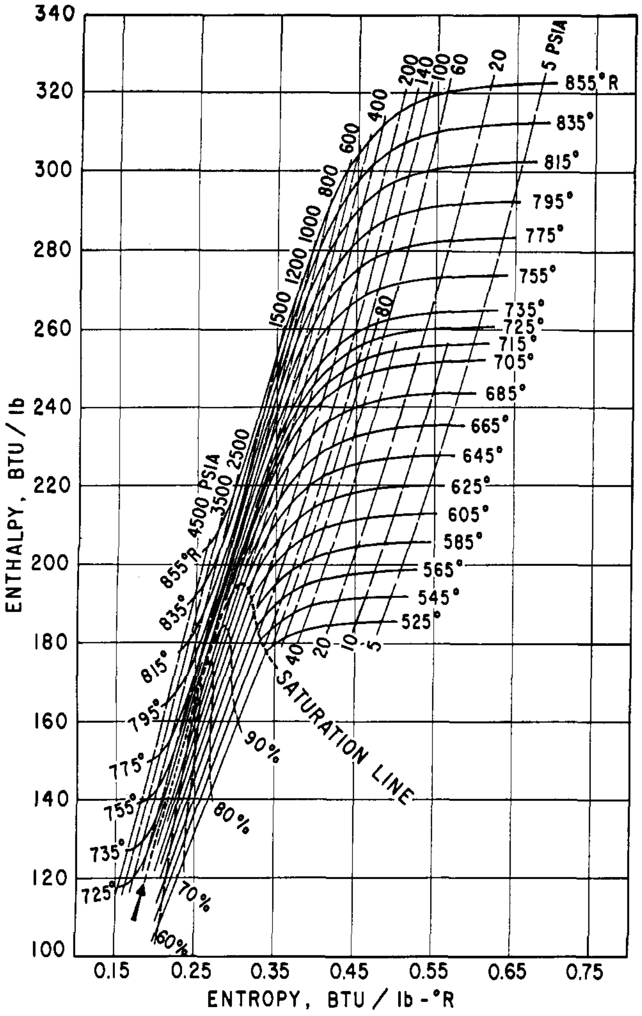

Figure 1. Mollier diagram of cyclopropane in vapor phase

NOMENCLATURE

C_P° = Heat capacity at constant pressure in ideal gas state, Btu/lb °R
f = Fugacity
H_g = Enthalpy of saturated vapor, Btu/lb
$\Delta H_{P,T}$ = Enthalpy at P,T above the saturated liquid state at P_0,T_0, Btu/lb
ΔH_T° = Change of ideal state enthalpy from T_0 to T, Btu/lb
$(\Delta H_v)_{T_0}$ = Heat of vaporization at the reference temperature T_0, 177.924 Btu/lb
H_x = Enthalpy of the vapor-liquid mixture, Btu/lb
J = Dimensional constant for cyclopropane, 0.004400354 (Btu/lb)(ft^3/lb-mol)$^{-1}$ (psia)$^{-1}$
P = Pressure, psia
P_0 = Reference pressure, 87.787 psia
R = Cyclopropane gas constant, 0.25502 (psi) (ft^3)/(°R) (lb), 0.047222 (Btu)/(°R) (lb)
S_g = Entropy of the saturated vapor, Btu/lb °R
$\Delta S_{P,T}$ = Entropy at P,T above the saturated liquid state at P_0,T_0, Btu/lb °R
ΔS_T° = Change of ideal state entropy from T_0 to T, Btu/lb °R
$(\Delta S_v)_{T_0}$ = Entropy of vaporization at the reference temperature T_0, 0.3389 Btu/lb °R
S_x = Entropy of vapor-liquid mixture, Btu/lb °R
T = Temperature, °R
T_0 = Reference temperature, 525°R
V = Specific volume, ft^3/lb
x = Quality of the vapor-liquid mixture, lb vapor/lb of mixture
γ = Volume residual, $\frac{RT}{P} - V$, ft^3/lb
ν = Fugacity coefficient, f/P

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Estimation of Heats of Formation of Binary Oxides

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Calculation of gas solid reaction equilibria requires a variety of thermodynamic data. When the available data on a solid compound are incomplete, well-known methods can be used to estimate absolute entropies or heat capacities (*18*). The remaining information needed is the standard enthalpy of formation from the elements at 298.15°K, ΔH_f°. The present investigation reports a method for estimating ΔH_f° for compounds formed from two oxides, such as $CaSO_4$ (from CaO and SO_3) or $Na_2Al_2O_4$ (from Na_2O and Al_2O_3).

