

Registry No. *N*-Methylmethanesulfinamide, 18649-17-7; *N,N*-dimethylmethanesulfinamide, 920-56-9; 1,4-dioxane, 123-91-1.

Literature Cited

- Ruostesuo, P.; Mattila, T. *Thermochim. Acta* **1966**, *104*, 153-158.
- Ruostesuo, P. *Acta Univ. Ouluensis, Ser. A* **1976**, *66*, Chem. 6.
- Ruostesuo, P.; Mattila, T.; Kurkisu, S.; Salmiinen, U., unpublished results.
- Ruostesuo, P.; Karjalainen, J. *Spectrochim. Acta, Part A* **1981**, *37*, 535-539.
- Häkkinen, A.-M.; Ruostesuo, P.; Kurkisu, S. *Magn. Reson. Chem.* **1985**, *23*, 311-314.
- Douglass, I. B.; Norton, R. V. *J. Org. Chem.* **1968**, *33*, 2104-2108.
- Moriarty, R. M. *J. Org. Chem.* **1965**, *30*, 600-603.
- Timmermans, J. *Physico-Chemical Constants of Binary Systems in Concentrated Solutions*; Interscience: New York, 1960; Vol. 4, pp 12, 13.
- Pikkarainen, L. *Acta Univ. Ouluensis, Ser. A* **1980**, *98*, Chem. 10.
- Sannigrahi, A. B.; Chandra, A. K. *J. Phys. Chem.* **1963**, *67*, 1106-1109.
- Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979; p 19.

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Thermochemistry of Inorganic Solids. 5. Empirical Relations among Enthalpies of Formation of Oxides, Carbonates, Sulfates, Hydroxides, and Nitrates

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Examination of the existing data of standard enthalpies of formation of solid metal oxides, carbonates, sulfates, hydroxides, and nitrates reveals the fact that the standard enthalpies of formation of any three compounds for a particular metal oxidation state can be correlated quantitatively by the following two-parameter linear equations: for mono- and divalent compounds, $(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) = 1.36(\Delta H^\circ_{(\text{CO}_3)} - \Delta H^\circ_{(\text{O})}) - 3.2$ kcal/mol (1); for monovalent compounds, $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.463(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 2.3$ kcal/mol (2), and $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.02(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 56.1$ kcal/mol (4); for divalent compounds, $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.318(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) + 22.6$ kcal/mol (3), and $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.025(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 119.6$ kcal/mol (5), where $\Delta H^\circ_{(\text{O})}$, $\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{NO}_3)}$, and $\Delta H^\circ_{(\text{OH})}$ are the standard enthalpies of formation in kcalories per mole of the oxide, sulfate, carbonate, nitrate, and hydroxide of the metal. These equations are recast into linear equations which permit deducing ΔH_f° for monovalent and divalent metal salts from the ΔH_f° of their oxides and any of their other salts. Considering the accuracy involved in the reference compounds, for different compounds of various metals examined the maximum absolute deviation is only 3 kcal/mol.

Introduction

As part of a program to understand the bonding and the kinetic behavior of solid inorganic catalysts, we have been exploring the known thermochemistry of inorganic solids. In the course of this, we have discovered a number of empirical relations which permit us to make estimations of the enthalpies of formation of inorganic salts and their hydrates. No comparable estimation methods now exist for these substances. In

Table I. Standard Enthalpies of Formation ($\Delta H_f^\circ_{298}$) of Solid Metal Oxides, Sulfates, Carbonates, Nitrates, and Hydroxides

metal	valence state	$-\Delta H_f^\circ_{298}$, kcal/mol of metal				
		oxide	sulfate	carbonate	nitrate	hydroxide
Li	1	71.5	171.7	145.3	115.5	115.9
Na	1	49.5	165.8	135.1	111.8	101.7
K	1	43.2	171.8	137.6	118.2	101.5
Rb	1	40.5	171.6	135.8	118.3	99.9
Cs	1	41.3	172.4	136.2	120.9	99.7
Tl	1	21.4	111.4	83.7	58.3	57.1
Ag	1	3.7	85.6	60.4	29.7	
Be	2	145.7	288.0	245.0		215.7
Mg	2	143.4	307.1	261.9	189.0	221.0
Ca	2	151.8	341.0 ^a	288.5	224.3	235.7
Sr	2	141.5	346.9 ^a	291.6	233.8	229.0
Ba	2	132.3	351.3 ^a	290.7	237.1	225.8
Ra	2	125.0	351.6		237.1	
Pb	2	52.1	219.9	167.1	108.0	
Cd	2	61.7	223.1	179.4	109.1	134.0
Mn	2	92.0	254.6	213.7	137.7	166.2
Fe	2	65.0	221.9	177.0		136.0
Co	2	56.9	212.3	170.4	100.5	129.0
Ni	2	57.3	208.6		99.2	126.6
Cu	2	37.6	184.4		72.4	107.5
Zn	2	83.2	234.9	194.3	115.6	153.4

^aAn average values is taken for these compounds where more than one value is reported depending upon the structural types.

