(2) Franchini, G. C.; Marchetti, A.; Preti, C.; Tassi, L.; Tosi, G. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1697.
(3) Marchetti, A.; Picchioni E.; Tassi, L.; Tosi, G. *Anal. Chem.* **1989**, *61*, 1971.
(4) Banerjee, P. C. *J. Indian Chem. Soc.* **1942**, *19*, 35.
(5) Maryott, A. A.; Smith, E. R. *Table of Dielectric Constant of Pure Liquids*; Natl. Bur. Stand. Circ. No. 514; U.S. Government Printing Office: Washington, DC, 1951.
(6) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *J. Chem. Eng. Data* **1991**, *36*, 365.
(7) Van Hippel, A. R. *Dielectric and Waves*, 3rd ed.; Wiley: New York, 1962; Chapter 1.
(8) Marchetti, A.; Preti, C.; Tagliazucchi, M.; Tassi, L.; Tosi, G. *J. Chem. Eng. Data* **1991**, *36*, 360.
(9) Fuoss, R. M.; Hsia, K. L. *J. Am. Chem. Soc.* **1968**, *90*, 3055.
(10) Roberts, J. H. *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1976; Vol. IV, Chapter 1.
(11) *Time Series Processor-TSP-User's Guide*; Hall, Bronwyn H., Ed.; TSP International: Stanford, CA, July 1963.
(12) Nakahara, M. *J. Phys. Chem.* **1984**, *88*, 2138.
(13) Fuoss, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1959**, *45*, 807.
(14) Stokes, J. M.; Stokes, R. H. *J. Phys. Chem.* **1958**, *62*, 497.

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Thermochemistry of Inorganic Solids. 10. Empirical Relations between the Enthalpies of Formation of Solid Halides and the Corresponding Gas-Phase Halide Anions

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Equation 4, $\Delta(MX_n) = a\Delta(M'X_n) + b$, where M and M' are two different metals, both with formal valence n, $\Delta(MX_n)$ is defined by eq 3, $\Delta(MX_n) = \Delta_fH^\circ(MX_n,cr) - \Delta_fH^\circ(X^-,g)$, and for a selected pair of metals, M and M', X can be any of the halogens, has been found to correlate the standard enthalpies of formation, Δ_fH°, at 298 K for any solid halides with the corresponding gas-phase halide ions. While values of b vary over a broad range, values of a are usually close to unity. The deviations from these relations are always within the claimed accuracy of the Δ_fH° reported. For 40 monovalent halides, the average deviation is 0.7 kcal/mol with a maximum deviation of 2.0 kcal/mol. For 82 divalent halides, the average deviation is 1.2 kcal/mol with a maximum of 5.0 kcal/mol. For 68 trivalent halides, the average deviation is 2 kcal/mol with a maximum of 6.5 kcal/mol. For 16 tetravalent halides, the average deviation is 0.9 kcal/mol with a maximum of 1.8 kcal/mol. For six pentavalent halides, the average deviation is 0.9 kcal/mol with a maximum of 1.5 kcal/mol.

Introduction

In a recent paper (*1*), we have presented evidence that a quantitative, linear relationship exists among the standard enthalpies of formation, Δ_fH°, of any three classes of crystalline halides. We have noted that there is no simple relationship between any pair of classes of compounds. However, when the differences in the values of $\Delta_fH^\circ_{298}$ between two classes of compounds are considered, a two-parameter linear relationship is found.

A typical example is provided by

$$\Delta_fH^\circ(MX_n) - \Delta_fH^\circ(MY_n) = a[\Delta_fH^\circ(MZ_n) - \Delta_fH^\circ(MY_n)] + b \quad (1)$$

where M is any metal of formal valence n in a group of the periodic table. Such relations lead to equations of the form

$$\Delta_fH^\circ(MX_n) = a\,\Delta_fH^\circ(MZ_n) - (a-1)\Delta_fH^\circ(MY_n) + b \quad (2)$$

When the values of a and b are known for a particular group of metals, then it is possible to estimate $\Delta_fH^\circ(MX_n)$ for unknown members of the class. Using oxides and chlorides of metals as prime data, it is now possible to estimate Δ_fH° for almost all crystalline salts (*4*).