This problem of estimating ΔH_f° arose during a study of processes for removing sulfur oxides from flue gas, using dry

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A method suggested previously by Erdös (CA, 57, 9297e, 1962) was modified and applied to estimation of ΔH_f° of sulfates, carbonates, sulfites, ferrites, chromates, vanadates, titanates, tungstates, molybdates, and aluminates. Standard heats of reaction of the pair of oxides which make up the compound are predicted from a term, $(K_i - A_j)^{n_j}$, where K_i is a cation parameter and A_j and n_j are anion parameters. Adding ΔH_f° for the two oxides to this heat of reaction gives ΔH_f° for the compound. A set of 92 literature values of ΔH_f° was used to determine 30 values of K_i and 10 values of A_j and n_j. Comparison of measured and calculated values showed RMS Errors (kcal/mol anion) of ±1.3 for sulfates, ±3.2 for carbonates, ±2.5 for sulfites, and ±4.1 for the seven types of metal-metal oxides.

metal oxide sorbents. For example, a divalent oxide might sorb SO_2 by forming sulfite:

$$\mathrm{MeO} + \mathrm{SO_2} \rightarrow \mathrm{MeSO_3} \quad (1)$$

An attractive possibility would be to develop a sorbent which could be thermally regenerated to yield a salable by-product. In terms of the above reaction, the thermodynamic requirement is to find an oxide for which the reaction can be reversed by a moderate alteration in temperature or other conditions. Quantitative specification of this equilibrium requires, among other things, data on ΔH_f° of all compounds involved.

The possible reactions between a metal oxide and a typical flue gas can involve sulfate and carbonate formation as well as sulfite formation. Further, there is no reason to restrict the choice of sorbents to single metal oxides. A wide variety of binary metal oxide systems exists; some of these involve well-defined stoichiometric compounds, such as $Na_2Al_2O_4$. Evaluation of the reaction equilibria for these compounds again requires ΔH_f° data.

The objective of the present study was to develop a method for predicting ΔH_f° for binary oxides, including both metal–nonmetal oxides, such as carbonates, sulfates, and sulfites, and metal–metal oxides.

ESTIMATION METHODS

Several general methods have been developed for estimating ΔH_f° of inorganic compounds. In these methods, parameters are assigned to each atom or ion in the compound, and ΔH_f° is expressed as a function of these parameters. The parameters are then determined by regression analysis using known values of ΔH_f°.

The simplest method is due to Pauling (*32*) who assigned electronegativities, X_i, to each element i. The heat of formation of compound $\alpha\beta$ from elements α and β is then expressed by an equation of the form

$$-\Delta H_f^\circ{,}\alpha\beta = (X_\alpha - X_\beta)^2 \quad (2)$$

Anderson and Bromley (*2*) modified Pauling's expression by adding a contribution, Y_i, for each atom (or ion) in the compound:

$$-\Delta H_f^\circ{,}\alpha\beta = (X_\alpha - X_\beta)^2 + Y_\alpha + Y_\beta \quad (3)$$

This equation was used to correlate heats of formation of metal halides, with an average deviation from reported values of 0.9 kcal, and a maximum deviation of 10 kcal.

Wilcox and Bromley (*43*) further extended this method by using a third parameter, W_i:

$$-\Delta H_f^\circ{,}\alpha\beta = (X_\alpha - X_\beta)^2 + Y_\alpha + Y_\beta + (W_\alpha/W_\beta) \quad (4)$$

These authors applied this equation to a very wide range of compounds including, for example, halides, silicates, bisulfates, and amides. For the various classes of compounds, average deviations ranged from 0.5 to 3.9 kcal/mol, and maximum deviations were 1.0 to 10.2 kcal/mol. Some difficulty was experienced by these authors in obtaining a unique set of parameters, although consistent values of ΔH_f° were obtained. This suggests that further improvement would require a change in the basic form of the equation rather than an addition of further terms.