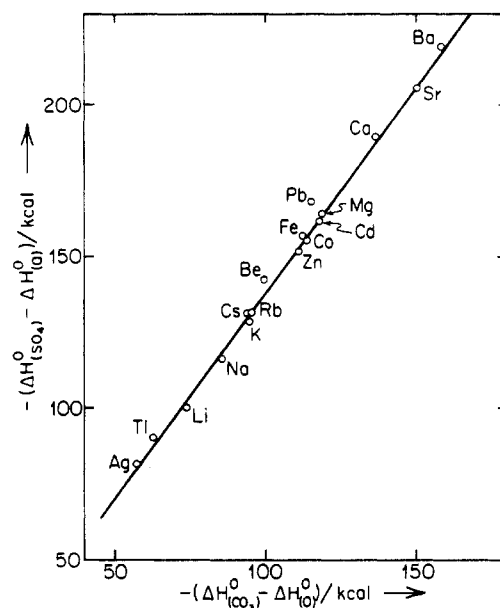
recent papers (1, 2), we have presented evidence that a quantitative relationship exists between the standard enthalpies of formation of the different valence states of solid polyvalent binary metal compounds of the formula MX_z (where X is either metal or nonmetal) and the value of z . We have also shown (3) that for solid metal oxyhalide compounds of different valence states, the standard enthalpies of formation can be related quantitatively to the corresponding halides and oxides of the same oxidation states.

Table II. Differences in $\Delta H_f^{\circ 298}$ Metal Salts and the Corresponding Oxides

metal	valence state	$-(\Delta H^{\circ}_{(\text{SO}_4)} - \Delta H^{\circ}_{(\text{O})})$, kcal/mol	$-(\Delta H^{\circ}_{(\text{CO}_3)} - \Delta H^{\circ}_{(\text{O})})$, kcal/mol	$-(\Delta H^{\circ}_{(\text{NO}_3)} - \Delta H^{\circ}_{(\text{O})})$, kcal/mol	$-(\Delta H^{\circ}_{(\text{OH})} - \Delta H^{\circ}_{(\text{O})})$, kcal/mol
Li	1	100.2	73.8	44.0	44.4
Na	1	116.3	85.6	62.3	52.2
K	1	128.6	94.4	75.0	58.3
Rb	1	131.1	95.3	77.8	59.4
Cs	1	131.1	94.9	79.6	58.4
Tl	1	90.0	62.3	36.9	35.7
Ag	1	81.9	56.7	26.0	
Be	2	142.3	99.3		70.0
Mg	2	163.7	118.6	45.6	77.6
Ca	2	189.2	136.7	72.5	83.9
Sr	2	205.4	150.1	92.3	87.5
Ba	2	219.0	158.4	104.8	93.5
Ra	2	226.6		112.1	
Pb	2	167.8	115.0	55.9	
Cd	2	161.4	117.7	47.4	72.3
Mn	2	162.6	121.7	45.7	74.2
Fe	2	156.9	112.0		71.0
Co	2	155.4	113.5		72.1
Ni	2	151.3		43.6	69.3
Cu	2	146.8		41.9	69.9
Zn	2	151.7	111.1	34.8	70.2

Table III. Equations Involved in the Determination of $\Delta H_f^{\circ 298}$ for Oxides, Sulfates, Carbonates, Nitrates, and Hydroxides