An examination of the available data on the halides of various metals with $\Delta_fH^\circ_{298}$ of the corresponding gas-phase halide ion reveals another quantitative relation which can also be expressed by a set of two-parameter linear equations. Unless otherwise stated, thermochemical data used here are taken from National Bureau of Standards (NBS) tables (*2*), and values are given for $\Delta_fH^\circ_{298}$ per mole of metal atom and at 298 K in kilocalories.

We define $\Delta(MX_n)$ for a metal M with valence n by following eq 3. X (F, Cl, Br, or I) is a halide atom, M is a metal atom, and n is its valence state. $\Delta_fH^\circ(MX_n,cr)$ is the enthalpy of formation of solid metal halide MX_n, and $\Delta_fH^\circ(X^-,g)$ is the enthalpy of formation of the corresponding gas-phase monovalent halogen anion. The latter are known accurately.

$$\Delta(MX_n) = \Delta_fH^\circ(MX_n,cr) - \Delta_fH^\circ(X^-,g) \quad (3)$$

The values used for $\Delta(MX_n)$ where the data for at least three halides are available for a metal M with a valence n are listed in Table I. It is interesting to note that, for any given valence state n from 1 to 5, the values of $\Delta(MX_n)$ for any two metals within that particular valence group are linearly related, and the relation is given by the following two-parameter, linear equation (eq 4).

$$\Delta(MX_n) = a\Delta(M'X_n) + b \quad (4)$$

For monovalent ($n = 1$) halides, we have chosen to relate all metal halides to the halides of sodium. The typical plots obtained for some metals to illustrate the relations are shown in Figure 1, and the values for coefficients a and b obtained in eq 4 for the metals examined are summarized in Table II. The comparison between the calculated values using eq 4 and the

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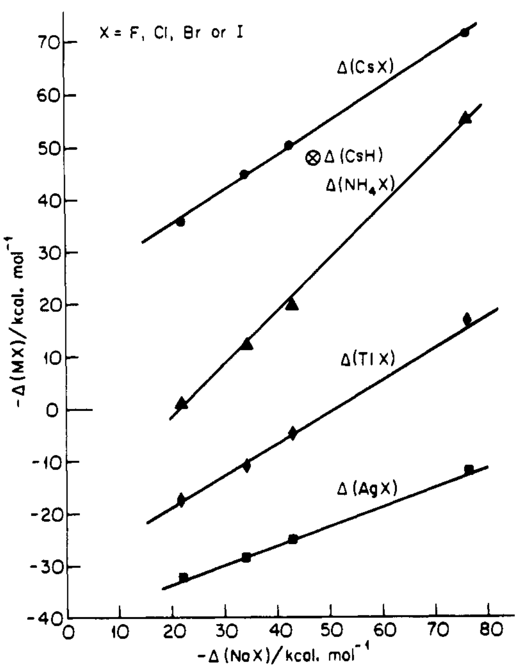

Figure 1. Relationship between Δ(MX) and Δ(NaX).

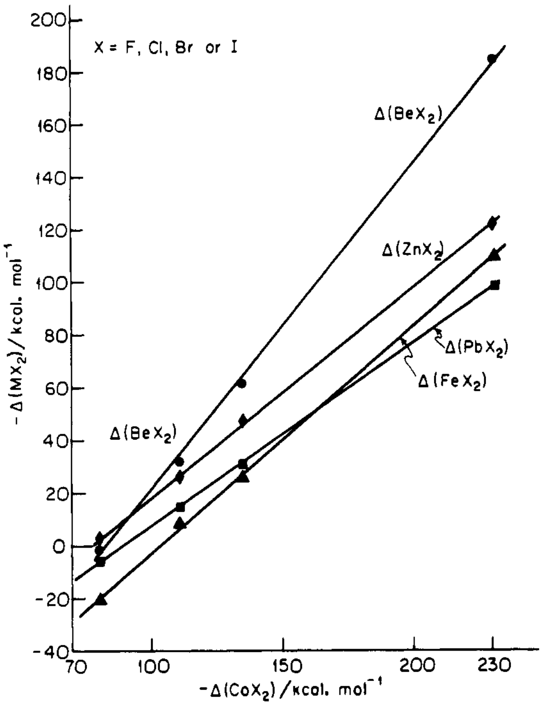

Figure 2. Relationship between Δ(MX$_2$) and Δ(CaX$_2$).

corresponding reported values for each metal halide shows remarkable agreement. As shown in Table III, for 11 different monovalent metals the maximum absolute deviation is only 2.0 kcal/mol while the average is 0.71 kcal/mol for the 40 compounds examined.