Erdös (*7*) correlated heats of formation of carbonates and sulfates using Equation 5:

$$-\Delta H_{R,\alpha\beta}^\circ = (K_\alpha - A_\beta)^c \quad (5)$$

An important distinction of this approach is that the reference states are not the elements, but compounds. For example $\Delta H_{R,\mathrm{CaSO_3}}^\circ$ is the standard heat of reaction of CaO and SO_2. The standard heat of formation of the compound from the elements is then obtained by adding to ΔH_R° the standard heats of formation of the two oxides. These latter values are known for nearly all oxides. Another interesting feature of Erdös' work is the use of an empirical exponent, c, instead of the quadratic form originated by Pauling. By using data on 17 sulfates and 17 carbonates, Erdös found that the best value of c was 5/3. This gave an average deviation of 1.5 kcal/mol and a maximum of 3.9 kcal/mol. Parameters were determined for 14 additional metal cations from sulfate data, and the unknown heats of formation of 30 sulfites were predicted from these parameters plus a single known value for Na_2SO_3.

When the last two methods are compared, that of Wilcox and Bromley is an extension of Pauling's original form and uses three parameters per atom or ion. The method is quite general and can be applied to most any type of compound. In contrast, the Erdös method uses a new form of equation which requires only one parameter per atom or ion. However, this method is restricted to binary oxides.

After comparison of the number of parameters required and the deviations obtained, the Erdös method was chosen for the present problem. The work presented here differs from Erdös' work in two respects. First, the exponent in Equation 5 was allowed to vary, thus increasing the number of parameters. Second, the method was evaluated for 10 different types of binary oxides, rather than just sulfates and carbonates.

LITERATURE SURVEY

A literature survey was performed to locate all available values for oxides, carbonates, sulfates, sulfites, and binary metal–metal oxides. In addition to the standard compilations (*12, 18, 19, 38*) *Chemical Abstracts* was covered through 1967. When uncertain or conflicting values were found, the original literature was examined, and often the conflicts were resolved. When wide differences between reported values could not be explained, the values were not used in the correlation.

Heats of formation of 38 single oxides are listed in Table I. In addition to these, heats of formation of 29 sulfates, 18 carbonates, and 10 sulfites were found. Among binary metal oxides, data were found for 6 ferrites, 4 chromates, 3 vanadates,

Table I. Heats of Formation of Oxides

Oxide	$-\Delta H_f°$, kcal/mol[a]	Oxide	$-\Delta H_f°$, kcal/mol[a]
Ag_2O	7.30	Na_2O	102.87
Al_2O_3	400.16	NiO	57.26
BaO	132.10	PbO	52.37
BeO	143.03	Rb_2O	78.84
Bi_2O_3	138.08	Sb_2O_3	169.40
CaO	151.73	SnO_2	138.75
CdO	61.18	SrO	140.74
CeO_2	232.93	ThO_2	294.09
CoO	57.07	UO_2	258.97
Cs_2O	75.85	ZnO	83.38
Cu_2O	40.78	ZrO_2	261.36
CuO	39.49[b]	$CO_2(g)$	94.01
FeO	63.76	$SO_2(g)$	70.93
Fe_2O_3	196.42	$SO_3(g)$	94.41
K_2O	86.36	CrO_3	142.03
Li_2O	142.50	MoO_3	177.88
MgO	143.63	TiO_2	225.50
MnO	91.93	$_2VO_5$	372.68
Mn_2O_3	229.11	WO_3	201.46

[a] All values from Landolt-Börnstein (*19*), except BaO (*8*), Sb_2O_3 (*24*), and WO_3 (*12*). [b] It was later found that this value from Landolt-Börnstein (*19*) is evidently in error, as the original source (*3*) gives 37.5. Rossini et al. (*38*) give 37.1.

4 titanates, 7 tungstates, 3 molybdates, and 8 aluminates. The computational problem was then to use these 92 known compound values to generate parameters for 30 cations and 10 anions; that is, for a set of 300 possible compounds.

