	323.5	323.60
Mg(OH) ₂	221.00	221.67	Ca(NO ₂) ₂	178.3	176.51
MgSO ₃	241.0	242.37	CaSiO ₃	382.9 ^l	379.06
MgSiO ₃	357.9	355.88	CaMoO ₄	367.3 ^q	366.58
MgMoO ₄	336.5 ^m	337.65	CaWO ₄	392.5	394.47
MgWO ₄	361.1 ^m	363.69	CaH ₂	45.1	44.37

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
CaSeO ₄	270.11 ^r	270.64	SrHPO ₄	431.3	347.07
CaHPO ₄	435.2	431.98	Sr(NH ₂) ₂	83.2	85.01
Ca(NH ₂) ₂	91.60	88.58	SrO ₂	150.8 ^s	151.73
CaO ₂	155.8 ^s	159.69	BaF ₂	286.9	292.98
SrF ₂	290.3	287.95	BaCl ₂	205.56	203.32
SrCl ₂	198.0	196.85	BaBr ₂	180.4	178.51
SrBr ₂	171.1	171.78	BaI ₂	144.0	145.96
SrI ₂	135.5	138.95	BaO	133.5 ^l	132.14
SrO	141.1	140.21	BaS	106.0 ^o	105.09
SrS	108.1 ^o	107.15	BaCO ₃	291.3	292.39
SrCO ₃	291.2	289.64	Ba(NO ₃) ₂	237.06	237.41
Sr(NO ₃) ₂	233.25	229.85	BaSO ₄	350.2	349.10
SrSO ₄	345.3	342.64	Ba(C ₂ H ₃ O ₂) ₂	355.1	356.77
Sr(C ₂ H ₃ O ₂) ₂	356.7	353.26	Ba(OH) ₂	226.2	229.76
Sr(OH) ₂	229.3	231.93	Ba(CN) ₂	47.9	49.85
Sr(CHO ₂) ₂	325.5	323.94	Ba(CHO ₂) ₂	326.5	328.03
Sr(NO ₂) ₂	179.3	178.42	BaSO ₃	282.6	280.71
SrSiO ₃	371.2	376.81	Ba(NO ₂) ₂	174.0	182.73
SrWO ₄	398.3	396.10	BaMoO ₄	373.4 ^m	370.88
SrH ₂	42.3	44.95	BaWO ₄	403.0 ^m	401.43
SrSeO ₄	275.37 ^t	272.89	BaH ₂	40.9	34.78

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
BaSeO ₄	279.2 ^u	278.90	MnF ₂	189.	196.97
Ba(ClO ₄) ₂	192.8	196.81	MnCl ₂	115.19 ^l	114.91
BaHPO ₄	465.8	457.70	MnBr ₂	90.7	91.65
Ba(ClO ₃) ₂	181.7	182.40	MnI ₂	59.3	60.58
Ba(NH ₂) ₂	78.9	80.21	MnO	92.05 ^l	92.83
BaO ₂	151.9 ^s	147.05	MnS	49.49 ^l	51.82
RaO	125.	125.99	MnCO ₃	213.9	210.37
Ra(NO ₃) ₂	237.	240.90	MnSO ₄	254.24	254.52
RaSO ₄	352.	251.49	Mn(C ₂ H ₃ O ₂) ₂	273.0	274.77
RaMoO ₄	375.0 ^m	372.14	Mn(OH) ₂	165.8	166.67
RaWO ₄	404.7 ^m	403.20	MnC ₂ O ₄	258.2	251.13
CrF ₂	181.0	181.11	Mn(CHO ₂) ₂	242.2	242.25
CrCl ₂	94.6	94.44	MnSiO ₃	307.87 ^l	305.12
CrBr ₂	70±5 ^v	69.83	MnMoO ₄	290.7 ^m	289.10
CrI ₂	37.8	37.90	MnWO ₄	312.5 ^w	311.31
MoCl ₂	44.	44.15	FeF ₂	168±2 ^x	164.33
MoBr ₂	29.	28.84	FeCl ₂	81.86 ^l	82.31
MoI ₂	12.	11.99	FeBr ₂	60.0	59.06
WCl ₂	38.	37.61	FeI ₂	30±2 ^l	28.00
WBr ₂	19.	19.52	FeO	63.8 ^l	64.31
WI ₂	1.	0.87	FeS	22.72	21.85

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
FeSO ₄	220.5	221.70	NiO	57.3 ^l	59.09
FeMoO ₄	258.1 ^m	257.21	NiS	17.5	18.25
FeWO ₄	281.5 ^m	278.83	Ni(NO ₃) ₂	102.2	98.25
FeSiO ₃	276.	273.99	NiSO ₄	213.0	213.04
CoF ₂	159.0	153.27	Ni(OH) ₂	128.6	129.28
CoCl ₂	77.8	77.23	NiC ₂ O ₄	206. ^y	210.54
CoBr ₂	55.5	55.14	NiMoO ₄	251.5 ^m	249.79
CoI ₂	24.4	25.24	NiWO ₄	271.0 ^w	270.48
CoO	57.2	60.08	NiH ₂	6.2	3.64
CoS	20.2	20.35	PdCl ₂	45.4	45.70
CoCO ₃	172.7	170.73	PdBr ₂	24.9	24.72
Co(NO ₃) ₂	102.9	98.96	PdO	20.4	20.58
CoSO ₄	207.5	213.60	Pd(OH) ₂	92.4	92.09
Co(OH) ₂	131.2	129.91	PtCl ₂	35.5	35.49
CoMoO ₄	246.6 ^m	250.67	PtS	20.8	20.85
CoWO ₄	269.3 ^m	271.10	Pt(OH) ₂	87.2	87.14
CoH ₂	10.2	8.12	CuCl	32.6 ^l	32.47
NiF ₂	156±2 ^l	153.65	CuBr	25.3 ^l	25.45
NiCl ₂	72.97	75.77	CuI	16.4 ^l	14.59
NiBr ₂	54.2	53.32	Cu ₂ O	40.4 ^l	38.96
NiI ₂	22±2 ^v	23.07	Cu ₂ S	21.20 ^z	23.73

Table I (Continued).

$-\Delta H_f^{\circ}$ (kcal/gM)			$-\Delta H_f^{\circ}$ (kcal/gM)		
Compound	Experimental	Calculated	Compound	Experimental	Calculated
Cu_2SO_4	179.2	180.90	Ag_2S	7.6	5.93
CuCNS	-15.0	-18.86	Ag_2CO_3	120.97	120.93
CuF_2	126.9 $\pm$ 4	122.93	AgNO_3	29.43	31.48
CuCl_2	49.2 $\pm$ 2	54.57	Ag_2SO_4	170.5	172.34
CuBr_2	33.2	33.96	$\text{AgC}_2\text{H}_3\text{O}_2$	93.41	98.87
CuI_2	5.1 ^{aa}	5.57	AgCN	-34.94	-33.13
CuO	37.1	41.63	$\text{Ag}_2\text{C}_2\text{O}_4$	159.1	161.67
CuS	11.6	4.28	Ag_2MoO_4	216.6 ^{bb}	213.10
CuCO_3	142.2	145.14	Ag_2WO_4	230.7 ⁱ	229.47
$\text{Cu}(\text{NO}_3)_2$	73.4	72.43	Ag_2SeO_4	105.05 ^{cc}	104.54
CuSO_4	184.0	186.91	AgClO_4	7.75	6.20
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	214.3	212.07	AgNO_2	10.105	12.99
$\text{Cu}(\text{OH})_2$	107.2	107.26	AgClO_3	5.73	8.29
$\text{Cu}(\text{CHO}_2)_2$	178.6	177.08	Ag_2O_2	6.3	6.46
CuMoO_4	225.7 ^m	226.68	AgCNS	-21.1	-21.84
CuWO_4	247.3 ^m	245.14	ZnF_2	176 $\pm$ 3 ^v	172.58
AgF	48.5	42.64	ZnCl_2	99.6 ^l	100.51
AgCl	30.362	29.58	ZnBr_2	78.4 ^l	79.18
AgBr	23.78	23.30	ZnI_2	49.8 ^l	50.06
AgI	14.91	13.23	ZnO	83.25 ^l	87.22
Ag_2O	7.306	7.92	ZnS	48.5	48.10

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
ZnCO ₃	194.2	192.85	Cd(CNS) ₂	-6. ^{ff}	-11.96 ⁵
Zn(NO ₃) ₂	115.12	120.04	CdMoO ₄	261.1 ^m	261.66
ZnSO ₄	233.88	234.72	CdWO ₄	282.3 ^m	282.24
Zn(C ₂ H ₃ O ₂) ₂	258.1	259.02	Cd(NH ₂) ₂	14.71	14.66
Zn(OH) ₂	153.5	154.14	Hg ₂ F ₂	77. ^{gg}	81.70
Zn(CN) ₂	-18.4	-24.11	Hg ₂ Cl ₂	63.32	61.77
Zn(CHO ₂) ₂	225.0	224.58	Hg ₂ Br ₂	49.42 ^{gg}	50.44
ZnSiO ₃	294.6	291.33	Hg ₂ I ₂	28.91	31.51
ZnMoO ₄	272.4 ^m	273.56	Hg ₂ O	21.8	21.60
CdF ₂	164.9	158.31	Hg ₂ SO ₄	177.34 ^{gg}	171.33
CdCl ₂	93.0	94.35	Hg ₂ (C ₂ H ₃ O ₂) ₂	201.1	200.51
CdBr ₂	75.8 ^l	74.56	HgF ₂	69.5 ^{gg}	76.24
CdI ₂	48.4 ^l	47.03	HgCl ₂	53.4 ^l	54.71
CdO	61.2 ^{dd}	60.93	HgBr ₂	40.7 ^l	43.08
CdS	34.5	33.25	HgI ₂	25.3 ^l	23.84
CdCO ₃	178.7	178.52	HgO	21.68	21.64
Cd(NO ₃) ₂	107.98	112.70	HgS	13.90	15.40
CdSO ₄	221.36	225.50	HgSO ₄	168.3	164.72
Cd(OH) ₂	133.26	134.15	Hg(C ₂ H ₃ O ₂) ₂	199.4	195.16
Cd(CN) ₂	-39.0	-35.81	Hg(CN) ₂	-62.5	-61.94
CdC ₂ O ₄	217.4 ^{ee}	219.39	HgC ₂ O ₄	161.8	157.36

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
Hg(CNS) ₂	-48.0	-46.84	Pb(CNS) ₂	-27.5	-22.21
SnF ₂	158. ^v	159.41	PbSiO ₃	258.8	265.14
SnCl ₂	83.6	84.37	PbMoO ₄	249.7 ^q	251.65
SnBr ₂	63.6	62.47	PbSeO ₄	148.	148.19
SnI ₂	34.4	32.77	TlF	74±5 ^l	74.36
SnO	68.35	67.04	TlCl	48.79 ^l	47.24
SnS	24.3 ^l	27.88	TlBr	41.9 ^l	38.26
Sn(OH) ₂	138.3	136.64	TlI	29.6 ^l	25.45
PbF ₂	158.5	150.07	Tl ₂ S	20.8	24.06
PbCl ₂	85.7 ^l	84.41	Tl ₂ O	41.9	38.67
PbBr ₂	66.21	64.28	Tl ₂ CO ₃	168.1 ⁱⁱ	169.21
PbI ₂	41.6 ^l	36.42	TlNO ₃	58.01	55.60
PbO	52.4	48.93	Tl ₂ SO ₄	221.7	221.89
PbS	22.54	20.55	TlOH	56.9	59.33
PbCO ₃	167.3	168.80	TlCNS	-11.4 ^{jj}	-5.84
Pb(NO ₃) ₂	106.25 ^q	103.85	Tl ₂ SeO ₄	152.84 ^{kk}	153.17
PbSO ₄	219.5	216.55	AuCl	8.4	8.63
Pb(C ₂ H ₃ O ₂) ₂	230.5	237.02	AuBr	4.4	4.15
Pb(OH) ₂	123.0	123.06 ⁺	AuI	-0.2	-0.20
PbC ₂ O ₄	206.2 ^{hh}	209.93	TiF ₂	205±15 ^{ll}	212.19
Pb(CHO ₂) ₂	200.1	202.93	TiCl ₂	120.1 ^{mm}	118.24

Table I (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
TiBr ₂	95±5 ^{ll}	92.73	ZrF ₂	230.	229.97
TiI ₂	61.	59.34	ZrCl ₂	130. ^{ll}	130.26
TiO	124.15 ^l	118.57	ZrBr ₂	97. ^{ll}	96.84
TiH ₂	32.9 ⁿⁿ	37.07	ZrI ₂	63. ^{ll}	62.95

^aFrom N. B. S. Circular 500 unless otherwise indicated; see reference 7.

^bSee reference 8

^cSee reference 9

^dSee reference 10

^eSee reference 11

^fSee reference 12

^gSee reference 13

^hSee reference 14

ⁱSee reference 15

^jSee reference 16

^kSee reference 17

^lSee reference 18

^mSee reference 19

ⁿSee reference 20

^oSee reference 21

^pSee reference 22

^qSee reference 23

^rSee reference 24

^sSee reference 25

^{ll}From personal consultation with Professor Leo Brewer, Department of Chemistry, University of California, Berkeley, California.

^{mm}See reference 43

^tSee reference 26

^uSee reference 27

^vSee reference 28

^wSee reference 29

^xSee reference 30

^ySee reference 31

^zSee reference 32

^{aa}See reference 33

^{bb}See reference 34

^{cc}See reference 35

^{dd}See reference 36

^{ee}See reference 37

^{ff}See reference 38

^{gg}See reference 39

^{hh}See reference 40

ⁱⁱSee reference 41

^{jj}See reference 42

^{kk}See reference 43

ⁿⁿSee reference 44

Table II. Solution of Eq. (7) for heat of formation. Experimental data are compared with calculated values of $-\Delta H_f^\circ$.