1. Oxide	
a. monovalent	
$\Delta H^{\circ}_{(\text{O})} = -0.862\Delta H^{\circ}_{(\text{SO}_4)} + 1.862\Delta H^{\circ}_{(\text{OH})} - 4.3$	(2 _{m,o})
$\Delta H^{\circ}_{(\text{O})} = 1.831\Delta H^{\circ}_{(\text{OH})} - 0.831\Delta H^{\circ}_{(\text{NO}_3)} + 42.4$	(4 _{m,o})
b. bivalent	
$\Delta H^{\circ}_{(\text{O})} = 1.466\Delta H^{\circ}_{(\text{OH})} - 0.466\Delta H^{\circ}_{(\text{SO}_4)} + 33.1$	(2 _{b,o})
$\Delta H^{\circ}_{(\text{O})} = 1.450\Delta H^{\circ}_{(\text{OH})} - 0.450\Delta H^{\circ}_{(\text{NO}_3)} + 86.6$	(4 _{b,o})
2. Sulfate	
a. monovalent	
$\Delta H^{\circ}_{(\text{SO}_4)} = 1.361\Delta H^{\circ}_{(\text{CO}_3)} - 0.361\Delta H^{\circ}_{(\text{O})} - 3.3$	(2 _{m,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.980\Delta H^{\circ}_{(\text{NO}_3)} + 0.020\Delta H^{\circ}_{(\text{O})} - 55$	(4 _{m,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.036\Delta H^{\circ}_{(\text{OH})} + 0.964\Delta H^{\circ}_{(\text{NO}_3)} - 54.2$	(5 _{m,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.070\Delta H^{\circ}_{(\text{CO}_3)} + 0.930\Delta H^{\circ}_{(\text{NO}_3)} - 52.3$	(6 _{m,s})
b. bivalent	
$\Delta H^{\circ}_{(\text{SO}_4)} = 1.361\Delta H^{\circ}_{(\text{CO}_3)} - 0.361\Delta H^{\circ}_{(\text{O})} - 3.3$	(2 _{b,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.976\Delta H^{\circ}_{(\text{NO}_3)} + 0.024\Delta H^{\circ}_{(\text{O})} - 116.7$	(4 _{b,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.035\Delta H^{\circ}_{(\text{OH})} + 0.965\Delta H^{\circ}_{(\text{NO}_3)} - 114.6$	(5 _{b,s})
$\Delta H^{\circ}_{(\text{SO}_4)} = 0.914\Delta H^{\circ}_{(\text{NO}_3)} + 0.086\Delta H^{\circ}_{(\text{CO}_3)} - 109.7$	(6 _{b,s})
3. Carbonate	
a. monovalent	
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.735\Delta H^{\circ}_{(\text{SO}_4)} + 0.265\Delta H^{\circ}_{(\text{O})} + 2.4$	(2 _{m,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.507\Delta H^{\circ}_{(\text{SO}_4)} + 0.493\Delta H^{\circ}_{(\text{OH})} + 1.3$	(3 _{m,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.276\Delta H^{\circ}_{(\text{O})} + 0.720\Delta H^{\circ}_{(\text{NO}_3)} - 38.0$	(4 _{m,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.488\Delta H^{\circ}_{(\text{NO}_3)} + 0.512\Delta H^{\circ}_{(\text{OH})} - 26.7$	(5 _{m,c})
b. bivalent	
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.735\Delta H^{\circ}_{(\text{SO}_4)} + 0.265\Delta H^{\circ}_{(\text{O})} + 2.4$	(2 _{b,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.389\Delta H^{\circ}_{(\text{OH})} + 0.611\Delta H^{\circ}_{(\text{SO}_4)} + 11.2$	(3 _{b,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.717\Delta H^{\circ}_{(\text{NO}_3)} + 0.283\Delta H^{\circ}_{(\text{O})} - 83.3$	(4 _{b,c})
$\Delta H^{\circ}_{(\text{CO}_3)} = 0.409\Delta H^{\circ}_{(\text{OH})} + 0.591\Delta H^{\circ}_{(\text{NO}_3)} - 58.7$	(5 _{b,c})
4. Nitrate	
a. monovalent	
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.020\Delta H^{\circ}_{(\text{SO}_4)} - 0.02\Delta H^{\circ}_{(\text{O})} + 56.1$	(2 _{m,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.388\Delta H^{\circ}_{(\text{CO}_3)} - 0.388\Delta H^{\circ}_{(\text{O})} + 52.8$	(3 _{m,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.037\Delta H^{\circ}_{(\text{SO}_4)} - 0.037\Delta H^{\circ}_{(\text{OH})} + 56.2$	(4 _{m,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.075\Delta H^{\circ}_{(\text{SO}_4)} - 0.075\Delta H^{\circ}_{(\text{CO}_3)} + 56.2$	(6 _{m,n})
b. bivalent	
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.025\Delta H^{\circ}_{(\text{SO}_4)} - 0.025\Delta H^{\circ}_{(\text{O})} + 119.6$	(2 _{b,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.395\Delta H^{\circ}_{(\text{CO}_3)} - 0.395\Delta H^{\circ}_{(\text{O})} + 116.2$	(3 _{b,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.037\Delta H^{\circ}_{(\text{SO}_4)} - 0.037\Delta H^{\circ}_{(\text{OH})} + 118.8$	(4 _{b,n})
$\Delta H^{\circ}_{(\text{NO}_3)} = 1.094\Delta H^{\circ}_{(\text{SO}_4)} - 0.094\Delta H^{\circ}_{(\text{CO}_3)} + 120.0$	(6 _{b,n})
5. Hydroxide	
a. monovalent	
$\Delta H^{\circ}_{(\text{OH})} = 0.630\Delta H^{\circ}_{(\text{CO}_3)} + 0.370\Delta H^{\circ}_{(\text{O})} + 0.8$	(1 _{m,h})
$\Delta H^{\circ}_{(\text{OH})} = 0.463\Delta H^{\circ}_{(\text{SO}_4)} + 0.537\Delta H^{\circ}_{(\text{O})} + 2.3$	(2 _{m,h})
$\Delta H^{\circ}_{(\text{OH})} = 0.546\Delta H^{\circ}_{(\text{OH})} + 0.454\Delta H^{\circ}_{(\text{NO}_3)} - 23.1$	(4 _{m,h})
b. bivalent	
$\Delta H^{\circ}_{(\text{OH})} = 0.433\Delta H^{\circ}_{(\text{CO}_3)} + 0.567\Delta H^{\circ}_{(\text{O})} - 23.7$	(1 _{b,h})
$\Delta H^{\circ}_{(\text{OH})} = 0.318\Delta H^{\circ}_{(\text{SO}_4)} + 0.682\Delta H^{\circ}_{(\text{O})} - 22.6$	(2 _{b,h})
$\Delta H^{\circ}_{(\text{OH})} = 0.690\Delta H^{\circ}_{(\text{O})} + 0.310\Delta H^{\circ}_{(\text{NO}_3)} - 59.7$	(4 _{b,h})