CALCULATION METHOD

Equation 5 can be written in a more general form as follows:

$$\Delta H_{R,ij}° = -b_{ij}(K_i - A_j)^{n_j} \qquad (6)$$

This is the standard heat of reaction of a_{ij} moles of oxide i with b_{ij} moles of oxide j. The standard heat of formation of compound ij is then,

$$\Delta H_{f,ij}° = a_{ij}\Delta H_{f,i}° + b_{ij}\Delta H_{f,j}° + \Delta H_{R,ij}° \qquad (7)$$

Oxide i can be regarded as the basic oxide. It loses b_{ij} oxide (O^{2-}) anions to acidic oxide j. Parameter K_i represents the base strength of oxide i or, alternatively, the stability of the resulting cation, which is also indexed i. Parameter A_j represents the acid strength of oxide j; $-A_j$ can also be regarded as the stability parameter of the polyoxygenated anion of the final compound. The exponent n_j is taken to be a characteristic of the anion of the compound, rather than being constant for all types of compounds. For example, if the compound is $Fe_2(SO_4)_3$, a_{ij} is 1 and b_{ij} is 3; K_i is the stability parameter of Fe^{3+}, and $-A_j$ is the stability parameter of SO_4^{2-}. The exponent n_j is a characteristic parameter of sulfates.

It is necessary to set an arbitrary zero point for either the K_i or the A_j scale. For this purpose, carbonates were indexed A_1, and A_1 was set equal to zero. For example, $-A_{SO_4^{2-}}$ represents the stability of SO_4^{2-} relative to CO_3^{2-} and values of K_i represent stabilities of carbonates containing different cations, i. However, all the available data, rather than just carbonate data, were used to determine K_i, as described next.

The best values of K_i, A_j, and n_j can be determined by a least-squares method. Basic required data are a set of $\Delta H_{f,i}°$ for I basic oxides and a set of $\Delta H_{f,j}°$ for J acidic oxides. There are then IJ possible compounds, and $I + 2J - 1$ parameters to be found. Values of $\Delta H_{f,ij}°$ are known for a portion of these compounds, and Equation 7 is then used to obtain the incomplete set of experimental values of $\Delta H_{R,ij}°/b_{ij}$.

The sum of the squares of the differences between experimental and calculated values is

$$E^2 = \sum_i \sum_j E_{ij}^2 = \sum_i \sum_j [\Delta H_{R,ij}°/b_{ij} + (K_i - A_j)^{n_j}]^2 \qquad (8)$$

where the summations are performed for all compounds for which experimental values are known. The best values of the parameters are found by minimizing E^2. This form minimizes the error per mole of O^{2-} transferred from the basic to the acidic oxide. Since all the anions in the compounds considered are divalent, it also minimizes the error per mole of anion. Taking the partial derivatives gives:

$$\frac{\partial E^2}{\partial K_i} = 2 \sum_j [\Delta H_{R,ij}°/b_{ij} + (K_i - A_j)^{n_j}]n_j \times$$
$$(K_i - A_j)^{n_j - 1} = 0;\ i = 1 \text{ to } I \qquad (9)$$

$$\frac{\partial E^2}{\partial A_j} = -2 \sum_i [\Delta H_{R,ij}°/b_{ij} + (K_i - A_j)^{n_j}]n_j \times$$
$$(K_i - A_j)^{n_j - 1} = 0;\ j = 2 \text{ to } J \qquad (10)$$

$$\frac{\partial E^2}{\partial n_j} = 2 \sum [\Delta H_{R,ij}°/b_{ij} + (K_i - A_j)^{n_j}] \times$$
$$(K_i - A_j)^{n_j} \ln (K_i - A_j) = 0;\ j = 1 \text{ to } J \qquad (11)$$

This is the required set of $I + 2J - 1$ equations which determines the unknown parameters.

The solution was obtained by a steepest descent technique. If we call the set of unknowns X_k, the condition for a minimum is,

$$\partial E^2/\partial X_1 = \partial E^2/\partial X_2 = \ldots \partial E^2/\partial X_k = 0 \qquad (12)$$

This condition can be put in a positive definite form by defining the function, ϕ:

$$\phi \equiv \sum_k (\partial E^2/\partial X_k)^2 \qquad (13)$$

If ϕ is zero then each partial derivative must individually be zero. The minimum of E^2 is thus found from the condition, $\phi = 0$.