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental ^a	Calculated		Experimental	Calculated
BiCl ₃	90.61	96.11	In(OH) ₃	214.	214.90
Bi ₂ O ₃	137.9	135.29	PtCl ₄	62.9	63.03
Bi ₂ S ₃	43.8	41.39	PtBr ₄	41.3	43.74
Bi ₂ (SO ₄) ₃	607.	609.96	PtI ₄	21.6	16.98
Bi(OH) ₃	169.6	168.23	PtS ₂	27.8	29.86
GaF ₃	255 ± 10 ^b	255.27	MoCl ₄	79.	80.58
GaCl ₃	125.4	130.75	MoBr ₄	45.	45.38
GaBr ₃	92.4	93.35	MoI ₄	18.	14.77
GaI ₃	51.2	46.97	MoO ₂	140.8 ^e	140.33
Ga ₂ O ₃	258.	256.83	MoS ₂	55.5	57.26
AuF ₃	83.3 ^c	83.60	MoCl ₃	65.	64.64
AuCl ₃	28.3	34.83	MoBr ₃	41.	41.64
AuBr ₃	13.0	8.03	MoI ₃	15.	14.70
Au(OH) ₃	100.	100.20	AlF ₃	356.3 ^f	357.05
Au ₂ O ₃	-19.3	-20.32	AlCl ₃	168.6 ^f	170.20
InCl ₃	128.4	130.49	AlBr ₃	125.8	125.41
InBr ₃	96.5	97.26	AlI ₃	74.4 ^g	71.66
InI ₃	55.	55.14	Al ₂ O ₃	400.29 ^h	396.96
In ₂ O ₃	221.27 ^d	223.39	Al ₂ S ₃	121.6	121.83
In ₂ (SO ₄) ₃	695.	690.95	Al ₂ (SO ₄) ₃	820.98	824.47

Table II(Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
CrF ₃	266 ± 5 ^f	266.03	LuCl ₃	227.9	227.89
CrCl ₃	134.6	133.00	LuI ₃	133.2	133.21
CrBr ₃	91 ± 7 ^b	94.14	VF ₃	275. ± 25 ^b	275.12
CrI ₃	47.8 ⁱ	46.26	VCl ₃	137. ± 10 ^f	142.30
Cr ₂ O ₃	272.7 ^f	272.69	VBr ₃	108. ± 7 ^b	102.82
FeF ₃	235 ± 10 ^b	234.03	V ₂ O ₃	296 ^f	295.39
FeCl ₃	95.7 ^f	98.78	ScF ₃	367 ± 7 ^b	366.59
FeBr ₃	63.8 ^b	60.94	ScCl ₃	220.8	212.85
Fe ₂ O ₃	196.8 ^f	197.82	ScBr ₃	179.4	177.50
Fe(OH) ₃	197.0	197.71	ScI ₃	127 ± 2 ^b	133.67
B ₂ O ₃	305.3 ^f	305.29	Sc ₂ O ₃	411 ± 9 ^b	412.81
B ₂ S ₃	57.0	57.14	TmCl ₃	229.5	229.49
TlF ₃	136.9 ^c	136.89	TmI ₃	137.8	137.81
TlCl ₃	83.9	83.32	ErCl ₃	231.8	227.99
TlBr ₃	59.0	59.59	ErI ₃	140.0	142.52
Tl(OH) ₃	122.6	122.61	Er ₂ O ₃	453.5 ^l	454.05
YCl ₃	234.8	232.62	Er(OH) ₃	340.5	340.72
YI ₃	148 ^j	149.44	HoCl ₃	232.8	232.77
Y ₂ O ₃	455.45 ^k	455.76	HoI ₃	141.7	141.70
Y(OH) ₃	337.6	337.72	Ho ₂ O ₃	449.55 ^m	449.57

Table II(Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
DyCl ₃	237.8	237.79	Ce ₂ S ₃	298.7	300.32
DyI ₃	144.5	144.49	CeO ₂	233.	233.03
Dy ₂ O ₃	445.84 ⁿ	445.85	CeS ₂	153.9	153.90
GdCl ₃	240.1 ^f	240.12	Ce(SO ₄) ₂	560.	559.98
GdI ₃	147.6	147.56	LaCl ₃	256.18 ^t	248.10
Gd ₂ O ₃	433.94 ^o	433.95	LaI ₃	167.4	167.42
SmCl ₃	249.8	249.85	La ₂ O ₃	428.57 ^u	429.53
SmI ₃	153.4	153.34	La ₂ S ₃	306.8	305.25
Sm ₂ O ₃	434.0 ^p	434.00	La ₂ (SO ₄) ₃	939.8 ^t	940.16
NdCl ₃	245.62 ^q	245.25	La(OH) ₃	466.2 ± 2.7 ^v	466.37
NdI ₃	158.9	158.90	PuCl ₃	230.0	230.45
Nd ₂ O ₃	432.15 ^r	432.19	PuBr ₃	187.8	187.01
Nd ₂ S ₃	281.8	281.88	PuI ₃	133.	133.36
Nd ₂ (SO ₄) ₃	948.1	948.18	NpF ₃	360.	359.99
PrCl ₃	257.8	257.86	NpCl ₃	216.	216.43
PrI ₃	162.0	161.93	NpBr ₃	174.	173.12
Pr ₂ O ₃	444.5	444.49	NpI ₃	120.	120.47
CeF ₃	410.4 ^s	410.28	NpF ₄	428.	428.00
CeCl ₃	252.84 ^q	253.78	NpCl ₄	237.	236.94
CeI ₃	164.4	160.33	NpBr ₄	183.	183.07

Table II (Continued).

Compound	$-\Delta H_f^\circ$ (kcal/gM)		Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
UF ₃	357.	356.99	WI ₄	0.	5.11
UCl ₃	213.	213.49	WO ₂	134.8 ^z	135.53
UBr ₃	170.1	169.09	WS ₂	53.97 ^{aa}	51.25
UI ₃	114.7	115.23	TiF ₃	315.	315.01
UF ₄	443 ± 5 ^f	442.54	TiCl ₃	172.4 ^{bb}	172.50
UCl ₄	251.2	249.72	TiBr ₃	132.	132.17
UBr ₄	196.6	195.66	TiI ₃	83. ± 5 ^b	82.79
UI ₄	127.0	129.54	Ti ₂ O ₃	363.4 ^f	363.37
UO ₂	259.2 ^f	263.16	TiF ₄	393.6 ^b	393.79
U(SO ₄) ₂	563.	559.39	TiBr ₄	147.9 ^{cc}	154.13
ThF ₄	482.4 ^w	484.08	TiI ₄	92.1 ^{dd}	87.02
ThCl ₄	285.	282.80	TiO ₂	225.75 ^f	224.42
ThBr ₄	227.1	228.97	ZrF ₃	350.	350.00
ThI ₄	160. ± 5 ^x	163.21	ZrCl ₃	186. ^b	185.76
ThO ₂	294.1 ^y	296.27	ZrBr ₃	142. ^b	142.37
Th(SO ₄) ₂	602.	591.77	ZrI ₃	90. ^b	89.88
Th(OH) ₄	421.5	425.01	ZrF ₄	456.9 ^{ee}	453.70
SnO ₂	138.8	138.70	ZrCl ₄	234.7 ^{ee}	238.77
Sn(OH) ₄	270.5	270.49	ZrBr ₄	180. ^b	180.42
Sn(SO ₄) ₂	393.4	393.53	ZrI ₄	114. ^b	109.85
WCl ₄	71.	68.78	ZrO ₂	261.5 ^f	268.68
WBr ₄	35.	34.05	Zr(OH) ₄	411.2	406.89

Table II (Continued).

$-\Delta H_f^\circ$ (kcal/gM)			$-\Delta H_f^\circ$ (kcal/gM)		
Compound	Experimental	Calculated	Compound	Experimental	Calculated
MnF ₃	238 ± 5 ^b	240.58	SeCl ₄	45.	44.98
MnCl ₃	110 ± 5 ^b	107.41	SeO ₂	57.5 ^{gg}	57.53
Mn ₂ O ₃	228.4 ^f	222.30	SbF ₃	217.2	217.09
Mn ₂ (SO ₄) ₃	666.9	671.95	SbCl ₃	91.4 ^f	87.55
Mn(OH) ₃	212.	214.12	SbBr ₃	62.1	59.84
PbF ₄	222.3	222.30	SbI ₃	23.0	24.18
PbCl ₄	78.85 ^{ff}	78.86	Sb ₂ S ₃	43.5	44.73
PbO ₂	66.12	66.11	Sb ₂ (SO ₄) ₃	575.3	576.58
TeCl ₄	77.2	77.19	HfCl ₄	237 ± .2 ^f	236.97
TeO ₂	77.69	77.70	HfO ₂	266.05 ^f	266.09

^aFrom N. B. S. Circular 500 unless otherwise indicated; see reference 7.

^bFrom personal consultation with Professor Leo Brewer, Department of Chemistry, University of California, Berkeley, California.

^cSee reference 45.

ⁱSee reference 50

^dSee reference 46.

^jSee reference 51.

^eSee reference 47.

^kSee reference 52.

^fSee reference 18.

^lSee reference 53.

^gSee reference 48.

^mSee reference 54.

^hSee reference 49.

ⁿSee reference 55.

Table II (Continued).

^o See Reference 56.	^y See reference 66.
^p See reference 57.	^z See reference 67.
^q See reference 58.	^{aa} See reference 68.
^r See reference 59.	^{bb} See reference 69.
^s See reference 60.	^{cc} See reference 70.
^t See reference 61.	^{dd} See reference 71.
^u See reference 62.	^{ee} See reference 11.
^v See reference 63.	^{ff} See reference 72.
^w See reference 64.	^{gg} See reference 73.
^x See reference 65.	

Table III. Solution of Eq. (8) for free energy of formation. Experimental data are compared with calculated values of $-\Delta F_f^\circ$.

Compound	$-\Delta F_f^\circ$ (kcal/gM)		Compound	$-\Delta F_f^\circ$ (kcal/gM)	
	Experimental ^a	Calculated		Experimental	Calculated
LiF	139.6	138.87	KBr	90.63	90.89
LiCl	94.5	92.89	KI	77.03	78.66
Li ₂ O	133.824 ^b	133.96	KNO ₃	93.96	93.47
Li ₂ CO ₃	270.66	271.90	K ₂ SO ₄	314.62	314.78
LiOH	106.1	104.91	KClO ₄	72.7	71.95
LiClO ₄	60.502 ^b	61.28	RbF	124.78 ^f	128.49
NaF	129.3	126.88	RbCl	97.05	96.25
NaCl	91.785	89.67	RbBr	90.88	90.77
NaBr	83.1 ^c	82.98	RbI	78.3	78.18
NaI	68.0 ^c	69.90	Rb ₂ O	70.	68.78
Na ₂ O	90.0	92.22	Rb ₂ S	81.1	82.61
Na ₂ S	86.368	85.03	Rb ₂ CO ₃	249.5	249.88
Na ₂ CO ₃	249.96 ^d	249.19	RbNO ₃	93.9	94.75
NaNO ₃	87.45	87.68	Rb ₂ SO ₄	318.9	316.77
Na ₂ SO ₄	302.78	305.66	RbClO ₄	73.19	72.60
NaOH	91.188 ^b	88.69	CsF	122.9 ^f	126.80
Na ₂ SiO ₃	338.537 ^b	337.89	CsCl	100.1	97.12
Na ₂ CrO ₄	301.5 ^e	301.47	CsBr	95.	92.11
KF	127.42	127.74	CsI	83.1	80.00
KCl	97.592	96.35	Cs ₂ O	69.	66.88

Table III (Continued).

$-\Delta F_f^0$ (kcal/gM)			$-\Delta F_f^0$ (kcal/gM)		
Compound	Experimental ^a	Calculated	Compound	Experimental	Calculated
Cs ₂ S	81.7	85.72	MgSiO ₃	342.014 ^b	340.63
Cs ₂ CO ₃	249.3	248.17	MgH ₂	8.589 ^b	9.49
CsNO ₃	95.4	94.63	CaF ₂	277.7	274.63
Cs ₂ SO ₄	314.2	315.89	CaCl ₂	179.3	179.30
CsClO ₄	73.28	74.19	CaBr ₂	156.8	161.26
BeO	136.12 ^b	135.63	CaI ₂	126.9	132.38
Be(OH) ₂	196.168 ^b	197.19	CaO	144.4	148.05
BeWO ₄	318.9 ^g	317.28	CaS	114.1	104.71
BeMoO ₄	293.6 ^g	294.69	CaCO ₃	269.78	271.26
MgF ₂	250.8	247.30	Ca(NO ₃) ₂	177.34	176.70
MgCl ₂	141.57	143.43	CaSO ₄	315.56	312.11
MgO	136.13	138.13	Ca(OH) ₂	214.77 ^b	216.61
MgS	81.672 ^b	78.83	CaMoO ₄	345.8 ^g	343.84
MgCO ₃	246.0	245.03	CaSiO ₃	362.5 ^c	364.53
Mg(NO ₃) ₂	140.63	140.88	CaCrO ₄	305.3	305.30
MgSO ₄	278.196 ^b	278.57	CaH ₂	35.8	35.37
Mg(OH) ₂	199.27	198.66	SrCl ₂	186.7	186.68
MgWO ₄	337.7 ^g	343.20	SrO	133.8	133.83
MgMoO ₄	314.3 ^g	312.72	SrCO ₃	271.9	271.67

Table III (Continued).

ΔF_f^0 (kcal/gM)			ΔF_f^0 (kcal/gM)		
Compound	Experimental	Calculated	Compound	Experimental	Calculated
SrSO ₄	318.9	318.72	Cr ₂ O ₃	253.2 ^c	253.21
SrSeO ₄	244.7 ^h	245.12	MnF ₂	180 ± 5 ^c	183.59
BaF ₂	274.5	276.17	MnCl ₂	105.5	106.04
BaCl ₂	193.8	193.88	MnO	86.8	86.77
BaO	126.3	126.47	MnS	50.5 ^c	51.48
BaCO ₃	272.2	271.80	MnCO ₃	195.4	190.56
Ba(NO ₃) ₂	190.0	190.64	MnSO ₄	228.48	227.21
BaSO ₄	323.64 ⁱ	322.78	Mn(OH) ₂	145.9	145.60
BaWO ₄	377.9 ^g	375.47	MnMoO ₄	267.5 ^g	266.91
BaMoO ₄	349.6 ^g	351.50	MnSiO ₃	289.05 ^l	289.07
BaSeO ₄	248.65 ⁱ	247.90	FeCl ₂	72.56 ^c	72.88
Ra(NO ₃) ₂	190.3	190.89	FeBr ₂	57.2 ^c	57.23
RaSO ₄	326.4	325.07	FeI ₂	30.8 ± 2 ^c	32.51
RaWO ₄	380.4 ^g	380.68	FeO	58.7 ^c	59.75
RaMoO ₄	351.9 ^g	352.36	FeS	22.81 ^c	21.24
CrF ₂	170.7 ± 3 ^j	169.51	FeCO ₃	161.06	159.57
CrCl ₂	87.4	91.85	Fe(OH) ₂	115.57	116.47
CrI ₂	55.3 ^k	52.03	FeMoO ₄	235.3 ^g	234.67
CrF ₃	249 ± 5 ^c	248.96	CoCl ₂	64.5 ± 2 ^c	63.96
CrCl ₃	115 ± 5 ^c	115.02	CoO	50.4 ^m	50.26

Table III . (Continued).

$-\Delta F_f^o$ (kcal/gM)			ΔF_f^o (kcal/gM)		
Compound	Experimental	Calculated	Compound	Experimental	Calculated
CoSO ₄	182.1	182.50	TiI ₃	82.5 ± 5 ^j	84.51
CoWO ₄	245.5 ^g	245.37	Ti ₂ O ₃	342.224 ^b	342.12
CoMoO ₄	224.0 ^g	224.41	TiF ₄	370.972 ^b	370.29
NiF ₂	144.7 ± 2 ^c	141.28	TiBr ₄	138.9 ^j	142.95
NiCl ₂	65.1	68.78	TiI ₄	92 ^j	88.50
NiO	50.6 ^c	50.18	TiO ₂	212.283 ^b	212.42
NiCO ₃	146.7	151.04	ZrF ₂	219.046 ^b	220.07
NiSO ₄	184.9	186.93	ZrCl ₂	119.8 ^j	115.56
Ni(OH) ₂	108.3	107.34	ZrBr ₂	93.5 ^j	94.43
NiMoO ₄	226.5 ^g	228.35	ZrI ₂	63.7 ^j	65.99
VCl ₃	120 ± 10 ^c	120.00	ZrF ₃	333.613 ^b	333.90
V ₂ O ₃	277 ^c	277.00	ZrCl ₃	169.2 ^j	168.08
TiF ₂	194 ± 15 ^j	194.93	ZrBr ₃	134.6 ^j	134.70
TiCl ₂	109.8 ^j	107.64	ZrI ₃	89.6 ^j	90.34
TiBr ₂	91.4 ± 5 ^j	90.09	ZrF ₄	435.676 ^b	434.32
TiI ₂	61.6 ^j	64.27	ZrCl ₄	212 ± 2 ^c	216.11
TiO	117.15 ^c	117.02	ZrBr ₄	172.5 ± 2 ^j	173.47
TiF ₃	298 ^j	298.80	ZrI ₄	116.6 ± 2 ^j	112.80
TiCl ₃	155.741 ^b	154.61	ZrO ₂	247.7 ^c	247.82
TiBr ₃	127.5 ^j	126.03	CeF ₃	392 ⁿ	392.00

Table III (Continued).