Similar relations described above are also found for di-, tri-, tetra-, and pentavalent halides, and typical plots obtained for these compounds are shown in Figures 2–5, respectively. Divalent halides are related to the halides of Ca, trivalent halides are related to the halides of Al, tetravalent halides are related to the halides of U, and pentavalent halides are related to the halides of Nb. The coefficients *a* and *b* obtained in eq 4 for each set of compounds of one metal are summarized in Table II. The deviations obtained between calculated values using eq 4 and the observed values are listed in Table III. For

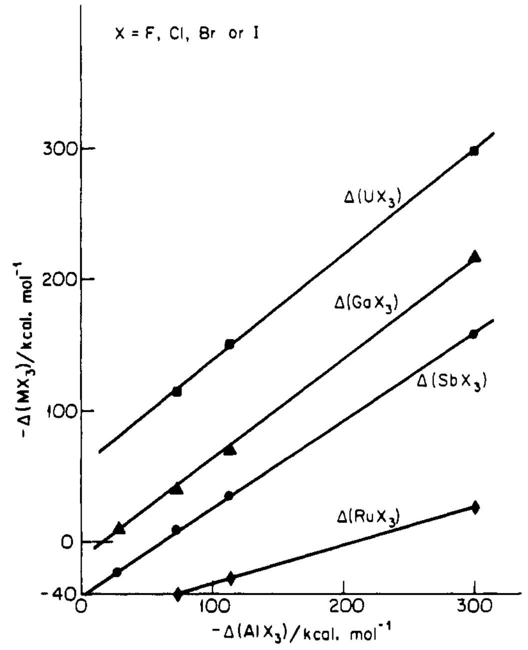

Figure 3. Relationship between Δ(MX$_3$) and Δ(AlX$_3$).

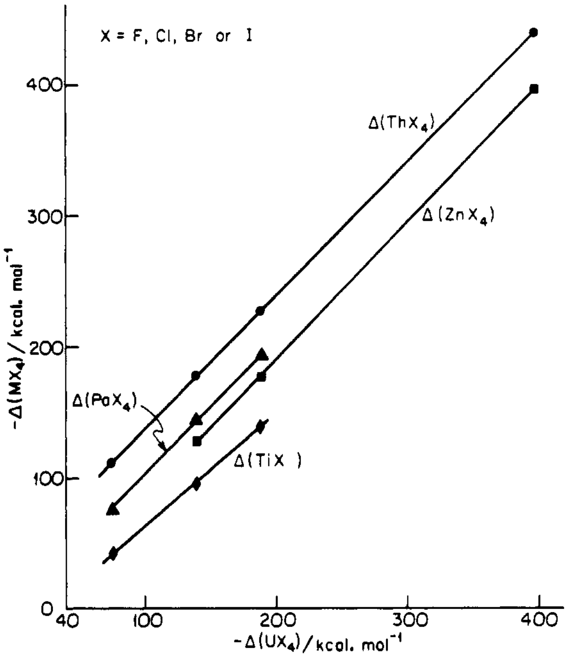

Figure 4. Relationship between Δ(MX$_4$) and Δ(UX$_4$).

divalent compounds (total of 62 compounds with 17 different metals) the maximum deviation is 5.0 kcal/mol with an average deviation of 1.2 kcal/mol. For trivalent compounds (total of 71 compounds and 21 different metals), the maximum deviation is 6.5 kcal/mol with an average deviation of 2.0 kcal/mol. For tetravalent compounds (total of 16 compounds and 5 metals), we obtained the maximum deviation of 1.8 kcal/mol with an average deviation of 0.9 kcal/mol. For pentavalent compounds (total of six), the maximum deviation is 1.5 with an average deviation of 0.9 kcal/mol. However, data exist for only two metals in this group.