**Figure 1. Relationship between $(\Delta H^{\circ}_{(\text{SO}_4)} - \Delta H^{\circ}_{(\text{O})})$ vs. $(\Delta H^{\circ}_{(\text{CO}_3)} - \Delta H^{\circ}_{(\text{O})})$.**

Examination of the existing data on the standard enthalpies of formation, ΔH_f° , of solid metal oxides, sulfates, carbonates, hydroxides, and nitrates of various metals reveals the fact that ΔH_f° for any three classes of compounds for the metal in a fixed valence state can be correlated quantitatively by a two-parameter linear equation. Unless otherwise stated, thermochemical data used here are taken from NBS tables (10), and values are given for standard enthalpies of formation $\Delta H_f^{\circ 298}$ per metal atom and at 298 K in kcal/mol.

The existing data on $\Delta H_f^{\circ 298}$ of all the mono- and divalent metal oxides ($\Delta H^{\circ}_{(\text{O})}$), hydroxides ($\Delta H^{\circ}_{(\text{OH})}$), sulfates ($\Delta H^{\circ}_{(\text{SO}_4)}$), carbonates ($\Delta H^{\circ}_{(\text{CO}_3)}$), and nitrates ($\Delta H^{\circ}_{(\text{NO}_3)}$) (where the data for at least three compounds are available for a particular metal) are listed in Table I. The differences in value between the particular compound and the corresponding oxide for each metal in a fixed oxidation state are listed in Table II. Although no relationship is found between the values of individual compounds, the values obtained for differences show a systematic and monotonic relation between the compounds, when compounds are classified according to the corresponding valence states of the metals. When $(\Delta H^{\circ}_{(\text{CO}_3)} - \Delta H^{\circ}_{(\text{O})})$ is plotted

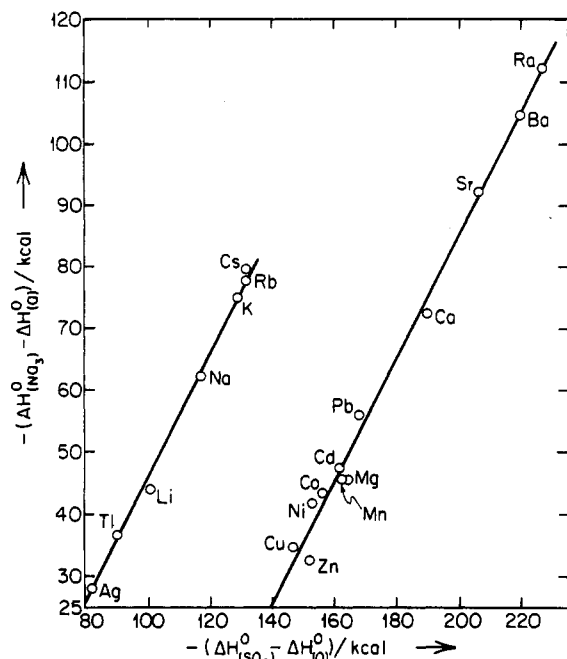


Figure 2. Relationship between $(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})})$ vs. $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})})$.