An initial estimate for K_i, A_j, and n_j was made and the estimate corrected with a modified Newton–Raphson technique based on the gradient. If the mth corrected value of the initial guess was ϕ^m, the $m + 1$ corrected value is given by Equation 14:

$$\phi^{m+1} = \phi^m + \Delta\phi^m \qquad (14)$$

Equation 15 describes $\Delta\phi^m$:

$$\Delta\phi^m = \sum_k \Delta X_k^m(\partial\phi/\partial X_k) = \Delta\vec{X}^m \cdot \nabla\phi^m \qquad (15)$$

The method requires that the correction vector $\Delta\vec{\mathbf{X}}^m$ have that direction causing the steepest descent of ϕ^m; that is, the direction of $\nabla\phi^m$. Equation 14 may be rewritten for the individual components $X(A, K, \text{and } n)$ using vector relationships as shown in Equation 16:

$$\mathbf{X}_i^{m+1} = \mathbf{X}_i^m - (\phi^m/|\nabla\phi|^2)(\partial\phi^m/\partial\mathbf{X}_i) \qquad (16)$$

In practice it was found that the scale of variation for K_i and A_j was markedly different from that for n_j. Convergence of the iteration process was therefore obtained by holding the n_j's constant and iterating the K_i's and A_j's and then holding the K_i's and A_j's constant and iterating the n_j's. By using this procedure, a unique set of parameters was obtained.

RESULTS AND DISCUSSION

Parameters estimated as described above are given in Tables II and III. The units of K_i and A_j are such that predicted values of $\Delta H_R°$ are in kcal/mol.

Table II. Cation Parameters

Cation	K_i	No. of exptl values in group i
Ag^+	8.97	6
Al^{3+}	4.37	1
Ba^{2+}	18.18	5
Be^{2+}	4.93	1
Bi^{3+}	7.75	1
Ca^{2+}	13.10	5
Cd^{2+}	8.53	3
Ce^{4+}	9.05	1
Co^{2+}	8.95	3
Cs^+	25.31	2
Cu^+	4.08	1
Cu^{2+}	4.53	3
Fe^{2+}	8.25	3
Fe^{3+}	4.29	1
K^+	23.73	3
Li^+	15.39	5
Mg^{2+}	8.68	8
Mn^{2+}	9.10	5
Mn^{3+}	5.47	1
Na^+	19.97	8
Ni^{2+}	7.46	6
Pb^{2+}	9.34	5
Rb^+	24.60	2
Sb^{3+}	3.24	1
Sn^{4+}	1.41	1
Sr^{2+}	15.74	5
Th^{4+}	7.73	1
U^{4+}	6.79	1
Zn^{2+}	6.56	3
Zr^{4+}	9.87	1
		Total 92

Table III. Anion Parameters

Anion	A_j	n_j	No. of exptl values in group j
SO_4^{2-}	−9.77	1.45	29
CO_3^{2-}	0.00	1.43	18
SO_3^{2-}	−2.60	1.44	10
$Fe_2O_4^{2-}$	7.45	1.39	6
CrO_4^{2-}	0.13	1.43	4
$V_2O_6^{2-}$	1.55	1.47	3
TiO_3^{2-}	5.13	1.40	4
WO_4^{2-}	0.87	1.48	7
MoO_4^{2-}	−2.87	1.38	3
$Al_2O_4^{2-}$	5.24	1.38	8
			Total 92

The majority of values of $K_i - A_j$ are positive, corresponding to an exothermic reaction between the two oxides. For a few of the binary metal oxides, negative values of $K_i - A_j$ can be found. In predicting values for these cases, the absolute value of $K_i - A_j$ should be used and the sign of $\Delta H_R°$ should be reversed, corresponding to an endothermic reaction. The worst case of this type is formation of the hypothetical compound $Sn(Fe_2O_4)_2$, for which the reaction is predicted to be endothermic by 12.2 kcal/mol of Fe_2O_3. It is expected that the compound $Fe_2(SnO_3)_3$ would instead be formed in an exothermic reaction, but the available data on stannates are not sufficient to test this possibility. All the experimental values of $\Delta H_R°$ were negative, and the few predicted positive values are probably devoid of physical meaning.