Compound	$-\Delta F_f^\circ$ (kcal/gM)		Compound	$-\Delta F_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
CeCl ₃	235.16 ^o	235.16	CuS	11.7	7.22
NdCl ₃	227.93 ^o	228.18	CuCO ₃	123.8	123.22
Nd ₂ O ₃	410.6 ^j	410.99	CuSO ₄	158.2	156.64
Nd(OH) ₃	299.6 ^p	298.57	CuWO ₄	223.1 ^g	219.72
UF ₃	339.	340.53	CuMoO ₄	202.7 ^g	202.90
UCl ₃	196.	192.00	AgF	44.2	40.39
UBr ₃	164.7	162.33	AgCl	26.22 ⁴	25.22
UI ₃	115.3	120.44	AgBr	22.93	21.80
UH ₃	17.353 ^a	17.06	AgI	15.85	14.11
UF ₄	421 ± 5 ^c	422.44	Ag ₂ O	2.586	1.64
UCl ₄	230.	225.75	Ag ₂ S	9.62	11.11
UBr ₄	188.5	186.93	Ag ₂ CO ₃	104.48	104.30
UI ₄	126.1	130.56	AgNO ₃	7.69	8.93
UO ₂	246.6 ^c	246.52	Ag ₂ SO ₄	147.17	147.03
CuCl	28.5 ^c	30.33	Ag ₂ WO ₄	198.5 ^t	203.00
CuBr	24.4 ^c	24.83	Ag ₂ MoO ₄	197.7 ^t	195.79
CuI	16.8 ^c	15.12	Ag ₂ SeO ₄	80.78 ^u	80.47
Cu ₂ O	35.44 ^r	35.33	Ag ₂ CrO ₄	150.78 ^t	150.81
Cu ₂ S	20.36 ^s	20.17	AuCl ₃	11.5 ± 1.6 ^v	12.81
CuCl ₂	39.0 ^j	45.80	Au ₂ O ₃	-39.0	-36.97
CuO	30.52 ^r	33.51			

Table III (Continued).

Compound	$-\Delta F_f^o$ (kcal/gM)		Compound	$-\Delta F_f^o$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
Au(OH) ₃	69.3 ^k	63.93	Hg ₂ Cl ₂	50.35	51.15
ZnCl ₂	88.255	89.61	Hg ₂ Br ₂	42.714	42.40
ZnBr ₂	74.142	75.02	Hg ₂ I ₂	26.60	26.43
ZnI ₂	50.01	51.81	Hg ₂ SO ₄	149.12	148.81
ZnO	76.05	78.37	HgF ₂	56.9 ^j	60.90
ZnS	47.4	43.85	HgCl ₂	42.4 ± 1 ^c	39.93
ZnCO ₃	147.8	173.12	HgBr ₂	36.6 ^c	34.28
ZnSO ₄	208.31	206.79	HgI ₂	24.3 ^c	21.52
ZnWO ₄	270.1 ^g	270.13	HgO	13.99	9.57
ZnMoO ₄	249.4 ^g	249.78	HgS	11.67	18.66
CdF ₂	154.8	149.78	AlF ₃	337.351 ^b	339.82
CdCl ₂	81.88	83.14	AlCl ₃	150.7 ^c	153.65
CdBr ₂	70.14	69.82	AlBr ₃	120.7	117.70
CdI ₂	48.00	47.26	AlI ₃	75.0	67.66
CdO	54.1 ^w	55.11	Al ₂ O ₃	378.074 ^c	375.31
CdS	33.6	30.91	Al ₂ S ₃	117.7	122.31
CdCO ₃	160.2	160.42	Al ₂ (SO ₄) ₃	738.99	739.61
CdSO ₄	195.99	198.83	In ₂ O ₃	196.4 ^y	195.99
Cd(OH) ₂	113.37 ^x	114.43	In ₂ S ₃	101 ^z	100.81
CdWO ₄	258.5 ^g	258.94	In(OH) ₃	182.	183.18
CdMoO ₄	238.3 ^g	240.24	TlF	69 ± 5 ^c	69.09

Table III (Continued).

Compound	$-\Delta F_f^\circ$ (kcal/gM)		Compound	$-\Delta F_f^\circ$ (kcal/gM)	
	Experimental	Calculated		Experimental	Calculated
TlCl	44.19	44.50	PbI ₂	41.53	40.61
TlBr	39.7	39.61	PbO	45.25	43.28
TlI	29.7	29.73	PbS	22.15	20.22
Tl ₂ O	32.5	31.15	PbCO ₃	149.7	154.10
TlNO ₃	36.07	33.72	PbSO ₄	193.89	194.33
TlOH	45.5	48.79	Pb(OH) ₂	100.6	105.36
Tl ₂ SeO ₄	126.88 ^{aa}	127.61	PbWO ₄	256.6 ^g	253.33
SnO	61.5	61.31	PbMoO ₄	236.4 ^g	234.11
SnS	23.8 ^c	23.71	BiCl ₃	76.23	76.30
Sn(OH) ₂	117.6	117.88	Bi ₂ O ₃	118.7	118.71
SnO ₂	123.9	123.90	Bi ₂ S ₃	39.4	39.35
SnS ₂	47.552 ^{bb}	47.55	NH ₄ Cl	48.743 ^b	49.65
PbF ₂	148.1	145.30	NH ₄ NO ₃	43.82	43.26
PbCl ₂	75.04	77.15	NH ₄ ClO ₄	13.383 ^b	13.07
PbBr ₂	62.24	63.70			

^a From N. B. S. Circular 500 unless otherwise indicated; see reference 7.

^b See reference 11.

^c See reference 18.

^d See reference 74.

^e See reference 75.

^f All N. B. S. data for Rb and Cs compounds were corrected for errors in S° of Rb⁺ and ΔH° of Cs⁺ noted in Appendix 7 of reference 18.

Table III (Continued).

^gSee reference 19.

^hSee reference 33.

ⁱSee reference 76.

^jCalculated by Latimer's method with recent ΔH_f data; see reference 1.

^kSee reference 1.

^tSee reference 26.

^lSee reference 77.

^uSee reference 34.

^mSee reference 78.

^vSee reference 83.

ⁿSee reference 60.

^wSee reference 84.

^oSee reference 58.

^xSee reference 85.

^pSee reference 79.

^ySee reference 86.

^qSee reference 80.

^zSee reference 87.

^rSee reference 81.

^{aa}See reference 42.

^sSee reference 82.

^{bb}See reference 88.

better known compounds may be attributed to the fact that other compounds whose experimental ΔH_f° may be in error were given equal weight in the solution of Eqs. (A-1), and would therefore have improperly influenced the values of the characteristic parameters X, Y, and W. A possible remedy to this is the use of a set of weighting factors for the compounds. This is discussed in more detail in a later section on Improvement of Correlation, along with one method of determining appropriate weighting factors.

Tables IV through VI compare for each anion the average and maximum deviations obtained in the back-calculated values. These indicate that correlation of data of one set of compounds is approximately as good as that of another when data are accurate. However, this is contrary to what one would expect. The results of Anderson and Bromley show that better agreement may be obtained with a correlation of this sort for the halides than for the compounds with more complex bond structure. This again points out the need of a system of weighting factors as a means of improving the overall correlation.

Table VII compares the electronegativities of Pauling with those obtained from Eqs. (A-1). The values are generally similar except for the alkali and alkaline earth metals, for which the order of decreasing X is reversed. The extent to which the least-squares values differ from those of Pauling may be related to the magnitude of the Y values for the elements. The deviation of the alkali metals from the Pauling scale is greatest for Cs and least for Li. The Y values follow the same trend in decreasing from Cs through the group to Li. This is true also of the other elements, and seems quite logical in light of the previous discussion.

There appears to be no relationship between the values of W and those of X or Y. However, the absolute value of W appears to be larger in general for anions whose compounds would not be expected to closely follow Eq. (5).

Table VIII lists the experimental data for $-\Delta H_f^\circ$ of 10 chromates along with values calculated from a preliminary program. The agreement

Table IV. Solution of Eq. (7) for heat of formation. Deviation of calculated values are compared for the correlation of monovalent and divalent cation compounds.

Anion	Number of compounds	Average deviations (kcal/gM)	Maximum deviations (kcal/gM)	Compound of maximum deviations
F^-	26	3.86	8.43	PbF_2
Cl^-	33	1.01	5.37	$CuCl_2$
Br^-	32	1.01	3.64	$TlBr$
I^-	31	1.55	5.18	PbI_2
$O^{=}$	27	1.87	5.59	TiO
$S^{=}$	24	2.46	7.90	CaS
$CO_3^{=}$	17	1.23	3.53	$MnCO_3$
NO_3^-	19	2.13	4.92	$Zn(NO_3)_2$
$SO_4^{=}$	25	1.95	6.10	$CoSO_4$
$C_2H_3O_2^-$	12	2.56	6.52	$Pb(C_2H_3O_2)_2$
OH^-	21	1.62	5.28	$Be(OH)_2$
CN^-	8	2.85	5.71	$Zn(CN)_2$
$C_2O_4^{=}$	8	3.21	7.07	MnC_2O_4
CHO_2^-	9	1.13	2.83	$Pb(CHO_2)_2$
$SO_3^{=}$	5	1.69	2.82	K_2SO_3
NO_2^-	8	3.52	8.73	$Ba(NO_2)_2$
HSO_4^-	5	0.85	1.09	NH_4HSO_4
HCO_3^-	5	0.81	1.66	$KHCO_3$
CNS^-	9	2.93	5.96	$TlCNS$
ReO_4^-	5	1.82	3.70	$KReO_4$

Table IV. (Continued).

Anion	Number of compounds	Average deviation (kcal/gM)	Maximum deviation (kcal/gM)	Compound of maximum deviation
SiO_3^-	8	3.67	6.34	PbSiO_3
MoO_4^-	16	1.79	4.07	CoMoO_4
WO_4^-	14	1.88	4.73	FeWO_4
H^-	10	2.82	6.12	BaH_2
SeO_4^-	8	0.81	2.48	SrSeO_4
ClO_4^-	8	1.85	4.01	$\text{Ba}(\text{ClO}_4)_2$
HPO_4^-	4	5.65	8.10	BaHPO_4
HS^-	5	0.50	0.98	KHS
ClO_3^-	6	1.02	2.39	NH_4ClO_3
NH_2^-	9	1.92	3.26	NaNH_2
O^-	10	2.57	5.43	K_2O_2
Total	427	1.98	8.73	$\text{Ba}(\text{NO}_2)_2$

Table V. Solution of Eq. (7) for heat of formation. Deviations of calculated values are compared for the correlation of trivalent and tetravalent cation compounds.

Anion	Number of compounds	Average deviation (kcal/gM)	Maximum deviation (kcal/gM)	Compound of maximum deviation
F^-	21	0.53	3.20	ZrF_4
Cl^-	41	1.84	8.08	$LaCl_3$
Br^-	24	1.63	6.23	$TiBr_4$
I^-	31	1.77	6.67	ScI_3
$O^{=}$	33	1.15	7.18	ZrO_2
$S^{=}$	11	1.24	2.65	WS_2
$SO_4^{=}$	11	2.84	10.23	$Th(SO_4)_2$
OH^-	12	1.19	4.31	$Zr(OH)_4$
Total	184	1.51	10.23	$Th(SO_4)_2$

Table VI. Solution of Eq. (8) for free energy of formation. Deviations of calculated values are compared.

Anion	Number of compounds	Average Deviation (kcal/gM)	Maximum deviation (kcal/gM)	Compound of maximum deviation
F^-	27	2.03	5.02	CdF_2
Cl^-	38	1.71	6.80	$CuCl_2$
Br^-	23	1.28	4.46	$CaBr_2$
I^-	24	2.47	7.34	AlI_3
$O^{=}$	35	1.00	4.42	HgO
$S^{=}$	19	2.58	9.39	CaS
$CO_3^{=}$	16	1.50	4.54	$MnCO_3$
NO_3^-	11	0.78	2.36	$TlNO_3$
$SO_4^{=}$	19	1.27	3.45	$CaSO_4$
OH^-	15	1.75	5.37	$Au(OH)_3$
$WO_4^{=}$	10	2.16	5.50	$MgWO_4$
$MoO_4^{=}$	14	1.18	2.29	$PbMoO_4$
$SiO_3^{=}$	4	1.02	2.03	$CaSiO_3$
$SeO_4^{=}$	4	0.56	0.77	$BaSeO_4$
$CrO_4^{=}$	3	0.02	0.03	Ag_2CrO_4
H^-	3	0.54	0.89	MgH_2
ClO_4^-	5	0.67	0.91	$CsClO_4$
Total	270	1.57	9.39	CaS

Table VII. Pauling electronegativity scale compared to x values.

Element	Pauling electro- negativity	0.22 X	Element	Pauling electro- negativity	0.22 X
H	2.1	2.28	Pd	2.2	1.64
Li	1.0	1.28	Pt(4)	2.2	2.29
Na	0.9	1.60	Cu(1)	1.9	2.16
K	0.8	1.75	Cu(2)	2.0	1.66
Rb	0.8	1.73	Ag	1.9	2.26
Cs	0.7	1.81	Au(1)	2.4	2.21
Be	1.5	0.82	Zn	1.6	1.62
Mg	1.2	1.01	Cd	1.7	1.73
Ca	1.0	1.22	Hg(2)	1.9	2.35
Sr	1.0	1.33	B	2.0	1.68
Ba	0.9	1.35	Al	1.5	1.18
Ra	0.9	1.43	Ga	1.6	1.58
Sc	1.3	1.59	In	1.7	1.78
Y	1.2	1.57	Tl	1.8	1.91
Ti(4)	1.5	1.38	Sn(2)	1.8	1.57
Zr(4)	1.4	1.25	Sn(4)	1.9	1.54
Hg(4)	1.3	1.26	Pb	1.8	1.70
Th(4)	1.3	1.39	Sb	1.8	1.92
V(3)	1.4	1.45	Bi	1.9	1.85
Cr(3)	1.6	1.35			

Table VII (Continued).

Element	Pauling electro- negativity	0.22 X	Element	Pauling electro- negativity	0.22 X
Mo(3)	1.8	1.81	F	4.0	3.99
Mn(2)	1.4	1.47	Cl	3.0	2.91
Fe(2)	1.8	1.47	Br	2.8	2.74
Fe(3)	1.9	1.56	I	2.5	2.57
Co(2)	1.8	1.55	O	3.5	3.58
Ni	1.8	1.53	S	2.5	2.50

Table VIII. Solution of Eq. (7) for $-\Delta H_f^\circ$ of chromates. Experimental data and calculated values are compared.

Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental ^a	Calculated
Na_2CrO_4	318.6 ^b	311.6
K_2CrO_4	332.8 ^c	303.9
MgCrO_4	318.3	341.2
CaCrO_4	329.6	345.4
BaCrO_4	341.3	332.8
FeCrO_4	341.9	309.4
Ag_2CrO_4	172.4 ^d	190.0
PbCrO_4	217.7	239.1
Tl_2CrO_4	223.3 ^e	224.1
$(\text{NH}_4)_2\text{CrO}_4$	275.2	273.4

^aFrom N. B. S. circular 500 unless indicated otherwise (see reference 7).

^bSee reference 16.

^cSee reference 89.

^dSee reference 26.

^eSee reference 90.

is in general quite poor, with an average deviation of 15.5 kcal/M resulting. There is no explanation for this, except that certain experimental data appear to be questionable. Rather than remove some of the data, the entire set was eliminated from the correlation. There is no reason to suspect that the method of correlation is not valid for the chromates. Application of the method to only the more recent data would probably yield considerably better agreement than that obtained here.