Discussion

It is important to note that where in our earlier observations (*1*, *4*) the span of $\Delta_f H°$ values for different metals or anions in a given class usually ranged over 50–100 kcal/mol, in the present finding the range for a given class can span 200 or

Table I. Values Used for $\Delta(MX_n)$[a]

M (n)	$-\Delta(MX_n)$/(kcal/mol) X = F	X = Cl	X = Br	X = I
Li (1)	86.3	41.9	31.5	17.5
Na (1)	76.1	42.6	33.9	21.7
K (1)	74.6	48.7	41.7	31.3
Rb (1)	72.3	48.4	41.9	32.7
Cs (1)	71.3	50.2	44.6	35.7
NH_4 (1)	50.0	19.5	12.3	1.0
Cu (1)		−22.9	−27.4	−30.9
Ag (1)	−12.1	−25.4	−28.4	−32.3
Au (1)		−47.4	−49.1	−47.1
Hg (1)		−29.3	−27.7	−32.6
In (1)		−11.2	−10.5	−19.3
Tl (1)	16.6	−6.9	−11.0	−17.5
Be (2)	184.4	61.5	32.1	−1.1
Mg (2)	207.5	97.6	72.9	39.9
Ca (2)	230.5	134.5	110.6	80.4
Sr (2)	229.7	142.4	119.1	86.3
Ba (2)	227.5	149.5	128.6	96.8
Fe (2)	109.0	26.0	7.3	−20.1
Co (2)	104.4	19.0 $(20.4)_J$	0.4	−25.9
Ni (2)	94.7	17.3	−1.7	−28.4
Zn (2)	121.7	43.5	26.1	2.6
UO_2 (2)	332.9	214.6	219.5	
Cd (2)	106.4	37.9	23.2	1.5
Hg (2)		−2.1	−11.6	−22.2
Sn (2)		22.0	5.8	−12.8
Pb (2)	97.7	30.2	14.2	−5.2
Ti (2)		67.1	43.6	16.0
V (2)		52.3	34.9	13.0
Cr (2)	124.9	38.8	19.8	−9.6
Pd (2)		−8.2	−27.5	−32.0
Al (3)	298.5	112.6	73.6	27.9
Ga (3)	217.0	69.7	40.0	10.0
In (3)		72.7	50.1	9.8
Sb (3)	157.8	35.6	9.6	−23.1
Au (3)	25.9	−27.6	−39.7	
Sc (3)	328.4	165.3	119.2	
V (3)		83.1	51.2	17.6
Cr (3)	216.0	77.3		1.9
Ru (3)		−6.7	−19.4	−31.4
U (3)	298.0	151.3	114.7	
Fe (3)		39.8	11.7	−33.1
Y (3)	349.8	183.3		100.3
La (3)	345.1	200.8	164.4	112.3
Ce (3)	346.0	197.2		108.3
Pr (3)	342.7	197.4	160.6	109.2
Nd (3)	340.3	193.3	156.3	105.6
Sm (3)	337.9	189.5	152.5	101.1
Eu (3)	314.5	168.1	133.8	
Gd (3)	345.1	185.1	145.7	94.9
Dy (3)	343.4	181.8	146.9	98.0
Ho (3)	344.8	182.1		101.9
Er (3)	343.9	182.0	148.1	99.4
Tm (3)	334.8	181.2		96.7
Ti (4)		140.0	95.0	42.7
Zr (4)	395.8	178.6	129.4	
Pt (4)		−0.3	−15.0	−29.7
Th (4)	438.9	227.9	178.3	111.8
U (4)	396.5	187.9	139.4	75.3
Pa (4)		193.6	144.6	75.9
Nb (5)	372.5	134.9	80.5	17.1
Ta (5)	394.0	149.6	90.6	
U (5)	435.0	197.4	141.4	

[a] Value labeled with J subscript is from the JANAF tables.

even 400 kcal/mol. Despite this, the average deviations are comparable in the two studies.

Also of interest was our earlier observation that different valence groups could all be related if comparisons were made on an equimolar basis. Thus, the differences such as $\Delta_f H°(M_n X_p) - \Delta_f H°(M_n O_q)$ would be divided by n, the number of moles of metal per formula in making the comparisons.