There are two interesting redundant cases: $Fe_2(Fe_2O_4)_3$, and $Al_2(Al_2O_4)_3$. The actual values of $\Delta H_R°$ should of course be zero, and the calculated values of $|K_i - A_j|^{n_j}$, which are 4.9 and 0.8 kcal/mol, respectively, represent errors in the correlation.

All the experimental values used in determining the parameters are listed, with references, in Table IV which also gives the calculated value and the error. The rms error per mole of anion, which is used as a measure of the uncertainty of the correlation method, is given in Table V. This quantity was calculated for each j by summing E_{ij}^2 over i, dividing by the number of values, and taking the square root of the result. The rms error per mole anion for the sum over all 92 values is ±3.1 kcal/mol.

It is difficult to estimate confidence limits for the present method, since the experimental values contain some uncertainty. The most accurate experimental values are probably the sulfate values. Heats of formation of many of these have been found by solution calorimetry near 25°C. The most direct method is to dissolve the oxide in H_2SO_4 solution; the heat of solution of the sulfate can be determined in a separate experiment. The same method is not so simple for sulfites and carbonates because of the possibility of side reactions such as conversion of sulfite to thiosulfate, or formation of basic carbonates. Hence, these values are less certain than the sulfate values. Considering the uncertainties in all the necessary values in the thermodynamic cycles used, the authors believe that the rms uncertainty per mole of anion for the sulfate data is about ±0.7 kcal; for sulfites and carbonates it is estimated at about ±1.5 kcal. These numbers are intended to reflect both the uncertainties in the experimental techniques and the fact that the original data arise from many different methods and laboratories and cover a lengthy time span.

Kubaschewski, Evans, and Alcock (*18*) give uncertainty estimates for individual values of $\Delta H_f°$. For sulfates, these range from ±1 to ±5 kcal/mol sulfate and average about ±3 kcal/mol sulfate. These limits are considerably broader than the authors' above estimate. It is unfortunate that too few completely independent measurements have been reported to allow a reliable statistical estimate of the uncertainty in the reported values of $\Delta H_f°$.

The rms error for the calculated values turns out to be about twice the present estimates of the rms error in the data. The individual deviations appear to be randomly distributed. In particular, the maximum error in each class of compound is two to three times the rms error. This is reasonable since, in 20 estimates, each subject to random rms error R, one would expect about one value with error $2R$.

For the binary metal–metal oxides the rms uncertainty in the data should be considerably larger, probably about ±4 kcal/mol. Values for these compounds often involve high-temperature equilibrium measurements and multistep thermodynamic cycles. The rms error in the calculated values is here about the