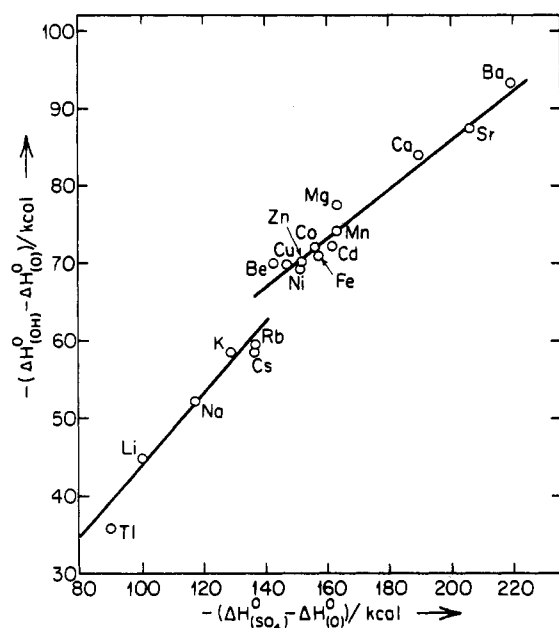


Figure 3. Relationship between $(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})})$ vs. $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})})$.

against $(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})})$ as shown in Figure 1, all the points irrespective of the nature of the metals and the valence states lie close to a straight line represented by eq 1. Similar plots

$$(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) = 1.36(\Delta H^\circ_{(\text{CO}_3)} - \Delta H^\circ_{(\text{O})}) - 3.2 \text{ kcal/mol} \quad (1)$$

are also obtained for nitrates and hydroxides. These are shown in Figures 2 and 3 where $(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})})$ and $(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})})$ are plotted against $(\Delta H^\circ_{(\text{CO}_3)} - \Delta H^\circ_{(\text{O})})$, respectively. However, unlike $\Delta H^\circ_{(\text{CO}_3)} - \Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}$ plots, in these cases mono- and divalent compounds are represented by two separate lines. The lines obtained for $\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{SO}_4)} -$

$\Delta H^\circ_{(\text{O})}$ are almost parallel with a slope of approximately 1. The relations between these compounds can be given by eq 2-5.

$$\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})} \text{ For monovalent compounds} \\ (\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.463(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 2.3 \text{ kcal/mol} \quad (2)$$

For divalent compounds

$$(\Delta H^\circ_{(\text{OH})} - \Delta H^\circ_{(\text{O})}) = 0.318(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) + 22.6 \text{ kcal/mol} \quad (3)$$

$\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}$ For monovalent compounds

$$(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.020(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 56.1 \text{ kcal/mol} \quad (4)$$

For divalent compounds

$$(\Delta H^\circ_{(\text{NO}_3)} - \Delta H^\circ_{(\text{O})}) = 1.025(\Delta H^\circ_{(\text{SO}_4)} - \Delta H^\circ_{(\text{O})}) - 119.6 \text{ kcal/mol} \quad (5)$$

Discussion

The set of eq 1-5 given above can be written in a number of equivalent forms. For example, eq 5 can be rearranged into eq 5_{b,s}, 5_{b,n}, and 5_{b,o}. In principle, we can estimate ΔH°_f for $\Delta H^\circ_{(\text{SO}_4)} = 0.976\Delta H^\circ_{(\text{NO}_3)} + 0.014\Delta H^\circ_{(\text{O})} - 116.7$ (5_{b,s})

$$\Delta H^\circ_{(\text{NO}_3)} = 1.025\Delta H^\circ_{(\text{SO}_4)} - 0.025\Delta H^\circ_{(\text{O})} + 119.6 \quad (5_{b,n})$$

$$\Delta H^\circ_{(\text{O})} = 41.0\Delta H^\circ_{(\text{SO}_4)} - 40.0\Delta H^\circ_{(\text{NO}_3)} + 4784 \quad (5_{b,o})$$

any compound of interest using these equations. However, when coefficients involved in these equations are larger than unity, larger deviations are obtained. This is because all uncertainties involved in the values of reference compounds are correspondingly magnified. According to eq 5_{b,o} even an error of 1 kcal in the reference compounds, $\Delta H^\circ_{(\text{SO}_4)}$ and $\Delta H^\circ_{(\text{NO}_3)}$, may yield deviations as much as 81 kcal in the estimated value of $\Delta H^\circ_{(\text{O})}$. It is thus not recommended to use such equations to try to estimate ΔH°_f for unknown compounds. In Table III, only eq 1-5 whose coefficients involved are smaller than or close to unity are listed. Table IV shows the deviations obtained between the calculated values by using these equations and the reported values for oxides, sulfates, carbonates, nitrates, and hydroxides. When a value is calculated for a particular compound, the observed values reported in the literature are taken for the other two corresponding reference compounds.