We have also tried to relate metal hydrides with the halides. However, no relationship was found among these two groups.

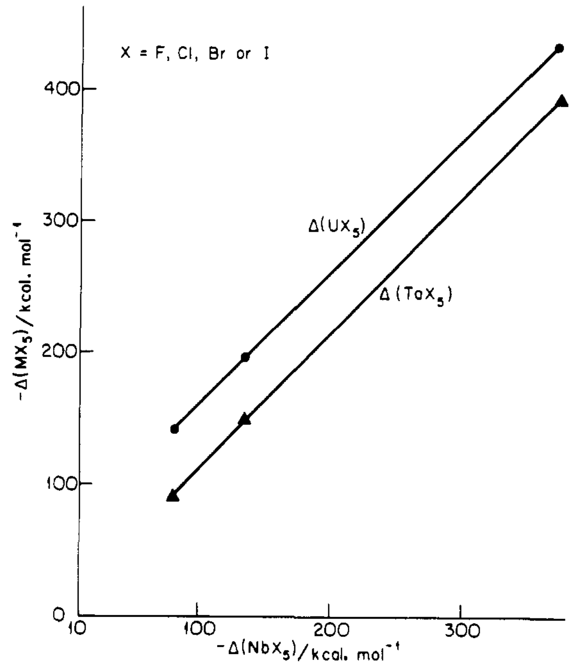

Figure 5. Relationship between $\Delta(MX_5)$ and $\Delta(NbX_5)$.

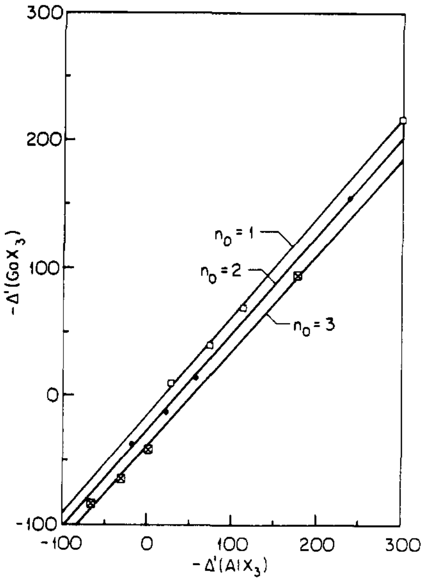

Figure 6. Relationship between $\Delta'(AlX_3)$ and $\Delta(GaX_3)$ for n_0 = 1–3.

These are shown in Figures 1 and 2 for NaH, CsH, BeH_2, and CaH_2. Although a quantitative relationship exists among $\Delta_f H°$ of metal halides and the corresponding gas-phase halide ions, the reason for such a relationship is difficult to understand theoretically. In practice, we can estimate $\Delta_f H°$ for any halides of interest using the above relations.

We also examined relationships among $\Delta'(MX_n)$ defined by eq 5, where n_0 takes the value 1, 2, ..., n, for certain metals with different values of n_0. In all cases, the values of $\Delta'(MX_n)$

$$\Delta'(MX_n) = \Delta_f H°(MX_n,cr) - n_0 \Delta_f H°(X^-,g) \qquad (5)$$

between any two metals with the same valence are linearly related by the following equation:

$$\Delta'(MX_n) = a'\Delta'(M'X_n) + b' \qquad (6)$$

It is interesting to note that in most cases lower deviations are used when n_0 = 1, although no remarkable differences either in maximum or in average deviations are found for different values of n_0. The results are summarized in Table IV, and

Table II. Parameters a and b (Equation 2) Obtained for Different Metal Halides[a]