Table IX lists six other compounds which were not included in the correlation. These were deleted because the data are inconsistent with expected trends in $-\Delta H_f^\circ$ of compounds of the cation and anion and appear to be incorrect. Figure 6 points out the inconsistencies by comparing the experimental $-\Delta H_f^\circ$ profiles of these compounds with others. Within a given group of the Periodic Table, the $-\Delta H_f^\circ$ profiles of various compounds would be expected to be similar, since the contribution characteristic of the anion would be approximately the same. Thus, one would expect the heat of formation of the molybdates to follow the same trend through a group as that of the tungstates, and so on. However, for the six compounds of Table IX this is not the case. The experimental $-\Delta H_f^\circ$ of $\text{Mn}(\text{NO}_3)_2$ appears to be approximately 20 kcal/M too high, while those of BaSiO_3 , SrMoO_4 , ZnWO_4 , PbWO_4 , and $\text{Fe}(\text{OH})_2$ seem unreasonably low.

Application

From values of the characteristic parameters X, Y, and W developed in the solution of Eqs. (A-1), unknown values of $-\Delta H_f^\circ$ and $-\Delta F_f^\circ$ were estimated for solid compounds of all cations and anions included in these correlations. These data are given in Tables A-5 through A-7 of Appendix II.

A measure of the reliability that may be attached to these estimates is directly obtained by comparing $-\Delta F_f^\circ$ values with estimates obtained by the Latimer method. The Latimer data for the entropy

Table IX. Solution of Eq. (7) for $-\Delta H_f^\circ$ of compounds not included in the correlation. Experimental data and calculated values are compared.

Compound	$-\Delta H_f^\circ$ (kcal/gM)	
	Experimental ^a	Calculated
$Mn(NO_3)_2$	166.3	145.4
$Fe(OH)_2$	135.8	147.8
$BaSiO_3$	359.5	373.6
$SrMO_4$	346.2 ^b	364.2
$ZnWO_4$	270.4 ^b	284.8
$PbWO_4$	250.0 ^b	267.8

^aFrom N. B. S. Circular 500 unless indicated otherwise (see reference 7).

^bSee reference 19.

Fig. 6. Comparison of experimental $-\Delta H_f^0$ profiles.

contribution are usually as accurate as experimental data for ΔH_f^O , and the ΔF_f^O values may then be considered the approximate equivalent of experimental data.

Table X compares the estimated values of Eq. (8) with those of Latimer for compounds not included in the correlation. The agreement is in general acceptable, although not as good as that for compounds included in the original solution of Eqs. (A-1). The average deviation of 119 calculated values is 8.4 kcal/M, and the maximum deviation is 45.7 kcal/M for BeS. Only the estimated values for $U(OH)_3$, $U(SO_4)_2$, $Sn(SO_4)_2$, $Bi_2(SO_4)_3$, AuF_3 and the beryllium compounds are in serious disagreement. Special attention should be given to these in an effort to explain their large deviations.

The parameters for Sn^{4+} were evaluated using only two experimental values of $-\Delta F_f^O$, and those of Bi^{+++} and Au^{+++} were determined with three. With three parameters and only two or three data to fit, nearly perfect agreement is obtained, as expected. However, when these parameters are extended to the calculation of additional values, large deviations result, again as expected.

The Latimer estimate for $U(OH)_3$ is regarded only as a rough approximation. However, any error in the Latimer value for $U(SO_4)_2$ should be small, and the large deviation cannot be left unexplained. This probably is because four of the five compounds used to evaluate the parameters for U^{4+} were halides, with bond structure significantly different from that of $U(SO_4)_2$. As might be expected if this were the case, the calculated value for the more stable $U(SO_4)_2$ is much smaller than Latimer's estimate of the true value.

Undoubtedly the errors in the data for the Be compounds are so large because BeO was one of four compounds used to evaluate the constants. Since this compound is an exceptionally stable oxide, the other estimated values of $-\Delta F_f^O$ would be expected to be high. Such was the case with four of the six estimated values.

Table X. Estimated values of $-\Delta F_f^0$ obtained from Eq. (8) compared with estimates obtained by the Latimer method.

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
LiBr	81.2	84.4	6	23
LiI	64.	70.0	6	24
Li ₂ S	104.8	106.9	6	19
LiNO ₃	93.1	92.4	6	11
Li ₂ SO ₄	316.0	318.8	6	19
NaClO ₄	61.4	62.3	12	5
K ₂ O	76.2	80.5	7	35
K ₂ S	96.6	91.2	7	19
K ₂ CO ₃	252.5	251.4	7	16
KOH	89.5	86.2	7	15
K ₂ CrO ₄	306.1 ^b	312.1	7	3
RbOH	87.5 ^b	82.9	10	15
CsOH	88.3 ^b	82.0	10	15
BeF ₂	230 ± 3	208.7	4	27
BeCl ₂	111.8	128.7	4	38
BeBr ₂	84.6	112.0	4	23
BeI ₂	51.0	88.4	4	24
BeS	55.9	101.6	4	19
BeSO ₄	260.2	246.5	4	19
MgBr ₂	119.3	123.4	12	23

Table X. (Continued).

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
MgI ₂	86.0	93.5	12	24
Mg(ClO ₄) ₂	79.4	70.9	12	5
CaWO ₄	368.7	371.8	14	10
SrF ₂	277.8	276.9	5	27
SrBr ₂	166.4	170.0	5	23
SrI ₂	135.	141.5	5	24
SrS	107.0 ^b	102.4	5	19
Sr(NO ₃) ₂	186.0 ^b	185.1	5	11
Sr(OH) ₂	204.7	209.6	5	15
SrSiO ₃	350.8	362.7	5	4
SrCrO ₄	315.3	312.4	5	3
SrWO ₄	366.5	374.2	5	10
BaBr ₂	174.4	178.8	9	23
BaI ₂	143.1	151.6	9	24
BaS	104.5 ^b	106.2	9	19
Ba(OH) ₂	204.3 ^b	205.9	9	15
BaCrO ₄	316.0	317.6	9	3
Ba(ClO ₄) ₂	127.9	134.8	9	5
RaO	117.5	137.2	4	35
RaCO ₃	281 ^b	277.8	4	16

Table X (Continued).

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
CrBr ₂	67 ± 5 ^b	76.2	3	23
Cr(OH) ₂	140.5	141.3	3	15
CrBr ₃	84 ± 5 ^b	88.2	3	23
CrI ₃	47.8 ^b	48.8	3	24
Cr(OH) ₃	215.3	203.5	3	15
MnBr ₂	87.4 ± 2	90.7	9	23
MnI ₂	59.9	66.1	9	24
FeF ₂	157 ± 2 ^b	151.6	8	27
FeSO ₄	198.3	194.1	8	19
FeSiO ₃	257.	258.4	8	4
FeWO ₄	250.4	257.1	8	10
CoF ₂	148.4 ^b	138.0	5	27
CoBr ₂	52.3 ^b	49.1	5	23
CoI ₂	25.3 ^b	25.4	5	24
CoS	20.6 ^b	15.4	5	19
CoCO ₃	155.6	148.0	5	16
Co(NO ₃) ₂	57.2 ^b	47.7	5	11
Co(OH) ₂	111.1 ^b	105.9	5	15
NiBr ₂	50.8 ± 2	54.3	7	23
NiI ₂	21.3	30.8	7	24
NiS	17.7	18.2	7	19

Table X (Continued).

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
Ni(NO ₃) ₂	56.4	52.5	7	11
VF ₃	258 ± 25 ^b	257.2	2	27
VBr ₃	99.7 ± 7 ^b	92.5	2	23
Zr(OH) ₄	370. ^c	354.8	5	15
CeI ₃	163.1	160.2	2	24
Ce ₂ S ₃	293.1	308.9	2	19
Ce(OH) ₃	311.6	334.7	2	15
NdI ₃	157.7	158.1	3	24
Nd ₂ S ₃	276.2	262.8	3	19
Nd ₂ (SO ₄) ₃	866.1	849.5	3	19
U(OH) ₃	263.2 ^c	298.1	5	15
U(SO ₄) ₂	516.	486.3	5	19
U(OH) ₄	351.6 ^c	351.9	5	15
Cu ₂ SO ₄	156.	167.8	5	19
CuF ₂	116 ± 4 ^b	106.9	7	27
CuBr ₂	29.7 ^b	33.1	7	23
CuI ₂	5.7	12.2	7	24
Cu(NO ₃) ₂	27.3	22.8	7	11
Cu(OH) ₂	85.3	85.0	7	15
AgClO ₄	-21.	- 1.2	13	5

Table X (Continued).

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
AuF ₃	66.3 ^b	104.6	3	27
AuBr ₃	5.9	- 6.0	3	23
Zn(NO ₃) ₂	71.4	72.0	9	11
Zn(OH) ₂	132.6	132.5	9	15
ZnSiO ₃	274.8	273.5	9	4
Cd(NO ₃) ₂	61.	65.5	11	11
Hg ₂ F ₂	63.9 ^b	88.8	4	27
Hg ₂ O	13.3 ^b	34.8	4	35
Hg ₂ CO ₃	105.8	115.4	4	16
Hg ₂ CrO ₄	155.8	151.8	4	3
HgSO ₄	141.0	129.2	6	19
Al(OH) ₃	271.9	270.0	7	15
InCl ₃	110.7	125.1	3	38
InBr ₃	88.5	103.5	3	23
InI ₃	53.9	68.4	3	24
In ₂ (SO ₄) ₃	613.4	603.5	3	19
Tl ₂ S	21.	30.7	8	19
Tl ₂ CO ₃	150.3 ^b	151.1	8	16
Tl ₂ SO ₄	196.8	197.6	8	19
Tl ₂ CrO ₄	200.2 ^b	198.0	8	3

Table X (Continued).

Compound	Latimer ^a estimate (kcal/gM)	Eq. (8) estimate (kcal/gM)	Number of compounds	
			cation	anion
SnF ₂	146.6 ^b	152.5	3	27
SnCl ₂	72.2	74.8	3	38
SnBr ₂	59.5	59.4	3	23
SnI ₂	34.4	34.9	3	24
SnSO ₄	193.4 ^b	195.5	3	19
Sn(SO ₄) ₂	346.8	372.0	2	19
Sn(OH) ₄	227.5	229.3	2	15
Pb(NO ₃) ₂	60.3	61.2	11	11
PbSiO ₃	239.0	251.8	11	4
PbCrO ₄	193.0 ^b	192.0	11	3
PbSeO ₄	122.	125.9	11	4
Bi ₂ (SO ₄) ₃	526 ^b	484.4	3	19
Bi(OH) ₃	137 ^b	135.9	3	15
(NH ₄) ₂ CrO ₄	230.6 ^b	219.1	3	3

^aFrom reference 1 unless otherwise indicated.

^bValues calculated using recent ΔH_f° data with Latimer's data for the entropy contributions; see reference 1.

^cLittle certainty is attached to these values; see reference 1.

Figures 7 to 9 provide an indirect measure of the accuracy of the estimates of unknown ΔH_f^0 values. The average and maximum deviations from Table I are plotted as a function of the number of entries for several elements. An approximately linear relationship is obtained which may be extrapolated to include the total number of possible compounds for each element. The extrapolated value then represents approximately the maximum error to be expected in the estimation of all unknown values. Thus, from Figs. 7 and 8 one would expect an error no larger than 6.5 kcal/M for ΔH_f^0 of the alkali metal compounds and 11.0 kcal/M for ΔH_f^0 of the alkaline-earth compounds.

Similar plots may be constructed for all of the cations in each correlation. From plots of the free-energy data, one would expect a maximum error of 6.5 kcal/M for ΔF_f^0 of the alkali metal compounds and 11.5 kcal/M for the alkaline-earth compounds. If it is assumed that the Latimer estimates are not in error and if the Be and Ra compounds are not considered, this is found to be approximately correct. The maximum deviation for the alkali metals was 6.3 kcal/M, and that for the alkaline earths was 11.9 kcal/M. Table XI compares the estimated and actual deviations in ΔF_f^0 for other elements. It must be emphasized that the validity of these plots requires that the experimental data to which they are compared be accurate. This may not be true with certain of the data of Tables X and XI.

Extension of the Parameters

It would increase the range of applicability of the equations if they could be extended to include intermetallic or simple organic compounds. Although the equations are written for binary compounds, they are not restricted to them. They can be readily applied to more general compounds, such as those with two cations and one anion, or vice-versa:

$$\begin{aligned}
 -\Delta H_f^0 = & n_{AB} (X_B - X_A)^2 + n_{CB} (X_B - X_C)^2 + n_A Y_A \\
 & + n_B Y_B + n_C Y_C + n_{AB} \left(\frac{W_B}{W_A} \right) + n_{CB} \left(\frac{W_B}{W_C} \right). \quad (9)
 \end{aligned}$$

MU-27691

Fig. 7. Estimated maximum deviation in $-\Delta H_f^0$ for alkali metal compounds.

MU-27692

Fig. 8. Estimated maximum deviation in $-\Delta H_f^\circ$ for alkaline earth compounds.

MU-27693

Fig. 9. Estimated maximum deviation in $-\Delta H_f^0$ for Mn⁺⁺, Fe⁺⁺, Co⁺⁺, Ni⁺⁺, Sn⁺⁺, and Pb⁺⁺ compounds.

Table XI. Accuracy of estimated maximum deviation in $-\Delta F_f^0$. Predicted and actual deviations from Latimer values are compared.

Cations	Predicted maximum deviation (kcal/M)	Actual max. deviation from Latimer value (kcal/M)	Compound of maximum deviation
alkali metals	6.5	6.3	CsOH
alkaline earth metals (excluding Be & Ra)	11.5	11.9	SrSiO ₃
U ⁺⁺⁺	17	34.9	U(OH) ₃
Cr ⁺⁺	17	9.2	CrBr ₂
Mn, ⁺⁺ Fe, ⁺⁺ Co, ⁺⁺ Ni ⁺⁺	10	10.4	CoF ₂
Al, ⁺⁺⁺ In, ⁺⁺⁺ Ga, ⁺⁺⁺ Tl ⁺	17.5	15	InBr ₃
Pb ⁺⁺	7.0	12.8	PbSiO ₃
Zn, ⁺⁺ Cd ⁺⁺	6.8	4.5	Cd(NO ₃) ₂
Ag, ⁺ Cu, ⁺ Hg ⁺	6.8	24.9	Hg ₂ F ₂
Au, ⁺⁺⁺ Cu, ⁺⁺ Hg ⁺⁺	20	37.6	AuF ₃

The method can be very readily applied to other inorganic compounds for which experimental data are available. Additional individual values for X , Y , and W can be evaluated if data for at least three compounds of the particular cation or anion are known. When many experimental data are available for an element, they are likely to be more accurate than that for compounds which have been less extensively investigated. Thus the more data used in the solution of Eqs. (A-1) for X , Y , and W , the more accurate will generally be the estimate of $-\Delta H_f^\circ$ or $-\Delta F_f^\circ$ from the results. Examination of Tables III and X bears this out. Beryllium and radium, for which only four data were included in the correlation of $-\Delta F_f^\circ$, show very large deviations when the estimated values of the other compounds are compared with the estimates of Latimer. However, the deviations of estimated values are much less for Mg and Ca compounds, for which many more data were included.

Improvement of Correlation

The solution of Eqs. (A-1) yields a method of estimation which is of acceptable accuracy for most compounds. However, the fact that better agreement is not always obtained for compounds whose data are well-known indicates the need for a system of weighting factors or other means of improving the correlation.

It would be very difficult to assign a weighting factor to each individual compound, since this would require that the accuracy of its datum be known. In many cases this is not reasonable. Such a designation would then have to be almost arbitrary. A set of weighting factors could much more easily be assigned to each element or radical. A combination of the weighting factor for the anion and that for the cation may then be evaluated for the compound of interest. One method of evaluating weighting factors is suggested upon examination of Table I with regard to the number of compounds and average deviations for each cation and anion included in the correlation.