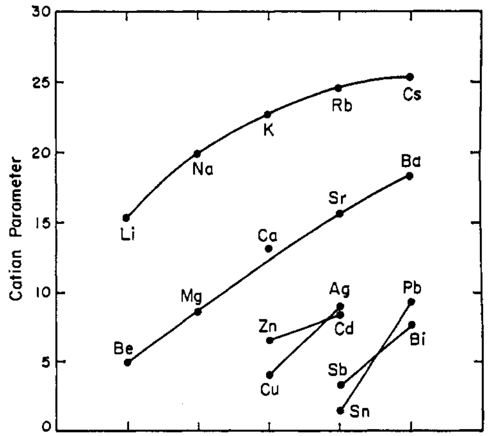

Figure 1. Cation parameter vs. periodic row

Table IV. Calculated and Experimental Heats of Formation

Compd	$-\Delta H_f°$, kcal/mol		Error, per mole anion	Ref
	Calcd	Exptl		
Ag_2SO_4	170.8	170.4	0.4	*19*
$Al_2(SO_4)_3$	821.4	820.4	0.3	*19*
$BaSO_4$	349.6	350.0	−0.4	*19*
$BeSO_4$	286.1	285.7	0.4	*38*
$Bi_2(SO_4)_3$	609.3	608.1	0.4	*41*
$CaSO_4$	338.2	340.2	−2.0	*19*
$CdSO_4$	222.4	221.2	1.2	*19*
$Ce(SO_4)_2$	560.8	560.0	0.4	*38*
Cs_2SO_4	341.2	339.0	2.2	*19*
Cu_2SO_4	179.8	179.5	0.3	*19*
$CuSO_4$	180.6	184.2	−3.6	*19*
$FeSO_4$	223.5	220.4	3.1	*19*
$Fe_2(SO_4)_3$	616.5	615.6	0.3	*4*
K_2SO_4	340.7	342.3	−1.6	*19*
Li_2SO_4	342.7	342.6	0.1	*19*
$MgSO_4$	305.6	305.5	0.1	*12*
$MnSO_4$	256.1	254.0	2.1	*19*
$Mn_2(SO_4)_3$	666.2	666.9	−0.2	*38*
Na_2SO_4	331.9	330.6	1.3	*19*
$NiSO_4$	212.9	213.5	−0.6	*19*
$PbSO_4$	217.9	219.3	−1.4	*19*
Rb_2SO_4	339.2	340.2	−1.0	*19*
$Sb_2(SO_4)_3$	575.4	574.2	0.4	*41*
$Sn(SO_4)_2$	393.1	393.4	−0.2	*38*
$SrSO_4$	343.0	345.0	−2.0	*19*
$Th(SO_4)_2$	608.1	607.3	0.4	*27*
$U(SO_4)_2$	563.4	563.0	0.2	*38*
$ZnSO_4$	234.4	233.7	0.7	*19*
$Zr(SO_4)_2$	598.0	597.0	0.5	*19*
Ag_2CO_3	124.0	120.9	3.1	*19*
$BaCO_3$	290.1	287.2	2.9	*19*
$CaCO_3$	284.6	288.1	−3.5	*19*
$CdCO_3$	176.5	178.5	−2.0	*19*
$CoCO_3$	176.3	173.3	3.0	*13*
Cs_2CO_3	272.6	274.2	−1.6	*42*
$CuCO_3$	140.0	142.1	−2.1	*19*
$FeCO_3$	178.0	178.6	−0.6	*19*
K_2CO_3	273.8	271.9	1.9	*19*
Li_2CO_3	287.4	290.3	−2.9	*19*
$MgCO_3$	259.5	264.0	−4.5	*19*
$MnCO_3$	207.2	213.7	−6.5	*19*
Na_2CO_3	270.4	269.7	0.7	*19*
$NiCO_3$	164.7	163.0	1.7	*19*
$PbCO_3$	171.3	167.2	4.1	*19*
Rb_2CO_3	271.4	269.5	1.9	*19*
$SrCO_3$	286.6	291.0	−4.4	*19*
$ZnCO_3$	197.5	193.7	3.8	*19*
Ag_2SO_3	112.1	114.4	−2.3	*39*
$BaSO_3$	281.5	282.6	−1.1	*38*
$CaSO_3$	275.1	275.9	−0.8	*25*
$CdSO_3$	164.1	163.9	0.2	*40*
K_2SO_3	267.6	266.9	0.7	*38*
Li_2SO_3	277.3	279.4	−2.1	*40*
$MgSO_3$	247.2	241.0	6.2	*38*
Na_2SO_3	262.2	260.4	1.8	*19*
$PbSO_3$	158.7	157.0	1.7	*39*
$SrSO_3$	277.2	279.4	−2.2	*39*
$BaFe_2O_4$	355.6	350.5	5.1	*26*
$CuFe_2O_4$	231.5	237.5	−6.0	*34*
$Li_2Fe_2O_4$	356.7	347.4	9.3	*18*
$MgFe_2O_4$	341.4	349.2	−7.8	*35*
$MnFe_2O_4$	290.4	293.0	−2.6	*9*
$NiFe_2O_4$	253.7	256.5	−2.8	*44*
Ag_2CrO_4	171.8	172.4	−0.6	*17*
$CaCrO_4$	332.6	329.4	3.2	*19*
Na_2CrO_4	316.2	318.6	−2.4	*28*
$PbCrO_4$	218.2	217.5	0.7	*19*
CaV_2O_6	561.0	558.7	2.3	*14*
MgV_2O_6	534.3	527.9	6.4	*14*
$Na_2V_2O_6$	548.3	552.9	−4.6	*15*
$CoTiO_3$	289.1	289.5	−0.4	*30*
$MgTiO_3$	375.0	371.5	3.5	*5*
$NiTiO_3$	286.0	287.8	−1.8	*10, 30*
$ZnTiO_3$	310.5	309.3	1.2	*31*
Ag_2WO_4	230.9	230.7	0.2	*11*
$BaWO_4$	401.8	406.1	−4.3	*22*
$MgWO_4$	366.1	373.4	−7.3	*37*
$MnWO_4$	316.1	312.6	3.5	*33*
Na_2WO_4	383.3	382.6	0.7	*16*
$NiWO_4$	275.0	271.6	3.4	*33*
$SrWO_4$	396.7	392.7	4.0	*23*
Ag_2MoO_4	215.5	216.6	−1.1	*17*
Na_2MoO_4	355.8	354.1	1.7	*16*
$PbMoO_4$	261.9	265.7	−3.8	*19*
$CoAl_2O_4$	463.4	466.5	−3.1	*30*
$FeAl_2O_4$	468.5	474.4	−5.9	*29, 36*
$Li_2Al_2O_4$	567.3	568.6	−1.3	*19*
$MgAl_2O_4$	549.3	551.0	−1.7	*1*
$MnAl_2O_4$	498.6	501.1	−2.5	*20*
$Na_2Al_2O_4$	544.2	541.3	2.9	*19*
$NiAl_2O_4$	460.4	463.3	−2.9	*21*
$SrAl_2O_4$	566.7	559.8	6.9	*6*