M (n)	M′ (n)	a	b/(kcal/mol)
Li (1)	Na	1.2744	-11.2
K (1)		0.7964	14.3
Rb (1)		0.7236	17.2
Cs (1)		0.6436	22.2
NH_4 (1)		0.8991	18.5
Cu (1)		0.3762	-39.7
Ag (1)		0.3817	-41.3
Au (1)		0.0523	-48.8
Hg (1)		0.2640	-38.6
In (1)		0.2800	-21.6
Tl (1)		0.6425	-32.5
Be (2)	Ca	1.2466	-104.1
Mg (2)		1.1077	-49.3
Sr (2)		0.9485	12.7
Ba (2)		0.8654	30.1
Fe (2)		0.8623	-89.3
Co (2)		0.8669	-95.9
Ni (2)		0.8231	-93.8
Zn (2)		0.7900	-61.7
UO_2 (2)		0.9500	113.5
Cd (2)		0.6923	-54.2
Hg (2)		0.3745	-52.6
Sn (2)		0.6455	-65.1
Pb (2)		0.6900	-62.0
Ti (2)		0.9382	-59.4
V (2)		0.7272	-45.5
Cr (2)		0.8864	-79.5
Pd (2)		0.4091	-67.7
Ga (3)	Al (3)	0.7732	-14.9
In (3)		0.7333	-6.8
Sb (3)		0.6651	-40.2
Au (3)		0.2884	-60.5
Sc (3)		0.9127	56.5
V (3)		0.7875	-6.6
Cr (3)		0.7948	-18.7
Ru (3)		0.2788	-38.7
U (3)		0.8095	58.0
Fe (3)		0.8321	-52.6
Y (3)	Gd (3)	1.0079	-0.7
La (3)		0.9350	25.0
Ce (3)		0.9520	18.5
Pr (3)		0.9388	21.3
Nd (3)		0.9450	17.1
Sm (3)		0.9439	13.2
Eu (3)		0.9045	1.9
Dy (3)		0.9750	4.5
Ho (3)		0.9762	6.8
Er (3)		0.9831	1.8
Tm (3)		0.9402	7.7
Ti (4)	U (4)	0.8570	-22.8
Zr (4)		1.0326	-15.0
Pt (4)		0.2500	-48.3
Th (4)		1.0166	36.2
Pa (4)		1.0500	-2.8
Ta (5)	Nb (5)	1.0331	8.7
U (5)		1.0038	61.2

[a] The a and b parameters are obtained from individual graphs. We have given greater weight to those data which are known most accurately.

Table III. Deviations Found for $\Delta_f H°$ from Linear Relations (Equation 4) Given in Table II

	dev(obsd - calcd)/(kcal/mol)			
M (n)	MF_n	MCl_n	MBr_n	MI_n
Li (1)	-0.3	1.2	0.5	-1.0
K (1)	0.3	-0.5	-0.4	0.3
Rb (1)	0	-0.4	-0.2	0.2
Cs (1)	-0.1	0.6	-0.6	0.5
NH_4 (1)	-0.1	0.3	-0.3	0
Cu (1)		0.8	0.5	-0.6
Ag (1)	-0.2	0.4	0	-0.7
Au (1)		0.8	2.0	-1.7
Hg (1)		1.9	-1.9	-0.3
In (1)		1.5	-1.6	-2.3
Tl (1)	-0.2	1.0	0.3	-1.1
		average 0.71		
Be (2)	-1.1	2.1	1.7	-2.8
Mg (2)	-1.5	2.1	0.3	-0.1
Sr (2)	1.6	-2.1	-1.5	2.7
Ba (2)	2.1	-3.0	-2.8	2.8
Fe (2)	0.5	0.7	-1.2	0.1
Co (2)	-0.5	1.7	0.4	-0.3
Ni (2)	1.2	-2.1	2.3	-1.7
Zn (2)	-1.3	1.1	-0.4	-0.8
UO_2 (2)	0.4	-0.3	-0.9	
Cd (2)	-1.0	1.0	-0.8	0
Hg (2)		-0.1	-0.8	-0.3
Sn (2)		-0.3	0.5	-0.4
Pb (2)	-0.7	0.6	0.1	-1.3
Ti (2)		-0.3	0.8	0
V (2)		0	0	0
Cr (2)	-0.1	0.9	-1.3	1.4
Pd (2)		4.4	5.0	-2.8
		average 1.19		
Ga (3)	-1.1	2.5	2.0	-3.3
In (3)		-3.1	-2.9	3.9
Sb (3)	0.7	-0.9	-0.8	1.5
Au (3)	-0.3	-0.4	0.4	
Sc (3)	0.5	-6.0	4.4	
V (3)		-1.0	0.2	2.3
Cr (3)	2.5	-6.5		1.6
Ru (3)		-0.6	1.2	0.5
U (3)	1.6	-2.2	2.9	
Fe (3)		1.3	-3.1	3.7
		average 2.10		
Y (3)	-2.7	2.6		-5.4
La (3)	2.6	-2.7	-3.1	1.4
Ce (3)	1.0	-2.5		0.5
Pr (3)	2.6	-2.3	-2.5	1.1
Nd (3)	2.9	-1.3	-1.5	1.2
Sm (3)	1.0	-1.6	-1.8	1.7
Eu (3)	-0.5	1.2	-0.1	
Dy (3)	-2.4	3.2	-0.3	-1.0
Ho (3)	-1.1	5.5		-2.5
Er (3)	-2.8	1.8	-1.9	-4.3
Tm (3)	-2.6	-3.1		0.2
		average 2.06		
Ti (4)		-1.8	1.7	-1.0
Zr (4)	-1.4	0.4	-0.5	
Pt (4)		-1.0	1.6	0.2
Th (4)	0.4	-0.7	-0.4	0.8
Pa (4)		0.9	-1.0	0.4
		average 0.92		
Ta (5)	-0.5	-1.5	1.3	
U (5)	-0.1	-0.8	0.06	
		average 0.90		