Within each group of the Periodic Table, it may be postulated that the element for which the largest number of data are available is in general also the one for which the data are the most accurate, since both are the result of extensive investigation. Thus, of the alkali-metal data, those for Na and K would be expected to be more accurate than that for Cs compounds. Data for Ba and Ca compounds would similarly be expected to be more accurate than that for Be and Ra compounds. It then seems reasonable to use the number of compounds of an ion included in the correlation as one measure of the relative accuracy of its data. The other criterion--the average deviation obtained in the present correlation--is obvious and needs no explanation.

It seems natural to assign a weighting factor of 1.0 to both Na^+ and Cl^- , since their respective compounds have been the most thoroughly investigated of all cations and anions. The relative accuracy of all data may then be referred to that of the datum for NaCl. In the same manner the trivalent and tetravalent cations may be referred to Al, with AlCl_3 as a reference compound.

The following empirical equation was used to evaluate weighting factors R_c for each cation of Table I:

$$R_c = 0.8 \left(\frac{N_c}{N_{\text{Na}}} + 0.25 \frac{\bar{\Delta}_{\text{Na}}}{\bar{\Delta}_c} \right) \quad (10)$$

Similarly, for each anion we have

$$R_a = 0.8 \left(\frac{N_a}{N_{\text{Cl}}} + 0.25 \frac{\bar{\Delta}_{\text{Cl}}}{\bar{\Delta}_a} \right), \quad (11)$$

where N is the number of compounds of the cation or anion included in the correlation, and $\bar{\Delta}$ is the average deviation obtained for compounds of the cation or anion included in this correlation.

Tables XII and XIII list the resultant weighting factors for each cation and anion. The appropriate value to be employed for each compound may then be determined by simply averaging the two over the

Table XII. Suggested weighting factors for the cations of Table I.

Cation	R_c	Cation	R_c	Cation	R_c
Li^+	0.76	Cr^{++}	0.4	Ag^+	0.70
Na^+	1.00	Mo^{++}	0.4	Au^+	0.4
K^+	0.92	W^{++}	0.4	Zn^{++}	0.61
Rb^+	0.87	Mn^{++}	0.58	Cd^{++}	0.61
Cs^+	0.61	Fe^{++}	0.48	Hg_2^{++}	0.36
Be^{++}	0.43	Co^{++}	0.50	Hg^{++}	0.46
Mg^{++}	0.77	Ni^{++}	0.54	Sn^{++}	0.43
Ca^{++}	0.77	Pd^{++}	0.4	Pb^{++}	0.56
Sr^{++}	0.70	Pt^{++}	0.4	Tl^+	0.49
Ba^{++}	0.79	Cu^+	0.43	Ti^{++}	0.26
Ra^{++}	0.34	Cu^{++}	0.52	Zr^{++}	0.4
				NH_4^+	0.63

Table XIII. Suggested weighting factors for the anions of Table I

Anion	R_a	Anion	R_a
F^-	0.68	HSO_4^-	0.36
Cl^-	1.00	HCO_3^-	0.37
Br^-	0.98	CNS^-	0.29
I^-	0.88	ReO_4^-	0.23
$O^{=}$	0.77	$SiO_3^{=}$	0.22
$S^{=}$	0.66	$MoO_4^{=}$	0.50
$CO_3^{=}$	0.58	$WO_4^{=}$	0.44
NO_3^-	0.56	H^-	0.31
$SO_4^{=}$	0.71	$SeO_4^{=}$	0.44
$C_2H_3O_2^-$	0.37	ClO_4^-	0.30
OH^-	0.56	$HPO_4^{=}$	0.13
CN^-	0.26	HS^-	0.52
$C_2O_4^{=}$	0.25	ClO_3^-	0.34
CHO_2^-	0.39	NH_2^-	0.32
$SO_3^{=}$	0.24	O^-	0.32
NO_2^-	0.25	$CrO_4^{=}$	0.26

number of ions in the compound by using the formula

$$R = \frac{1}{n} (n_c R_c + n_a R_a), \quad (12)$$

where R is the weighting factor for each compound, n_c and n_a are the numbers of cations or anions in the compound, respectively, and n is the total number of ions in the compound. Thus, for MgCl_2 , we have $n_c = 1$, $n_a = 2$, $n = 3$, and $R = 0.92$.

This leads to values for R of 1.00 and 0.95, respectively, for compounds such as NaCl and KBr whose ΔH_f are well known, and values of 0.46 and 0.37 for compounds such as BaHPO_4 and FeCrO_4 whose ΔH_f data are very uncertain. One can apply the values of R calculated in this manner by simply replacing Δ in Eqs. (A-1) by

$$\Delta' = R \cdot \Delta. \quad (13)$$

Values of R determined in this manner are not to be considered a set of complete and accurate weighting factors. In the case of silver, for instance, one would expect a somewhat higher value since many of the data for Ag compounds are known as accurately as those of Na . Wherever possible, Tables XII and XIII should be supplemented with more accurate estimates based on a knowledge of the accuracy of the thermochemical data. However, where better estimates are not available, this method should be useful as a starting point.

An alternative to the use of weighting factors is the modification of the existing parameters. There is no apparent way that Eqs. (7) and (8) might be modified to be consistent with Pauling's postulate of the geometric mean. Borrowing the basic idea of a geometric mean, one might change the first term of Eq. (7) to read $n_{AB} (X_B X_A)^{1/2}$. With the exception of the difference in power, however, this is essentially what was done with the W parameter, and there is no reason to believe that such a change would improve the correlation.

Perhaps a more promising alternative is the addition of a fourth characteristic parameter for each ion. One possible form is suggested by the weakening of a single bond as other atoms are added to a molecule. Thus, both the number of single bonds and the number of ions in the

compound contribute simultaneously to the bond energy. A product term may therefore improve the correlation. The following form is suggested:

$$n_{AB} n_A Z_A + n_{AB} n_B Z_B ,$$

where n_{AB} is the apparent number of single bonds, n_A and n_B are the number of cations and anions in the molecule, and Z is an empirically determined parameter for each valence state of each element.

CONCLUSION

A method has been developed for estimating the standard heat of formation and free energy of formation of inorganic compounds at 25°C. At least three compounds of the ion for which the parameters are to be evaluated should be known. In general, better agreement will be obtained if a large number of data are available for the ion, and the best estimate results if they are similar in nature to the compound of interest. The estimates may in general be expected to be within 15 kcal/M of the actual value or better. The accuracy to be assumed will depend on which experimental data are available. The heat of formation of a halide will be more accurately estimated with data for other halides than with data for the oxide and tungstate, for example.

Experimental heat-of-formation data for 427 compounds of monovalent and divalent cations and 184 compounds of trivalent and tetravalent cations have been correlated by using this method. Average deviations of 1.98 and 1.51 kcal/M and maximum deviations of 8.73 and 10.23 kcal/M, respectively, were obtained. Experimental data for the free energy of formation of 270 compounds have been correlated, with an average deviation of 1.57 kcal/M and a maximum deviation of 9.39 kcal/M. Estimated $-\Delta F_f^0$ values are compared with estimates obtained by the Latimer method for 119 compounds, with an average deviation of 8.4 kcal/M. Agreement is best for the better-known compounds, and poorest for those whose data are not considered to be as accurate.

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APPENDICES

I. SOLUTION OF EQUATIONS

A. Least-Squares Equations

To evaluate a set of parameters X, Y, and W, one may conveniently use the least-squares method to fit the experimental data. Let

$$\Delta = (-\Delta H_f^O) - (-\Delta H_f^O)_{\text{exptl.}}$$

The least-squares requirement is the $\sum \Delta^2$ be a minimum, or that $\partial/\partial \xi [\sum \Delta^2]$ be zero. Then we have $\sum \frac{\partial}{\partial \xi} \Delta^2 = \sum \Delta \frac{\partial \Delta}{\partial \xi} = 0$, where

$$\xi = X_{A_i}, X_{B_j}, Y_{A_i}, Y_{B_j}, W_{A_i}, W_{B_j}. \text{ The result is}$$

$$\xi = X_{A_m} : \sum_{B_j=B_1}^{B_n} -2 \Delta_{mj} n_{A_m B_j} (X_{B_j} - X_{A_m}) = 0,$$

$$\xi = X_{B_n} : \sum_{A_i=A_1}^{A_m} 2 \Delta_{in} n_{A_i B_n} (X_{B_n} - X_{A_i}) = 0,$$

$$\xi = Y_{A_m} : \sum_{B_j=B_1}^{B_n} \Delta_{mj} n_{A_m} = 0, \tag{A-1}$$

$$\xi = Y_{B_n} : \sum_{A_i=A_1}^{A_m} \Delta_{in} n_{B_n} = 0,$$

$$\xi = W_{A_m} : \sum_{B_j=B_1}^{B_n} -\Delta_{mj} n_{A_m B_j} W_{B_j} = 0,$$

and

$$\xi = W_{B_n} : \sum_{A_i=A_1}^{A_m} \frac{\Delta_{in} n_{A_i B_n}}{W_{A_i}} = 0.$$

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

B. Iterative Solution⁶

The set of simultaneous equations

$$f_1(X, Y, W) = 0,$$

$$f_2(X, Y, W) = 0,$$

and

$$f_3(X, Y, W) = 0,$$

(A-2)

may be expressed in the form

$$X = F_1(X, Y, W),$$

$$Y = F_2(X, Y, W),$$

and

$$W = F_3(X, Y, W).$$

(A-3)

If an approximate solution is (X_0, Y_0, W_0) , then the solution by iteration proceeds as follows:

$$X_1 = F_1(X_0, Y_0, W_0),$$

$$Y_1 = F_2(X_1, Y_0, W_0),$$

$$W_1 = F_3(X_1, Y_1, W_0),$$

$$X_2 = F_1(X_1, Y_1, W_1),$$

(A-4)

For convergence, the coefficient of the unknown for which a particular equation is solved must be greater than the sum of the absolute values of all the other coefficients of that equation. 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.

The set of equations of this correlation are partially nonlinear. To apply the criterion of convergence, one must express Eqs. (A-1) in the form of Eqs. (A-3). Since these are in the form of a summation, however, this may not be done in some cases. The convergence of the equations may therefore be determined only by attempting the solution and testing the results.

Table A-1. Iterative solution of Eqs. (A-1). Values of X, Y, and W at 800 iterations for anions. Correlation of $-\Delta H_f^\circ$ for compounds of monovalent and divalent cations.

Anion	X (kcal) ^{1/2}	Y (kcal)	W (kcal)	Anion	X (kcal) ^{1/2}	Y (kcal)	W (kcal)
F ⁻	17.236	-2.38	0.94	HSO ₄ ⁻	14.444	181.60	-2.02
Cl ⁻	13.331	24.16	0.43	HCO ₃ ⁻	15.055	130.66	4.20
Br ⁻	12.586	21.91	0.39	CNS ⁻	13.045	-27.13	1.75
I ⁻	11.822	14.88	0.28	ReO ₄ ⁻	12.713	187.40	3.02
O ⁼	16.901	-147.60	33.19	SiO ₃ ⁼	15.648	146.50	12.51
S ⁼	13.620	-56.27	21.05	MoO ₄ ⁼	15.016	162.38	6.36
CO ₃ ⁼	16.000	47.12	7.45	WO ₄ ⁼	15.205	185.65	1.79
NO ₃ ⁻	14.626	20.72	-3.21	H ⁻	10.373	-24.13	43.34
SO ₄ ⁼	15.102	136.78	-0.91	SeO ₄ ⁼	15.117	66.14	0.19
C ₂ H ₃ O ₂ ⁻	15.084	72.91	6.31	ClO ₄ ⁻	14.074	9.17	-9.40
OH ⁻	16.546	-18.21	19.05	HPO ₄ ⁼	18.719	85.74	-38.28
CN ⁻	13.538	-54.93	13.46	HS ⁻	13.946	-23.32	-0.56
C ₂ O ₄ ⁼	15.901	95.04	5.33	ClO ₃ ⁻	13.778	6.67	-7.20
CHO ₂ ⁻	15.451	51.76	4.60	NH ₂ ⁻	14.389	-52.34	27.14
CO ₃ ⁼	15.743	44.55	-1.36	O ⁻	16.703	-62.55	25.06
NO ₂ ⁻	14.706	-7.58	4.66				

Table A-2. Iterative solution of Eqs. (A-1). Values of X, Y and W at 800 iterations for cations. Correlation of $-\Delta H_f^\circ$ for compounds of mono-valent and divalent cations.

Cation	X (kcal) ^{1/2}	Y (kcal)	W	Cation	X (kcal) ^{1/2}	Y (kcal)	W
NH ₄ ⁺	7.651	18.08	-23.39	Co ⁺⁺	7.083	-49.98	1.02
Li ⁺	5.841	17.44	6.18	Ni ⁺⁺	6.964	-54.44	1.04
Na ⁺	7.298	35.56	-14.84	Pd ⁺⁺	7.454	-72.48	1.07
K ⁺	7.946	51.30	-2.74	Pt ⁺⁺	10.399	-31.81	0.48
Rb ⁺	7.842	48.94	-1.85	Cu ⁺	9.794	-4.81	0.70
Cs ⁺	8.229	55.67	-1.73	Cu ⁺⁺	7.586	-60.74	0.87
Be ⁺⁺	3.736	-111.61	1.21	Ag ⁺	10.289	-4.33	0.87
Mg ⁺⁺	4.608	-48.61	1.76	Zn ⁺⁺	7.345	-20.42	0.92
Ca ⁺⁺	5.530	20.57	3.45	Cd ⁺⁺	7.851	-14.78	1.12
Sr ⁺⁺	6.064	42.83	6.53	Hg ₂ ⁺⁺	10.703	-0.78	0.71
Ba ⁺⁺	6.145	51.77	-19.33	Hg ⁺⁺	10.607	-9.73	0.67
Ra ⁺⁺	6.512	66.88	-7.24	Sn ⁺⁺	7.148	-41.25	1.01
Cr ⁺⁺	6.135	-54.77	-0.32	Pb ⁺⁺	7.738	-27.18	1.21
Mo ⁺⁺	8.236	-18.37	-0.02	Tl ⁺	8.460	-0.93	1.46
W ⁺⁺	7.116	-43.72	-0.02	Au ⁺	10.073	-2.20	-0.02
Mn ⁺⁺	6.687	-22.38	1.23	Ti ⁺⁺	5.938	-40.22	1.01
Fe ⁺⁺	6.693	-54.87	1.14	Zr ⁺⁺	1.886	-132.80	-0.02

Table A-3. Iterative solution of Eqs. (A-1). Values of X, Y, and W at 1600 iterations. Correlation of $-\Delta H_f^\circ$ for compounds of trivalent and tetravalent cations.