Considering the uncertainties involved in the reported values, the small deviations obtained in the bulk of the cases suggest that there is a quantitative relation among the ΔH°_f of these compounds. The equations, given above, where coefficients are smaller than unity, can be used to evaluate the ΔH°_f for compounds whose values are not known. We can now recommend eq 2_{m,c} and 2_{b,c}, 3_{m,c} and 3_{b,c}, 4_{m,c} and 4_{b,c}, and 5_{m,c} and 5_{b,c} for the estimation of $\Delta H^\circ_{(\text{CO}_3)}$, and eq 2_{m,n} and 2_{b,n}, 4_{m,n} and 4_{b,n}, and 6_{m,n} and 6_{b,n} for the estimation of $\Delta H^\circ_{(\text{NO}_3)}$. Estimation of $\Delta H^\circ_{(\text{OH})}$ can be made using eq 1_{m,h} and 1_{b,h}, 2_{m,h} and 2_{b,h}, and 4_{m,h} and 4_{b,h}. For $\Delta H^\circ_{(\text{SO}_4)}$, eq 4_{m,s} and 4_{b,s}, 5_{m,s} and 5_{b,s}, and 6_{m,s} and 6_{b,s} can be used. In all these cases, except for a few compounds, the maximum deviation is only 3 kcal. It is also now possible to use such equations to estimate missing values for compounds such as AgOH, Be(NO₃), RaCO₃, etc., given in Table I, and the estimated values from these equations for such compounds are listed in Table V. The results are consistent for various equations used. However, since we have found other independent methods for estimating ΔH°_f for some of the compounds listed here, a more detailed evaluation will be presented later.

Table IV. Deviations between Calculated and Reported Values

A. For Oxides									
deviation (calcd - obsd), kcal/mol					deviation (calcd - obsd), kcal/mol				
M	from		from		M	from		from	
	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$	$\Delta H^\circ_{(\text{NO}_3)}$		$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$	$\Delta H^\circ_{(\text{NO}_3)}$
	(eq 2 _{m,o} , 2 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})		(eq 2 _{m,o} , 2 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})	(eq 4 _{m,o} , 4 _{b,o})
Li	-0.6			-2.3	Ba	-1.9			-1.8
Na	-1.2			-1.4	Ra				
K	-2.0			-2.0	Pd				
Rb	-1.9			-1.7	Cd	2.3			3.1
Cs	0			1.6	Mn	0.1			-0.4
Tl	6.9			7.7	Fe	2.1			
Ag					Co	-0.2			1.7
Be	-3.2				Ni	2.0			5.0
Mg	-4.4			-5.4	Cu	-1.0			0.9
Cu	-1.7			-2.4	Zn	0.9			-0.6
Sr	0.5			-1.3					

B. For Sulfates									
deviation (calcd - obsd), kcal/mol					deviation (calcd - obsd), kcal/mol				
M	from		from		M	from		from	
	$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{NO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$	$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{NO}_3)}$		$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{NO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$	$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{NO}_3)}$
	(eq 2 _{m,s} , 2 _{b,s})	(eq 4 _{m,s} , 4 _{b,s})	(eq 5 _{m,s} , 5 _{b,s})	(eq 6 _{m,s} , 6 _{b,s})		(eq 2 _{m,s} , 2 _{b,s})	(eq 4 _{m,s} , 4 _{b,s})	(eq 5 _{m,s} , 5 _{b,s})	(eq 6 _{m,s} , 6 _{b,s})
Li	-3.5	2.1	2.0	1.8	Ba	0.1	0	0	-0.1
Na	-3.5	0.3	0.2	0.1	Ra		0.5		
K	-3.1	0.1	0	-0.1	Pb	8.0			-2.9
Rb	-1.9	-0.1	-0.2	-0.2	Cd	-2.1	-1.6	-1.5	-1.7
Cs	-1.4	-1.9	-2.0	-1.9	Mn	-6.3	1.3	1.3	0.7
Tl	1.9	-1.2	-1.1	-1.0	Fe	1.2			
Ag	1.4	1.4		1.5	Co	-2.4	-3.9	-3.8	-3.9
Be	3.9				Ni		-6.3	-6.2	
Mg	-0.9	2.5	2.4	2.1	Cu		-3.9	-3.8	
Ca	-0.1	1.7	1.7	1.5	Zn	-2.8	3.4	3.4	2.8
Sr	-2.2	-1.4	-1.3	-1.6					

C. For Carbonates									
deviation (calcd - obsd), kcal/mol					deviation (calcd - obsd), kcal/mol				
M	from		from		M	from		from	
	$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{NO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$		$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{NO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{NO}_3)}$
	(eq 2 _{m,c} , 2 _{b,c})	(eq 3 _{m,c} , 3 _{b,c})	(eq 4 _{m,c} , 4 _{b,c})	(eq 5 _{m,c} , 5 _{b,c})		(eq 2 _{m,c} , 2 _{b,c})	(eq 3 _{m,c} , 3 _{b,c})	(eq 4 _{m,c} , 4 _{b,c})	(eq 5 _{m,c} , 5 _{b,c})
Li	2.6	2.4	4.2	2.9	Ba	0.6	-0.6	0	-0.5
Na	2.5	3.3	2.8	1.8	Ra				
K	2.3	1.8	3.1	1.3	Pb	-5.9		-8.3	
Rb	1.3	0.8	1.3	0.2	Cd	1.5	2.2	0.4	1.4
Cs	0.9	0.9	-0.4	-0.5	Mn	4.6	4.7	5.6	5.6
Tl	-1.5	0.4	-2.2	-0.6	Fe	-0.9	-0.3		
Ag	-1.1		0		Co	1.7	1.7	-1.1	0.5
Be	-2.8	-3.7			Ni				
Mg	0.6	-0.5	2.5	1.1	Cu				
Ca	0	-0.3	1.4	0.8	Zn	2.0	2.3	4.6	4.5
Sr	1.5	1.8	0.6	1.1					