some examples are shown in Figures 6 and 7.

Uncertainties as small as ±2 kcal in reference compounds may cause uncertainties as much as ±10 kcal in the estimated values, particularly in the case of fluorides. The reasons for this are easy to understand. For most of the sequences the span of values compared covers 100–400 kcal/mol. Thus, the best lines are most sensitive to the end points. For the halogens these are the iodides and fluorides. If values for these are available, then interpolation to the chlorides and bromides is quite reliable. However, if iodide or fluoride values are missing, extrapolations are subject to much greater errors.

For example, we have estimated the values for bromides from corresponding chlorides and iodides by interpolations, and the values for iodides from corresponding bromides and chlorides by extrapolations. The deviations obtained from observed values are compared in Table V, and we find very good agreement for bromides which were determined by interpolation methods. The occassionally high deviations obtained for a few

Table IV. Parameters and Deviations Obtained for Equation 6

M (M′)	n	n_o	a'	b'/(kcal/mol)	dev(obsd − calcd)/(kcal/mol)					
					MF_n	MCl_n	MB_{rn}	MI_n	max	av
Be (Ca)	2	1	1.2466	−104.1	−1.1	2.1	1.7	−2.8	2.8	1.93
	2	2	1.2706	−92.8	−0.8	1.5	1.4	−2.3	2.3	1.50
Ga (Al)	3	1	0.7732	−14.9	−1.1	2.5	2.0	−3.3	3.3	2.22
	3	2	0.7628	−26.4	−1.2	3.0	2.2	−3.9	3.9	2.56
	3	3	0.7516	−39.0	−1.3	3.6	2.4	−4.6	4.6	2.98
Sb (Al)	3	1	0.6651	−40.2	0.5	−0.9	0.8	1.5	1.5	0.93
	3	2	0.6488	−57.1	0.2	−0.1	−0.5	0.6	0.6	0.35
	3	3	0.6312	−75.8	−0.2	0.8	−0.3	−0.3	0.8	0.40
Th (U)	4	1	1.0166	36.2	0.4	−0.7	−0.4	0.8	0.8	0.58
	4	2	1.0172	37.0	0.4	−0.7	−0.4	0.9	0.9	0.60
	4	3	1.0179	37.8	0.3	−0.8	−0.5	0.9	0.9	0.63
	4	4	1.9186	38.8	0.4	−0.8	−0.4	1.0	1.0	0.65
U (Nb)	5	1	1.0038	61.2	0.1	−0.8	0.6		0.8	0.50
	5	2	1.0039	61.4	0.1	−0.8	0.6		0.8	0.50
	5	3	1.0040	61.6	0.1	−0.8	0.6		0.8	0.50
	5	4	1.0041	61.9	0.2	−0.7	0.7		0.7	0.53
	5	5	1.0042	62.1	0.1	−0.8	0.6		0.8	0.50