Ion	X (kcal) ^{1/2}	Y (kcal)	W	Ion	X (kcal) ^{1/2}	Y (kcal)	W
F ⁻	18.141	-25.53	9.74	Dy ⁺⁺⁺	7.628	56.26	-0.15
Cl ⁻	13.244	10.61	-2.72	Gd ⁺⁺⁺	8.072	61.98	-0.12
Br ⁻	12.474	7.39	-2.39	Sm ⁺⁺⁺	8.579	58.62	-0.09
I ⁻	11.687	0.26	-1.88	Nd ⁺⁺⁺	8.410	87.09	-0.15
O ⁼	16.286	-74.95	-2.68	Pr ⁺⁺⁺	8.729	68.11	-0.08
S ⁼	11.368	1.63	-1.22	Ce ⁺⁺⁺	5.941	57.24	-1.73
SO ₄ ⁼	15.064	117.65	-3.76	La ⁺⁺⁺	8.649	107.82	-0.18
OH ⁻	16.125	-6.50	-12.69	Pu ⁺⁺⁺	6.116	24.48	-0.38
				Np ⁺⁺⁺	5.797	9.77	-0.96
Bi ⁺⁺⁺	8.418	-9.71	-1.98	U ⁺⁺⁺	5.595	-3.65	-0.84
Ga ⁺⁺⁺	6.986	-23.56	-1.63	U ⁴⁺	6.305	8.07	-1.64
Au ⁺⁺⁺	9.321	-49.71	-1.25	Th ⁴⁺	6.305	43.00	-2.27
In ⁺⁺⁺	7.887	7.61	-1.64	Sn ⁴⁺	2.050	-529.01	-1.53
Pt ⁴⁺	10.813	48.31	0.21	W ⁴⁺	4.288	-37.72	0.04
Mo ⁴⁺	4.563	-24.41	0.05	Ti ⁺⁺⁺	6.354	-6.84	-1.59
Al ⁺⁺⁺	5.311	-52.57	-3.82	Ti ⁴⁺	6.222	-39.75	-1.20
Cr ⁺⁺⁺	6.674	-33.46	-1.59	Zr ⁺⁺⁺	5.680	-22.40	-1.74
Fe ⁺⁺⁺	6.852	-59.14	-2.32	Zr ⁴⁺	5.627	-43.31	-1.43
B ⁺⁺⁺	4.617	-83.39	0.13	Mn ⁺⁺⁺	6.652	-60.02	-1.56
Tl ⁺⁺⁺	9.867	15.28	-4.07	Mo ⁺⁺⁺	8.236	24.11	0.12
Y ⁺⁺⁺	7.115	81.14	-1.17	Pb ⁴⁺	7.380	-109.31	-1.32
Lu ⁺⁺⁺	5.573	21.96	3.35	Te ⁴⁺	6.950	42.51	0.07
V ⁺⁺⁺	6.561	-29.42	-1.38	Se ⁴⁺	6.334	-206.98	-0.59

Table A-3 (Continued).

Ion	$X^{1/2}$		Y	W	Ion	$X^{1/2}$		Y	W
	(kcal)					(kcal)			
Sc ⁺⁺⁺	7.217		74.94	2.85	Sb ⁺⁺⁺	8.757		2.80	1.09
Tm ⁺⁺⁺	5.630		34.14	0.79	Ce ⁴⁺	8.373		99.99	-0.33
Er ⁺⁺⁺	6.907		67.62	-1.01	Hf ⁴⁺	5.667		-32.80	4.70
Ho ⁺⁺⁺	7.267		56.78	-0.22	Np ⁴⁺	6.337		-3.04	-1.61

Table A-4. Iterative solution of Eqs (A-1). Values of X, Y, and W at 800 iterations. Correlation of $-\Delta F_f^o$.

Ion	X (kcal) ^{1/2}	Y (kcal)	W	Ion	X (kcal) ^{1/2}	Y (kcal)	W
F ⁻	16.904	-11.35	-1.72	Cs ⁺	2.552	-60.68	0.24
Cl ⁻	14.858	-26.65	7.95	Be ⁺⁺	9.665	126.84	12.80
Br ⁻	14.528	-31.83	9.92	Mg ⁺⁺	5.134	-4.55	1.32
I ⁻	14.068	-39.51	11.46	Ca ⁺⁺	4.486	-6.03	0.68
O ⁼	14.321	-12.17	-9.22	Sr ⁺⁺	3.735	-40.17	0.49
S ⁼	13.074	-49.12	4.19	Ba ⁺⁺	3.706	-40.99	0.40
Co ₃ ⁼	15.844	20.95	-0.57	Ra ⁺⁺	3.124	-64.41	0.50
NO ₃ ⁻	15.981	-49.46	5.88	Cr ⁺⁺	8.075	39.28	1.15
SO ₄ ⁼	16.111	35.89	4.06	Cr ⁺⁺⁺	7.465	18.41	1.90
OH ⁻	15.103	5.60	-5.02	Mn ⁺⁺	7.096	18.34	0.78
WO ₄ ⁼	16.019	109.59	0.74	Fe ⁺⁺	7.333	-4.99	0.89
MoO ₄ ⁼	15.360	102.41	3.72	Co ⁺⁺	7.806	-0.84	0.85
SiO ₃ ⁼	15.401	136.41	-1.40	Ni ⁺⁺⁺	7.673	-1.94	0.77
SeO ₄ ⁼	15.811	-16.87	2.55	V ⁺⁺⁺	7.510	28.51	2.53
CrO ₄ ⁼	15.760	41.17	5.40	Ti ⁺⁺⁺	7.777	52.74	2.01
H ⁻	13.628	-67.58	3.19	Ti ⁺⁺⁺	6.932	36.55	2.51
ClO ₄ ⁻	14.584	-60.93	12.29	Ti ⁴⁺	7.369	53.97	3.51
				Zr ⁺⁺	7.994	82.33	-2.07
Li ⁺	3.611	-23.02	0.50	Zr ⁺⁺⁺	7.679	109.19	-1.51
Na ⁺	3.362	-39.96	0.33	Zr ⁴⁺	5.843	-8.37	5.32
K ⁺	3.100	-45.03	0.27	Ce ⁺⁺⁺	6.153	80.79	3.42
Rb ⁺	2.226	-68.68	0.25	Nd ⁺⁺⁺	5.469	18.20	0.94

Table A-4 (Continued).

Ion	X (kcal) ^{1/2}	Y (kcal)	W	Ion	X (kcal) ^{1/2}	Y (kcal)	W
U ⁺⁺⁺	7.333	100.17	12.61	Hg ⁺⁺	12.453	50.68	0.51
U ⁴⁺	6.661	50.84	2.51	Al ⁺⁺⁺	4.655	-76.74	-11.81
Cu ⁺	9.407	14.46	0.62	In ⁺⁺⁺	7.770	23.39	0.77
Cu ⁺⁺⁺	9.264	17.07	0.82	Tl ⁺	7.802	1.82	0.41
Ag ⁺	10.350	12.83	0.43	Sn ⁺⁺	4.424	-0.59	0.88
Au ⁺⁺⁺	8.741	-53.82	0.70	Sn ⁴⁺	8.214	34.99	1.03
Zn ⁺⁺	8.154	35.16	0.89	Pb ⁺⁺	7.221	-13.60	0.58
Cd ⁺⁺	7.733	9.69	0.63	Bi ⁺⁺⁺	9.355	36.81	0.83
Hg ₂ ⁺⁺	11.497	29.17	0.68	NH ⁴⁺	7.790	23.59	3.90

II. ESTIMATION OF UNKNOWNNS

Tables A-5 through A-7 list estimates for unknown values of $-\Delta H_f^\circ$ and $-\Delta F_f^\circ$ for solid compounds of all cations and anions included in the correlations. The values of Tables A-5 and A-7 may generally be considered accurate to within ± 15 kcal/M. The values of Table A-6 are less accurate, however, and uncertainty limits have been placed on each value. While only an estimate itself, the uncertainty limit provides some measure of the reliability of the ΔH_f° value.

In no event should the difference between ΔH_f° and ΔF_f° be regarded as an estimation of the entropy of formation. Since these values were determined independently and are only approximations, such an assumption would yield large errors in many cases.

With several of the cations of Tables A-2 and A-3, small values of W cause very large contributions by the term (W_B/W_A) in Eq. (7), thus yielding unreasonable values for $-\Delta H_f^\circ$. Therefore estimates for compounds of these cations are not included in Tables A-5 and A-6, nor are estimates given where the calculated values are considered unreliable for any other reason. Thus the listed estimates may be considered to be accurate approximately to within 15 kcal/M or the corresponding uncertainty limits.

Table A-5. Estimation of unknown values of $-\Delta H_f^\circ$. The estimated uncertainty is ± 15 kcal/M.

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
NH_4F	107	11	26
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	146	11	12
NH_4OH	78	11	21
NH_4CN	-3	11	8
NH_4CHO_2	131	11	9
NH_4CNS	20	11	9
NH_4ReO_4	231	11	5
NH_4H	-0.5	11	10
NH_4HS	34	11	5
NH_4NH_2	10	11	9
$(\text{NH}_4)_2\text{O}$	56	11	27
$(\text{NH}_4)_2\text{S}$	49	11	24
$(\text{NH}_4)_2\text{CO}_3$	222	11	17
$(\text{NH}_4)_2\text{C}_2\text{O}_4$	267	11	8
$(\text{NH}_4)_2\text{SiO}_3$	309	11	7
$(\text{NH}_4)_2\text{MoO}_4$	306	11	16
$(\text{NH}_4)_2\text{WO}_4$	336	11	14
$(\text{NH}_4)_2\text{SeO}_4$	214	11	8
$\text{LiC}_2\text{H}_3\text{O}_2$	177	17	12
LiCN	24	17	8
LiCHO_2	162	17	9

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
LiHSO_4	273	17	5
LiHCO_3	234	17	5
LiCNS	42	17	9
LiClO_3	93	17	6
$\text{Li}_2\text{C}_2\text{O}_4$	334	17	8
Li_2SO_3	275	17	5
Li_2SiO_3	378	17	7
Li_2MoO_4	368	17	16
Li_2WO_4	396	17	14
Li_2SeO_4	273	17	8
K_2SiO_3	359	27	7
K_2WO_4	392	27	14
K_2SeO_4	271	27	8
$\text{RbC}_2\text{H}_3\text{O}_2$	171	19	12
RbCN	19	19	8
RbCHO_2	156	19	9
RbNO_2	86	19	8
$\text{Rb}_2\text{C}_2\text{O}_4$	317	19	8
Rb_2SO_3	269	19	5
Rb_2SiO_3	353	19	7
Rb_2MoO_4	356	19	16

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
Rb_2WO_4	390	19	14
Rb_2SeO_4	270	19	8
RbH	8	19	10
$\text{CsC}_2\text{H}_3\text{O}_2$	172	16	12
CsCN	21	16	8
CsCHO_2	157	16	9
CsNO_2	87	16	8
CsCNS	51	16	9
CsH	11	16	10
CsClO_4	104	16	8
CsClO_3	97	16	6
$\text{Cs}_2\text{C}_2\text{O}_4$	318	16	8
Cs_2SO_3	270	16	5
Cs_2SiO_3	353	16	7
Cs_2MoO_4	358	16	16
Cs_2WO_4	392	16	14
Cs_2SeO_4	272	16	8
$\text{Be}(\text{NO}_3)_2$	162	11	19
$\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$	302	11	12
$\text{Be}(\text{CN})_2$	7	11	8
$\text{Be}(\text{CHO}_2)_2$	274	11	9

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Be}(\text{NO}_2)_2$	122	11	8
$\text{Be}(\text{HSO}_4)_2$	478	11	5
$\text{Be}(\text{HCO}_3)_2$	413	11	5
$\text{Be}(\text{CNS})_2$	110	11	9
BeH_2	-0.4	11	10
$\text{Be}(\text{ClO}_4)_2$	105	11	8
$\text{Be}(\text{HS})_2$	49	11	5
$\text{Be}(\text{ClO}_3)_2$	92	11	6
$\text{Be}(\text{NH}_2)_2$	55	11	9
BeO_2	142	11	10
BeCO_3	249	11	17
BeC_2O_4	288	11	8
BeSO_3	219	11	5
BeSiO_3	339	11	7
$\text{Be}(\text{ReO}_4)_2$	429	11	5
$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$	324	17	12
$\text{Mg}(\text{CN})_2$	16	17	8
$\text{Mg}(\text{CHO}_2)_2$	295	17	9
$\text{Mg}(\text{NO}_2)_2$	145	17	8
$\text{Mg}(\text{HSO}_4)_2$	506	17	5
$\text{Mg}(\text{HCO}_3)_2$	436	17	5
$\text{Mg}(\text{CNS})_2$	41	17	9

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Mg}(\text{HS})_2$	78	17	5
$\text{Mg}(\text{ClO}_3)_2$	125	17	6
$\text{Mg}(\text{NH}_2)_2$	69	17	9
MgC_2O_4	308	17	8
MgSeO_4	239	17	8
$\text{Mg}(\text{ReO}_4)_2$	461	17	5
$\text{Ca}(\text{HSO}_4)_2$	542	22	5
$\text{Ca}(\text{HCO}_3)_2$	466	22	5
$\text{Ca}(\text{CNS})_2$	80	22	9
$\text{Ca}(\text{ClO}_4)_2$	179	22	8
$\text{Ca}(\text{HS})_2$	115	22	5
$\text{Ca}(\text{ClO}_3)_2$	166	22	6
CaC_2O_4	334	22	8
CaSO_3	273	22	5
$\text{Ca}(\text{ReO}_4)_2$	500	22	5
$\text{Sr}(\text{CN})_2$	49	20	8
$\text{Sr}(\text{HSO}_4)_2$	546	20	5
$\text{Sr}(\text{HCO}_3)_2$	467	20	5
$\text{Sr}(\text{CNS})_2$	87	20	9
$\text{Sr}(\text{ClO}_4)_2$	187	20	8
$\text{Sr}(\text{HS})_2$	120	20	5
$\text{Sr}(\text{ClO}_3)_2$	173	20	6

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
SrC_2O_4	333	20	8
SrSO_3	274	20	5
SrMoO_4	367	20	16
$\text{Sr}(\text{ReO}_4)_2$	500	20	5
$\text{Ba}(\text{HSO}_4)_2$	553	24	5
$\text{Ba}(\text{HCO}_3)_2$	471	24	5
$\text{Ba}(\text{CNS})_2$	93	24	9
$\text{Ba}(\text{HS})_2$	127	24	5
BaC_2O_4	337	24	8
BaSiO_3	378	24	7
$\text{Ba}(\text{ReO}_4)_2$	513	24	5
RaF_2	292	5	26
RaCl_2	208	5	33
RaBr_2	184	5	32
RaI_2	153	5	31
$\text{Ra}(\text{C}_2\text{H}_3\text{O}_2)_2$	358	5	12
$\text{Ra}(\text{OH})_2$	227	5	21
$\text{Ra}(\text{CN})_2$	52	5	8
$\text{Ra}(\text{CHO}_2)_2$	329	5	9
$\text{Ra}(\text{NO}_2)_2$	185	5	8
$\text{Ra}(\text{HSO}_4)_2$	556	5	5
$\text{Ra}(\text{HCO}_3)_2$	473	5	5

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Ra}(\text{CNS})_2$	97	5	99
RaH_2	36	5	10
$\text{Ra}(\text{ClO}_2)_2$	202	5	8
$\text{Ra}(\text{HS})_2$	131	5	5
$\text{Ra}(\text{ClO}_3)_2$	188	5	6
$\text{Ra}(\text{NH}_2)_2$	79	5	9
RaO_2	143	5	10
RaS	106	5	24
RaCO_3	292	5	17
RaC_2O_4	337	5	8
RaSO_3	282	5	5
RaSiO_3	377	5	7
RaSeO_4	281	5	8
$\text{Ra}(\text{ReO}_4)_2$	518	5	5
$\text{Mn}(\text{NO}_3)_2$	140	15	19
$\text{Mn}(\text{CN})_2$	-16	15	8
$\text{Mn}(\text{NO}_2)_2$	99	15	8
$\text{Mn}(\text{HSO}_4)_2$	456	15	5
$\text{Mn}(\text{HCO}_3)_2$	386	15	5
$\text{Mn}(\text{CNS})_2$	7	15	9
$\text{Mn}(\text{ReO}_4)_2$	430	15	5
MnH_2	27	15	10