Table V. Summary of Errors

Class of compd	No. of values	Rms error, kcal/mol	Max error, kcal/mol
Sulfate	29	±1.3	−3.6
Carbonate	18	±3.2	−6.5
Sulfite	10	±2.5	+6.2
Metal-Metal Oxide	35	±4.1	+9.3
	All 92	±3.1	+9.3

same as our estimate of the uncertainty in the data. Again, the maximum error of 9.3 kcal/mol is between two and three times the rms value.

It is interesting to note that the K_i parameters show a regular progression with position in the periodic table, as illustrated in Figure 1. The A_j values show anion stabilities in the order,

$$SO_4^{2-} > MoO_4^{2-} > SO_3^{2-} > CO_3^{2-} > CrO_4^{2-} > WO_4^{2-} > V_2O_6^{2-} > TiO_3^{2-} > Al_2O_4^{2-} > Fe_2O_4^{2-}$$

Table VI. Comparison of Average and Maximum Error[a]

Anion	Wilcox and Bromley (*43*)			Erdös (*7*)			This study		
	No. of compd	Av error	Max error	No. of compd	Av error	Max error	No. of compd	Av error	Max error
SO_4^{2-}	25	2.0	6.1	17	1.5	3.9	29	1.0	3.6
CO_3^{2-}	17	1.2	3.5	17	1.6	3.9	18	2.8	6.5
SO_3^{2-}	5	1.7	2.8	...	...	...	10	1.9	6.2
WO_4^{2-}	14	1.9	4.7	...	...	...	7	3.3	7.3

[a] Average and maximum of the absolute value of difference between experimental and calculated values of $\Delta H_f°$ (kcal/mol).

It is especially interesting that molybdate falls so high in the series.

Finally the n_j values are remarkably close, covering a range of only 0.10, with a mean of 1.43. The constancy of n_j is in accord with the findings of Erdös (*7*) although our mean value of 1.43 is significantly different from his value of 1.67.

Table VI compares error values obtained in this study with those of two previous ones (*7*, *43*). Since rms values were not available for comparison, average and maximum values were used. The present study appears to be more successful for sulfates, but less successful for the other types of compounds, than the other two investigations. It is difficult, however, to draw conclusions from the comparison, since each study used a different set of data as well as a different correlating equation.

In conclusion, correlation parameters for 30 cations and 10 anions have been derived for use in estimating heats of formation of binary oxides. Concerning the accuracy of the method, the authors suggest that an estimated value should be subject to about twice the uncertainty of a typical experimental value for a similar compound. Further, it appears that the errors in the present estimation method are randomly distributed, and hence that occasional large errors are possible. Unknown heats of formation of 206 compounds can be predicted using the information in Tables I, II, and III, and Equations 6 and 7.

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