D. For Nitrates									
deviation (calcd - obsd), kcal/mol					deviation (calcd - obsd), kcal/mol				
M	from		from		M	from		from	
	$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{CO}_3)}$		$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{CO}_3)}$, $\Delta H^\circ_{(\text{O})}$	$\Delta H^\circ_{(\text{OH})}$, $\Delta H^\circ_{(\text{SO}_4)}$	$\Delta H^\circ_{(\text{SO}_4)}$, $\Delta H^\circ_{(\text{CO}_3)}$
	(eq 2 _{m,n} , 2 _{b,n})	(eq 3 _{m,n} , 3 _{b,n})	(eq 4 _{m,n} , 4 _{b,n})	(eq 6 _{m,n} , 6 _{b,n})		(eq 2 _{m,n} , 2 _{b,n})	(eq 3 _{m,n} , 3 _{b,n})	(eq 4 _{m,n} , 4 _{b,n})	(eq 6 _{m,n} , 6 _{b,n})
Li	-2.1	-5.6	-2.1	-2.0	Ba	-0.1	0	0	0.1
Na	-0.2	-3.7	-0.2	-0.1	Ra	-0.6			
K	-0.1	-3.2	0	0	Pb	3.5	11.7		3.1
Rb	0.2	-1.7	0.2	0.2	Cd	1.6	-0.6	1.5	1.9
Cs	2.0	0.7	2.0	2.0	Mn	-1.4	7.9	-1.3	-0.7
Tl	1.2	7.4	1.1	1.0	Fe				
Ag	-4.7	-0.3		-1.6	Co	3.9	1.5	3.9	4.3
Be					Ni	6.4		6.4	
Mg	-2.6	-3.5	-2.5	-2.3	Cu	3.9		4.0	
Ca	-1.8	-2.0	-1.8	-1.6	Zn	-3.5	-6.4	-3.5	-3.1
Sr	1.4	-0.9	1.3	1.7					

Table IV (Continued)

E. For Hydroxides							
M	deviation (calcd - obsd), kcal/mol			M	deviation (calcd - obsd), kcal/mol		
	from	from	from		from	from	from
	$\Delta H_f^\circ(\text{CO}_3)$, $\Delta H_f^\circ(\text{O})$ (eq 1 _{m,h} , 1 _{b,h})	$\Delta H_f^\circ(\text{SO}_4)$, $\Delta H_f^\circ(\text{O})$ (eq 2 _{m,h} , 2 _{b,h})	$\Delta H_f^\circ(\text{O})$, $\Delta H_f^\circ(\text{NO}_3)$ (eq 4 _{m,h} , 4 _{b,h})		$\Delta H_f^\circ(\text{CO}_3)$, $\Delta H_f^\circ(\text{O})$ (eq 1 _{m,h} , 1 _{b,h})	$\Delta H_f^\circ(\text{SO}_4)$, $\Delta H_f^\circ(\text{O})$ (eq 2 _{m,h} , 2 _{b,h})	$\Delta H_f^\circ(\text{O})$, $\Delta H_f^\circ(\text{NO}_3)$ (eq 4 _{m,h} , 4 _{b,h})
Li	-1.3	0.3	1.3	Ba	1.2	1.3	1.3
Na	-0.9	0.7	0.8	Ra			
K	-0.4	1.1	1.1	Pb			
Rb	0.2	1.0	1.0	Cd	-2.4	-1.6	-2.1
Cs	-0.6	0	-0.8	Mn	-2.2	-0.1	0.6
Tl	-2.7	-3.7	-4.2	Fe	-1.2	-1.5	
Ag				Co	-0.7	0.1	-1.1
Be	3.3	2.1		Ni		-1.4	-3.4
Mg	2.6	2.9	3.8	Cu		0.6	-0.6
Ca	1.0	1.1	1.7	Zn	-1.6	-0.6	0.5
Sr	-1.2	-0.4	-0.8				