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Mn}(\text{ClO}_4)_2$	90	15	8
$\text{Mn}(\text{HS})_2$	35	15	5
$\text{Mn}(\text{ClO}_3)_2$	80	15	6
$\text{Mn}(\text{NH}_2)_2$	36	15	9
MnSO_3	184	15	5
MnSeO_4	186	15	8
$\text{Fe}(\text{NO}_3)_2$	107	9	19
$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$	243	9	12
$\text{Fe}(\text{OH})_2$	136	9	21
$\text{Fe}(\text{CN})_2$	-47	9	8
$\text{Fe}(\text{CHO}_2)_2$	210	9	9
$\text{Fe}(\text{NO}_2)_2$	67	9	8
$\text{Fe}(\text{HSO}_4)_2$	425	9	5
$\text{Fe}(\text{HCO}_2)_2$	354	9	5
$\text{Fe}(\text{CNS})_2$	-25	9	9
$\text{Fe}(\text{ReO}_4)_2$	398	9	5
FeH_2	0.2	9	10
$\text{Fe}(\text{ClO}_4)_2$	56	9	8
$\text{Fe}(\text{HS})_2$	3	9	5
$\text{Fe}(\text{ClO}_3)_2$	80	9	6
$\text{Fe}(\text{NH}_2)_2$	36	9	9
FeCO_3	179	9	17

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
FeC_2O_4	219	9	8
FeSO_3	151	9	5
$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$	236	13	12
$\text{Co}(\text{CN})_2$	-50	13	8
$\text{Co}(\text{CHO}_2)_2$	203	13	9
$\text{Co}(\text{NO}_2)_2$	60	13	8
$\text{Co}(\text{HSO}_4)_2$	418	13	5
$\text{Co}(\text{HCO}_3)_2$	347	13	5
$\text{Co}(\text{CNS})_2$	-30	13	9
$\text{Co}(\text{ReO}_4)_2$	394	13	5
$\text{Co}(\text{ClO}_4)_2$	48	13	8
$\text{Co}(\text{HS})_2$	-4	13	5
$\text{Co}(\text{ClO}_3)_2$	39	13	6
$\text{Co}(\text{NH}_2)_2$	5	13	9
CoC_2O_4	211	13	8
CoSO_3	142	13	5
CoSiO_3	268	13	7
CoSeO_4	146	13	8
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$	235	13	12
$\text{Ni}(\text{CN})_2$	-52	13	8
$\text{Ni}(\text{CHO}_2)_2$	202	13	9
$\text{Ni}(\text{NO}_2)_2$	59	13	8

Table A-5 (Continued).

Compound	Eq. (7). estimate	Number of compounds	
		Cation	Anion
$\text{Ni}(\text{HSO}_4)_2$	417	13	5
$\text{Ni}(\text{HCO}_3)_2$	346	13	5
$\text{Ni}(\text{CNS})_2$	-31	13	9
$\text{Ni}(\text{ReO}_4)_2$	392	13	5
$\text{Ni}(\text{ClO}_4)_2$	47	13	8
$\text{Ni}(\text{HS})_2$	-5	13	5
$\text{Ni}(\text{ClO}_3)_2$	38	13	6
$\text{Ni}(\text{NH}_2)_2$	3	13	9
PdF_2	116	4	26
$\text{Pd}(\text{NO}_3)_2$	66	4	19
$\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$	202	4	12
$\text{Pd}(\text{CN})_2$	-83	4	8
$\text{Pd}(\text{CHO}_2)_2$	168	4	9
$\text{Pd}(\text{NO}_2)_2$	26	4	8
$\text{Pd}(\text{HSO}_4)_2$	385	4	5
$\text{Pd}(\text{HCO}_3)_2$	312	4	5
$\text{Pd}(\text{CNS})_2$	-61	4	9
$\text{Pd}(\text{ReO}_4)_2$	363	4	5
PdCO_3	135	4	17
PdSO_4	180	4	25
PdC_2O_4	175	4	8
PdSO_3	107	4	5
PdSiO_3	232	4	7
PdMoO_4	216	4	16

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
PdWO_4	237	4	14
PdSeO_4	111	4	8
$\text{Cu}(\text{CN})_2$	-69	14	8
$\text{Cu}(\text{NO}_2)_2$	36	14	8
$\text{Cu}(\text{HSO}_4)_2$	392	14	5
$\text{Cu}(\text{HCO}_3)_2$	322	14	5
$\text{Cu}(\text{CNS})_2$	-51	14	9
$\text{Cu}(\text{ReO}_4)_2$	374	14	5
CuH_2	6	14	10
$\text{Cu}(\text{ClO}_4)_2$	20	14	8
$\text{Cu}(\text{HS})_2$	-28	14	5
$\text{Cu}(\text{ClO}_3)_2$	13	14	6
$\text{Cu}(\text{NH}_2)_2$	-10	14	9
CuO_2	37	14	10
CuC_2O_4	185	14	8
CuSO_3	114	14	5
CuSiO_3	245	14	7
CuSeO_4	119	14	8
$\text{Zn}(\text{NO}_2)_2$	83	15	8
$\text{Zn}(\text{HSO}_4)_2$	439	15	5
$\text{Zn}(\text{HCO}_3)_2$	369	15	5
$\text{Zn}(\text{CNS})_2$	-6	15	9

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Zn}(\text{ReO}_4)_2$	419	15	5
ZnH_2	44	15	10
$\text{Zn}(\text{ClO}_4)_2$	68	15	8
$\text{Zn}(\text{HS})_2$	19	15	5
$\text{Zn}(\text{ClO}_3)_2$	60	15	6
$\text{Zn}(\text{NH}_2)_2$	33	15	9
ZnO_2	83	15	10
ZnC_2O_4	233	15	8
ZnSO_3	162	15	5
ZnWO_4	293	15	14
ZnSeO_4	167	15	8
$\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2$	247	16	12
$\text{Cd}(\text{CHO}_2)_2$	212	16	9
$\text{Cd}(\text{NO}_2)_2$	72	16	8
$\text{Cs}(\text{HSO}_4)_2$	432	16	5
$\text{Cd}(\text{HCO}_3)_2$	358	16	5
$\text{Cd}(\text{ReO}_4)_2$	413	16	5
CdH_2	27	16	10
$\text{Cd}(\text{ClO}_4)_2$	64	16	8
$\text{Cd}(\text{HS})_2$	12	16	5
$\text{Cd}(\text{ClO}_3)_2$	56	16	6
CdO_2	60	16	10

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
CdSO_3	152	16	5
CdSiO_3	276	16	7
CdSeO_4	157	16	8
$\text{Hg}_2(\text{NO}_3)_2$	61	7	19
$\text{Hg}_2(\text{OH})_2$	83	7	21
$\text{Hg}_2(\text{CN})_2$	-58	7	8
$\text{Hg}_2(\text{CHO}_2)_2$	110	7	9
$\text{Hg}_2(\text{NO}_2)_2$	28	7	8
$\text{Hg}_2(\text{HSO}_4)_2$	466	7	5
$\text{Hg}_2(\text{HCO}_3)_2$	309	7	5
$\text{Hg}_2(\text{CNS})_2$	-40	7	9
$\text{Hg}_2(\text{ReO}_4)_2$	385	7	5
Hg_2H_2	74	7	10
$\text{Hg}_2(\text{ClO}_4)_2$	12	7	8
$\text{Hg}_2(\text{HS})_2$	-28	7	5
$\text{Hg}_2(\text{ClO}_3)_2$	11	7	6
$\text{Hg}_2(\text{NH}_2)_2$	-2	7	9
Hg_2O_2	15	7	10
Hg_2S	19	7	24
Hg_2CO_3	123	7	17
$\text{Hg}_2\text{C}_2\text{O}_4$	163	7	8
Hg_2SO_3	90	7	5

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
Hg_2SiO_3	229	7	7
Hg_2MoO_4	216	7	16
Hg_2WO_4	229	7	14
Hg_2SeO_4	104	7	8
$\text{Hg}(\text{NO}_3)_2$	54	11	19
$\text{Hg}(\text{OH})_2$	82	11	21
$\text{Hg}(\text{CHO}_2)_2$	155	11	9
$\text{Hg}(\text{NO}_2)_2$	23	11	8
$\text{Hg}(\text{HSO}_4)_2$	377	11	5
$\text{Hg}(\text{HCO}_3)_2$	304	11	5
$\text{Hg}(\text{ReO}_4)_2$	383	11	5
HgH_2	72	11	10
$\text{Hg}(\text{ClO}_4)_2$	4	11	8
$\text{Hg}(\text{HS})_2$	-36	11	5
$\text{Hg}(\text{ClO}_3)_2$	2	11	6
$\text{Hg}(\text{NH}_2)_2$	-4	11	9
HgO_2	14	11	10
HgCO_3	118	11	17
HgSO_3	83	11	5
HgSiO_3	225	11	7
HgMoO_4	211	11	16
HgWO_4	224	11	14

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
HgSeO_4	98	11	8
$\text{Sn}(\text{NO}_3)_2$	106	7	19
$\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$	243	7	12
$\text{Sn}(\text{CN})_2$	-43	7	8
$\text{Sn}(\text{CHO}_2)_2$	209	7	9
$\text{Sn}(\text{NO}_2)_2$	67	7	8
$\text{Sn}(\text{HSO}_4)_2$	424	7	5
$\text{Sn}(\text{HCO}_3)_2$	353	7	5
$\text{Sn}(\text{CNS})_2$	-23	7	9
$\text{Sn}(\text{ReO}_4)_2$	401	7	5
SnH_2	17	7	10
$\text{Sn}(\text{ClO}_4)_2$	54	7	8
$\text{Sn}(\text{HS})_2$	3	7	5
$\text{Sn}(\text{ClO}_3)_2$	46	7	6
$\text{Sn}(\text{NH}_2)_2$	13	7	9
SnCO_3	177	7	17
SnSO_4	220	7	25
SnC_2O_4	218	7	8
SnSO_3	148	7	5
SnSiO_3	274	7	7
SnMoO_4	258	7	16

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
SnWO_4	278	7	14
SnSeO_4	152	7	8
$\text{Pb}(\text{CN})_2$	-47	17	8
$\text{Pb}(\text{NO}_2)_2$	62	17	8
$\text{Pb}(\text{HSO}_4)_2$	423	17	5
$\text{Pb}(\text{HCO}_3)_2$	348	17	5
$\text{Pb}(\text{ReO}_4)_2$	402	17	5
PbH_2	10	17	10
$\text{Pb}(\text{ClO}_4)_2$	56	17	8
$\text{Pb}(\text{HS})_2$	2	17	5
$\text{Pb}(\text{ClO}_3)_2$	47	17	6
$\text{Pb}(\text{NH}_2)_2$	1	17	9
PbO_2	51	17	10
PbC_2O_4	210	17	8
PbSO_3	143	17	5
PbWO_4	273	17	14
$\text{TlC}_2\text{H}_3\text{O}_2$	120	12	12
TlCN	-21	12	8
TlCHO_2	103	12	9
TlNO_2	34	12	8
TlHSO_4	215	12	5
TlHCO_3	176	12	5

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
TlCNS	-6	12	9
TlReO ₄	207	12	5
TlH	8	12	10
TlClO ₄	33	12	8
TlHS	5	12	5
TlClO ₃	29	12	6
TlNH ₂	0.5	12	9
Tl ₂ O ₂	43	12	10
Tl ₂ C ₂ O ₄	211	12	8
Tl ₂ SO ₃	147	12	5
Tl ₂ SiO ₃	265	12	7
Tl ₂ MoO ₄	255	12	16
Tl ₂ WO ₄	277	12	14
Ti(NO ₃) ₂	146	6	19
Ti(C ₂ H ₃ O ₂) ₂	285	6	12
Ti(OH) ₂	186	6	21
Ti(CN) ₂	-8	6	8
Ti(CHO ₂) ₂	253	6	9
Ti(NO ₂) ₂	108	6	8
Ti(HSO ₄) ₂	464	6	5
Ti(HCO ₃) ₂	396	6	5
Ti(CNS) ₂	10	6	9
Ti(ReO ₄) ₂	432	6	5

Table A-5 (Continued).

Compound	Eq. (7) estimate	Number of compounds	
		Cation	Anion
$\text{Ti}(\text{ClO}_4)_2$	92	6	8
$\text{Ti}(\text{HS})_2$	40	6	5
$\text{Ti}(\text{ClO}_3)_2$	82	6	6
$\text{Ti}(\text{NH}_2)_2$	52	6	9
TiO_2	119	6	10
TiS	63	6	24
TiCO_3	224	6	17
TiSO_4	263	6	25
TiC_2O_4	264	6	8
TiSO_3	194	6	5
TiSiO_3	320	6	7
TiMoO_4	300	6	16
TiWO_4	321	6	14
TiSeO_4	195	6	8

Table A-6. Estimation of unknown values of $-\Delta H_f^\circ$.

Compound	Eq. (7) estimate	Estimated uncertainty ($\pm$ values)	Number of compounds	
			Cation	Anion
BiF_3	183	20	5	21
BiBr_3	65	5	5	24
BiI_3	26	5	5	31
Ga_2S_3	78	15	5	11
$\text{Ga}_2(\text{SO}_4)_3$	711	15	5	11
$\text{Ga}(\text{OH})_3$	231	10	5	12
AuI_3	- 28	10	5	31
Au_2S_3	- 64	15	5	11
InF_3	229	20	6	21
In_2S_3	97	10	6	11
$\text{Al}(\text{OH})_3$	289	15	7	12
Cr_2S_3	75	20	5	11
$\text{Cr}_2(\text{SO}_4)_3$	723	20	5	11
$\text{Cr}(\text{OH})_3$	239	20	5	12
FeI_3	14	10	5	31
Fe_2S_3	12	20	5	11
$\text{Fe}_2(\text{SO}_4)_3$	649	20	5	11
VI_3	54	5	4	31
V_2S_3	90	30	4	11
$\text{V}_2(\text{SO}_4)_3$	744	15	4	11

Table A-6 (Continued).

Compound	Eq. (7) estimate	Estimated uncertainty (± values)	Number of compounds	
			Cation	Anion
$V(OH)_3$	253	15	4	12
TlI_3	27	10	4	31
Tl_2O_3	57	10	4	33
Tl_2S_3	51	30	4	11
$Tl_2(SO_4)_3$	551	30	4	11
YBr_3	196	10	4	24
Y_2S_3	282	20	4	11
$Y_2(SO_4)_3$	914	20	4	11
ErF_3	341	30	4	21
$ErBr_3$	190	15	4	24
Er_2S_3	267	15	4	11
$Er_2(SO_4)_3$	910	15	4	11
$HoBr_3$	193	5	3	24
Ho_2S_3	252	10	3	11
$Ho_2(SO_4)_3$	933	15	3	11
$DyBr_3$	197	10	3	24
Dy_2S_3	251	15	3	11
$Dy_2(SO_4)_3$	950	30	3	11
$GdBr_3$	200	10	3	24
Gd_2S_3	253	15	3	11

Table A-6 (Continued).

Compound	Eq. (7) estimate	Estimated uncertainty ($\pm$ values)	Number of compounds	
			Cation	Anion
$\text{Ga}_2(\text{SO}_4)_3$	952	30	3	11
SmBr_3	209	5	3	24
Sm_2S_3	253	15	3	11
NdBr_3	208	10	5	24
PrBr_3	218	5	3	24
Pr_2S_3	270	20	3	11
CeBr_3	212	10	4	24
Ce_2O_3	541	20	4	33
$\text{Ce}_2(\text{SO}_4)_3$	980	30	4	11
$\text{Ce}(\text{OH})_3$	371	30	4	12
LaBr_3	214	10	6	24
Pu_2O_3	487	20	3	33
Pu_2S_3	239	20	3	11
$\text{Pu}_2(\text{SO}_4)_3$	942	20	3	11
Np_2O_3	471	20	4	33
Np_2S_3	218	15	4	11
$\text{Np}_2(\text{SO}_4)_3$	911	15	4	11
$\text{Np}(\text{OH})_3$	350	15	4	12
U_2O_3	473	30	4	33
U_2S_3	206	20	4	11

Table A-6 (Continued).

Compound	Eq. (7) estimate	Estimated uncertainty ($\pm$ values)	Number of compounds	
			Cation	Anion
$U_2(SO_4)_3$	911	30	4	11
$U(OH)_3$	355	30	4	12
Ti_2S_3	147	15	5	11
$Ti_2(SO_4)_3$	809	15	5	11
$Ti(OH)_3$	284	15	5	12
Zr_2O_3	415	20	4	33
Zr_2S_3	158	50	4	11
$Zr(OH)_3$	307	30	4	12
Mo_2S_3	53	15	3	11
US_2	117	10	6	11
$U(OH)_4$	399	30	6	12
ThS_2	151	20	7	11
TiS_2	74	30	4	11
$Ti(SO_4)_2$	521	30	4	11
ZrS_2	95	20	6	11
$Zr(SO_4)_2$	559	20	6	11
$PbBr_4$	31	15	3	24
$Pb(SO_4)_2$	374	30	3	11
$Pb(OH)_4$	209	30	3	12
$CeCl_4$	270	15	3	41

Table A-6 (Continued).

Compound	Eq. (7) estimate	Estimated uncertainty ($\pm$ values)	Number of compounds	
			Cation	Anion
CeBr ₄	226	15	3	24
CeI ₄	168	10	3	31
Ce(OH) ₄	469	20	3	12
NpI ₄	117	20	3	31
NpO ₂	250	20	3	33
NpS ₂	104	20	3	11
Np(SO ₄) ₂	546	20	3	11
Np(OH) ₄	386	20	3	12

Table A-7. Estimation of unknown values of ΔH_f° . The estimated uncertainty is ± 15 kcal/M.

Compound	Eq. (8) estimate	Number of compounds	
		cation	Anion
LiH	16	6	3
Li ₂ WO ₄	374	6	10
Li ₂ MoO ₄	347	6	14
Li ₂ SiO ₃	363	6	4
Li ₂ SeO ₄	245	6	4
Li ₂ CrO ₄	312	6	3
NaH	8	12	3
Na ₂ WO ₄	355	12	10
Na ₂ MoO ₄	333	12	14
Na ₂ SeO ₄	229	12	4
KH	10	7	3
K ₂ WO ₄	359	7	10
K ₂ MoO ₄	341	7	14
K ₂ SiO ₃	338	7	4
K ₂ SeO ₄	235	7	4
RbH	7	10	3
Rb ₂ WO ₄	359	10	10
Rb ₂ MoO ₄	340	10	14
Rb ₂ SiO ₃	335	10	4
Rb ₂ SeO ₄	235	10	4
Rb ₂ CrO ₄	314	10	3

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
CsH	8	10	3
Cs ₂ WO ₄	357	10	10
Cs ₂ MoO ₄	340	10	14
Cs ₂ SiO ₃	334	10	4
Cs ₂ SeO ₄	235	10	4
Cs ₂ CrO ₄	314	10	3
CuF	57	5	27
CuNO ₂	18	5	11
CuOH	45	5	15
CuH	- 30	5	3
CuClO ₄	0.1	5	5
Cu ₂ CO ₃	131	5	16
Cu ₂ WO ₄	228	5	10
Cu ₂ MoO ₄	214	5	14
Cu ₂ SiO ₃	233	5	4
Cu ₂ SeO ₄	102	5	4
Cu ₂ CrO ₄	168	5	3
AgOH	30	13	15
AgH	- 37	13	3
Ag ₂ SiO ₃	206	13	4
TlH	- 24	8	3

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
TlClO_4	17	8	5
Tl_2WO_4	252	8	10
Tl_2MoO_4	239	8	14
Tl_2SiO_3	249	8	4
NH_4F	95	3	27
NH_4Br	41	3	23
NH_4I	27	3	24
NH_4OH	81	3	15
NH_4H	- 9	3	3
$(\text{NH}_4)_2\text{O}$	114	3	35
$(\text{NH}_4)_2\text{S}$	57	3	19
$(\text{NH}_4)_2\text{CO}_3$	197	3	16
$(\text{NH}_4)_2\text{SO}_4$	224	3	19
$(\text{NH}_4)_2\text{WO}_4$	293	3	10
$(\text{NH}_4)_2\text{MoO}_4$	267	3	14
$(\text{NH}_4)_2\text{SiO}_3$	298	3	4
$(\text{NH}_4)_2\text{SeO}_4$	161	3	4
$\text{Hg}_2(\text{NO}_3)_2$	17	4	11
$\text{Hg}_2(\text{OH})_2$	81	4	15
Hg_2H_2	- 83	4	3
$\text{Hg}_2(\text{ClO}_4)_2$	- 8	4	5

Table A-7. (Continued)

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
Hg_2S	27	4	19
Hg_2WO_4	211	4	10
Hg_2MoO_4	202	4	14
Hg_2SiO_3	221	4	4
Hg_2SeO_4	86	4	4
$\text{Be}(\text{NO}_3)_2$	109	4	11
BeH_2	24	4	3
$\text{Be}(\text{ClO}_4)_2$	55	4	5
BeCO_3	224	4	16
BeSiO_3	329	4	4
BeSeO_4	186	4	4
BeCrO_4	243	4	3
MgSeO_4	211	12	4
MgCrO_4	271	12	3
$\text{Ca}(\text{ClO}_4)_2$	112	14	5
CaSeO_4	241	14	4
SrH_2	34	5	3
$\text{Sr}(\text{ClO}_4)_2$	124	5	5
SrMoO_4	348	5	14
BaH_2	37	9	3
BaSiO_3	362	9	4

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
RaF_2	286	4	27
RaCl_2	190	4	38
RaBr_2	172	4	23
RaI_2	142	4	24
$\text{Ra}(\text{OH})_2$	214	4	15
RaH_2	34	4	3
$\text{Ra}(\text{ClO}_4)_2$	126	4	5
RaS	101	4	19
RaSiO_3	368	4	4
RaSeO_4	251	4	4
RaCrO_4	318	4	3
$\text{Cr}(\text{NO}_3)_2$	76	3	11
CrH_2	- 29	3	3
$\text{Cr}(\text{ClO}_4)_2$	24	3	5
CrO	89	3	35
CrS	47	3	19
CrCO_3	180	3	16
CrSO_4	211	3	19
CrWO_4	276	3	10
CrMoO_4	254	3	14

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
CrSiO_3	281	3	4
CrSeO_4	147	3	4
$\text{Mn}(\text{NO}_3)_2$	92	9	11
MnH_2	- 123	9	3
$\text{Mn}(\text{ClO}_4)_2$	40	9	5
MnWO_4	289	9	10
MnSeO_4	160	9	4
MnCrO_4	224	9	3
$\text{Fe}(\text{NO}_3)_2$	59	8	11
FeH_2	- 54	8	3
$\text{Fe}(\text{ClO}_4)_2$	6	8	5
FeSeO_4	128	8	4
FeCrO_4	190	8	3
CoH_2	- 61	5	3
$\text{Co}(\text{ClO}_4)_2$	- 2	5	5
CoSiO_3	248	5	4
CoSeO_4	116	5	4
CoCrO_4	180	5	3
NiH_2	- 58	7	3
$\text{Ni}(\text{ClO}_4)_2$	4	7	5
NiWO_4	249	7	10

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
NiSiO_3	250	7	4
NiSeO_4	120	7	4
NiCrO_4	184	7	3
CuH_2	- 72	7	3
$\text{Cu}(\text{ClO}_4)_2$	- 18	7	5
CuSiO_3	225	7	4
CuSeO_4	92	7	4
CuCrO_4	156	7	3
ZnH_2	- 33	9	3
$\text{Zn}(\text{ClO}_4)_2$	24	9	5
ZnSeO_4	141	9	4
ZnCrO_4	204	9	3
CdH_2	- 46	11	3
$\text{Cd}(\text{ClO}_4)_2$	21	11	5
CdSiO_3	259	11	4
CdSeO_4	131	11	4
CdCrO_4	197	11	3
$\text{Hg}(\text{NO}_3)_2$	- 0.4	6	11
$\text{Hg}(\text{OH})_2$	57	6	15
HgH_2	- 69	6	3

Table A-7. (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
$\text{Hg}(\text{ClO}_4)_2$	- 14	6	5
HgCO_3	92	6	16
HgWO_4	189	6	10
HgMoO_4	185	6	14
HgSiO_3	199	6	4
HgSeO_4	66	6	4
HgCrO_4	135	6	3
$\text{Sn}(\text{NO}_3)_2$	60	3	11
SnH_2	- 51	3	3
$\text{Sn}(\text{ClO}_4)_2$	8	3	5
SnCO_3	161	3	16
SnWO_4	258	3	10
SnMoO_4	236	3	14
SnSiO_3	260	3	4
SnSeO_4	129	3	4
SnCrO_4	192	3	3
PbH_2	- 56	11	3
$\text{Pb}(\text{ClO}_4)_2$	15	11	5
$\text{Ti}(\text{NO}_3)_2$	94	5	11
$\text{Ti}(\text{OH})_2$	167	5	15
TiH_2	- 11	5	3

Table A-7 (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
$\text{Ti}(\text{ClO}_4)_2$	36	5	5
TiSO_4	232	5	19
TiWO_4	299	5	10
TiMoO_4	274	5	14
TiSiO_3	304	5	4
TiSeO_4	167	5	4
TiCrO_4	227	5	3
$\text{Zr}(\text{NO}_3)_2$	105	4	11
$\text{Zr}(\text{OH})_2$	200	4	15
ZrH_2	8	4	3
$\text{Zr}(\text{ClO}_4)_2$	35	4	5
ZrO	159	4	35
ZrS	81	4	19
ZrCO_3	227	4	16
ZrSO_4	246	4	19
ZrWO_4	320	4	10
ZrMoO_4	290	4	14
ZrSiO_3	330	4	4
ZrSeO_4	185	4	4
ZrCrO_4	239	4	3

Table A-7 (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
$\text{Cr}(\text{NO}_3)_3$	97	3	11
CrH_3	- 65	3	3
$\text{Cr}(\text{ClO}_4)_3$	7	3	5
VI_3	53	2	24
$\text{V}(\text{NO}_3)_3$	102	2	11
$\text{V}(\text{OH})_3$	214	2	15
VH_3	- 58	2	3
$\text{V}(\text{ClO}_4)_3$	10	2	5
CeBr_3	204	2	23
$\text{Ce}(\text{NO}_3)_3$	227	2	11
CeH_3	48	2	3
$\text{Ce}(\text{ClO}_4)_3$	122	2	5
NdF_3	371	3	27
$\text{Nd}(\text{NO}_3)_3$	220	3	11
NdH_3	25	3	3
$\text{Nd}(\text{ClO}_4)_3$	124	3	5
$\text{U}(\text{NO}_3)_3$	178	5	11
$\text{U}(\text{ClO}_4)_3$	78	5	5
AuI_3	- 38	3	24
$\text{Au}(\text{NO}_3)_3$	- 20	3	11

Table A-7 (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
$\text{Au}(\text{ClO}_4)_3$	- 81	3	5
InF_3	233	3	27
$\text{In}(\text{NO}_3)_3$	100	3	11
InH_3	- 64	3	3
$\text{In}(\text{ClO}_4)_3$	28	3	5
BiF_3	168	3	27
BiBr_3	57	3	23
BiI_3	26	3	24
$\text{Bi}(\text{NO}_3)_3$	41	3	11
BiH_3	-100	3	3
$\text{Bi}(\text{ClO}_4)_3$	- 20	3	5
$\text{Ti}(\text{NO}_3)_3$	141	5	11
$\text{Ti}(\text{OH})_3$	249	5	15
TiH_3	- 28	5	3
$\text{Ti}(\text{ClO}_4)_3$	44	5	5
$\text{Zr}(\text{NO}_3)_3$	156	4	11
$\text{Zr}(\text{OH})_3$	303	4	15
ZrH_3	6	4	3
$\text{Zr}(\text{ClO}_4)_3$	45	4	5
Zr_2O_3	483	4	35

Table A-7 (Continued).

Compound	Eq. (8) estimate	Number of compounds	
		Cation	Anion
$\text{Zr}(\text{NO}_3)_4$	209	5	11
ZrH_4	- 34	5	3
$\text{Zr}(\text{ClO}_4)_4$	63	5	5
$\text{U}(\text{NO}_3)_4$	210	5	11
UH_4	- 20	5	3
$\text{U}(\text{ClO}_4)_4$	78	5	5
$\text{Ti}(\text{NO}_3)_4$	160	4	11
$\text{Ti}(\text{OH})_4$	312	4	15
TiH_4	- 56	4	3
$\text{Ti}(\text{ClO}_4)_4$	32	4	5
$\text{Al}(\text{NO}_3)_3$	158	7	11
$\text{Al}(\text{ClO}_4)_3$	33	7	5
AlH_3	- 39	7	3

III. LATIMER ENTROPY CONTRIBUTION

The free energy of formation of a compound may be estimated if the heat of formation is known by employing the Latimer equation for the approximate entropy contribution of each element in a solid compound:¹

$$S_{298} = \frac{3}{2} R \ln M + S_0' , \quad (\text{A-5})$$

where S_{298} is the entropy contribution of each element at 298°C, R is the universal gas constant, M is the atomic weight, and S_0' is the constant characteristic of the constraint by which atoms are held, postulated constant at -0.94.

If the postulate is valid that the entropy of a compound is the sum of the entropies of the constituent elements, we have

$$\Delta S_f^0 = S_p - \sum S_r , \quad (\text{A-6})$$

where ΔS_f^0 is the standard entropy of formation at 298°C, S_p is the total entropy of a compound, the sum of the separate contributions given by Eq. (14), and S_r is the entropy of the reactant element, the summation being taken over all the atoms in the compound.

It follows that

$$\Delta S_f^0 = \frac{3}{2} R \ln \left[M_A^m \cdot M_B^n \right] - 0.94 (m + n) - \sum S_r \quad (\text{A-7})$$

for a polyatomic molecule with m cations and n anions. Latimer made slight corrections to account for the effect of ionic radii and constructed tables of entropy contributions for many ions. The Latimer estimates of Table X were calculated from these tabulated values.

NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
A	a cation	
B	an anion	
D	extra-ionic energy of a bond	kcal/M
n_A, n_B	number of atoms of A or B per molecule	
n_{AB}	number of single bonds A-B per molecule in the compound $A_m B_n$	
N	iteration number	
R_a, R_c	weighting factors for an anion or cation	
x	Pauling electronegativity	(kcal/M) ^{1/2}
X	least-squares electronegativity	(kcal/M) ^{1/2}
Y, W, Z	synthetic parameters characteristic of an anion or cation	
ΔH_f°	standard heat of formation of a solid compound at 25° and 1 atm.	kcal/M
Δ	$(-\Delta H_f^\circ)_{\text{calc.}} - (-\Delta H_f^\circ)_{\text{exp.}}$	kcal/M
ϕ	characteristic wave function	
ΔF_f°	standard free energy of formation of a solid compound at 25°C and 1 atm.	kcal/M
M	atomic weight	
S_{298}	entropy contribution of each element in a solid compound at 25°C	cal/M-°C
S_0'	constant characteristic of the constraint by which atoms are held	cal/M-°C
ΔS_f°	standard entropy of formation of a solid compound at 25° and 1 atm.	cal/M-°C
S_r	entropy of a reactant element	cal/M-°C
S_p	total entropy of a compound	cal/M-°C

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