Table V. Estimated ΔH_f° Values (kcal/mol)

compd	ref compds and (eq used)	ΔH_f° , kcal/mol	
		estimated value	av value
AgOH	$\Delta H_f^\circ(\text{CO}_3)$ and $\Delta H_f^\circ(\text{O})$ (1 _{m,h})	-38.6	
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{m,h})	-39.3	-38.8
	$\Delta H_f^\circ(\text{O})$ and $\Delta H_f^\circ(\text{NO}_3)$ (4 _{m,h})	-38.6	
Be(NO ₃) ₂	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,n})	-172.0	
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{OH})$ (4 _{b,n})	-171.9	-172.0
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{CO}_3)$ (6 _{b,n})	-172.0	
RaCO ₃	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,c})	-289.2	
	$\Delta H_f^\circ(\text{NO}_3)$ and $\Delta H_f^\circ(\text{O})$ (4 _{b,c})	-288.6	-288.9
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,h})	-219.6	
Ra(OH) ₂	$\Delta H_f^\circ(\text{O})$ and $\Delta H_f^\circ(\text{NO}_3)$ (4 _{b,h})	-219.5	-219.6
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,n})	-106.2	
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{OH})$ (4 _{b,n})	-106.3	-106.2
NiCO ₃	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{CO}_3)$ (6 _{b,n})	-106.1	
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,c})	-166.1	
	$\Delta H_f^\circ(\text{OH})$ and $\Delta H_f^\circ(\text{SO}_4)$ (3 _{b,c})	-165.5	-167.8
	$\Delta H_f^\circ(\text{NO}_3)$ and $\Delta H_f^\circ(\text{O})$ (4 _{b,c})	-170.6	
	$\Delta H_f^\circ(\text{OH})$ and $\Delta H_f^\circ(\text{NO}_3)$ (5 _{b,c})	-169.1	
CuCO ₃	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,c})	-143.1	
	$\Delta H_f^\circ(\text{OH})$ and $\Delta H_f^\circ(\text{SO}_4)$ (3 _{b,c})	-143.3	
	$\Delta H_f^\circ(\text{NO}_3)$ and $\Delta H_f^\circ(\text{O})$ (4 _{b,c})	-145.6	-144.4
	$\Delta H_f^\circ(\text{OH})$ and $\Delta H_f^\circ(\text{NO}_3)$ (5 _{b,c})	-145.5	
Pb(OH) ₂	$\Delta H_f^\circ(\text{CO}_3)$ and $\Delta H_f^\circ(\text{O})$ (1 _{b,h})	-136.4	
	$\Delta H_f^\circ(\text{SO}_4)$ and $\Delta H_f^\circ(\text{O})$ (2 _{b,h})	-135.6	-136.0
	$\Delta H_f^\circ(\text{O})$ and $\Delta H_f^\circ(\text{NO}_3)$ (4 _{b,h})	-136.1	

Recently Tardy et al. (6-9) and Sverjensky (4, 5) have also shown the existence of empirical relations among Gibbs free

energies and enthalpies of formation of solid compounds such as silicates, carbonates, and sulfates, etc. However, they related ΔH_f° (salts) to ΔH_f° for the corresponding aqueous cations. Moreover, the relationships given are based on limited groups of compounds and the compounds are classified according to structural types. With the relationships illustrated here, we are able to correlate any three types of compounds only on the basis of valence states. We have also found that the relationship described above are not confined to the oxygen-containing compounds. The halides also show similar relations, and these will be described later.

Literature Cited

- (1) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1985**, *89*, 1905.
- (2) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1985**, *89*, 3417.
- (3) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1986**, *90*, 885.
- (4) Sverjensky, D. A. *Geochim. Cosmochim. Acta* **1984**, *48*, 1127.
- (5) Sverjensky, D. A. *Geochim. Cosmochim. Acta* **1985**, *49*, 853.
- (6) Tardy, Y.; Garrels, R. M. *Geochim. Cosmochim. Acta* **1976**, *41*, 1051.
- (7) Tardy, Y.; Garrels, R. M. *Geochim. Cosmochim. Acta* **1977**, *41*, 87.
- (8) Tardy, Y.; Viellard, P. *Contrib. Mineral Petrol.* **1977**, *63*, 75.
- (9) Tardy, Y.; Gartner, L. *Contrib. Mineral Petrol.* **1977**, *63*, 89.
- (10) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data*, **1982**, Suppl. 11.

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Vapor-Liquid Equilibrium of the System Ethanol + Benzene + Cyclohexane at 760 mmHg

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Vapor-liquid equilibrium data for the ternary mixture ethanol + benzene + cyclohexane at a constant pressure of 760 mmHg have been determined experimentally and predicted by using the group contribution methods UNIFAC and ASOG-KT and the NRTL, UNIQUAC, and Wilson equations with parameters estimated from data for the corresponding binary mixtures. The predictions compare satisfactorily with the experimental results.

Introduction

Apart from their intrinsic value for the design of distilling plants, experimental VLE data provide an important means of testing the validity of thermodynamic models of liquid mixtures and the associated methods of data processing and prediction. For binary mixtures experimental VLE data are generally available and reliable, but the same is not true for most multicomponent systems. This article reports experimental VLE