Table V. Deviations Found (kcal/mol) for Bromides and Iodides

M	n	$\Delta\Delta_f H°(MBr_n)$ dev(calcd)	$\Delta\Delta_f H°(MI_n)$ dev(calcd)
Li	1	0	1
K	1	1	1
Rb	1	0	1
Cs	1	1	1
NH_4	1	0	1
Cu	1	−1	
Ag	1	0	1
Au	1	2	5
Hg	1	3	8
In	1	4	9
Tl	1	0	1
Be	2	2	4
Mg	2	1	2
Sr	2	1	4
Ba	2	3	4
Fe	2	1	4
Co	2	1	3
Ni	2	1	2
Zn	2	1	1
Cd	2	1	3
Hg	2	1	3
Sn	2	1	2
Pb	2	0	1
Ga	3	2	5
In	3	6	14
Sb	3	1	2
V	3	2	1
Ru	3	1	3
Y	3	1	
La	3	2	5
Pr	3	1	6
Nd	3	1	3
Sm	3	2	4
Dy	3	2	4
Er	3	2	5
Th	4	0	1
Pa	4	2	4
Pt	4	2	4
Ti	4	3	7

Table VI. Some Estimated $\Delta_f H°$ Values

halide	$-\Delta_f H(MX_n)$/(kcal/mol)	
	estimd	reported
$CeBr_3$	210	211,[a] 213[b]
$TbBr_3$	198	199,[a] 203[b]
$HoBr_3$	201	202,[a] 198[b]
$TmBr_3$	197	199,[a] 201[b]
$YbBr_3$	192	190,[a] 191[b]
$CrBr_3$	95	98,[a] 94[c]
$HfBr_4$	182	185[a]
CuI2	9	6.0[a]
UO_2I_2	237	252[d]
AuI_3	−5	−15[a]
ScI_3	129	122[a]
TbI_3	141	144,[a] 142[e]
YbI_3	142	135,[a] 134[e]
TiI_3	81	74[a]
MnI_2	62	60,[a] 58[f]
ZrI_4	110	
MoI_2	23.9	24.8 (JANAF)
MoI_4	26	23,[a] 29.4 (JANAF)
TeI_4	2	−1[a]
PtI	2	2[a]
PtI_2	6	6[g]
PtI_3	10	7[g]
MoF_2		129[h]
ReI_3	7	6[a]
WI_5	24	14[a]
TaI_5	73	61[a]
HfI_4	110	111[a]
PaI_5	126	114[a]
UI_5	125	112[a]

[a] Using method described in ref 1. [b] From ref 5. [c] Using method described in ref 6. [d] Using method described in ref 4. [e] From ref 7. [f] Using method described in ref 8. [g] Using method described in ref 9. [h] This is obtained by using the NBS values for $MoCl_2$ and the JANAF values for $MoBr_2$ and MoI_2.

iodides reflect the corresponding experimental uncertainties involved in the reference compounds, either bromides or chlorides or both.

Using this method, we are able to estimate values for 28 compounds for which the values are not currently listed. Whenever possible, the estimated values are compared with their independent methods which we suggested previously. The results are shown in Table VI. In the case of bromides, we find very good agreement. For iodides, however, the higher deviations obtained in a few cases are probably due to the uncertainties involved in the observed values of the corresponding reference compounds. It is thus not recommended to use the above relations to try to estimate $\Delta_f H°$ for iodides for which experimental uncertainties involved in the reference compounds are high (>2 kcal/mol). However, in these cases our previous methods (*4*) can be used to estimate $\Delta_f H°$ for these compounds with reasonable accuracy.

It is of interest to note that, in Table II, the parameters *a* tend to be near unity. Among the univalent metals this is true for the main-group elements (Na, Li, etc.) while the subgroup elements have much smaller *a* values. These have all been referenced to Na for the univalent metals. We note that Li has the largest *a* value in this group. If we had referenced all metals to Li, the corresponding *a* values would all be smaller by the ratio of a_M/a_{Li} where for metal M, a_M is its value against Na and a_{Li} is the corresponding value for Li against Na. For

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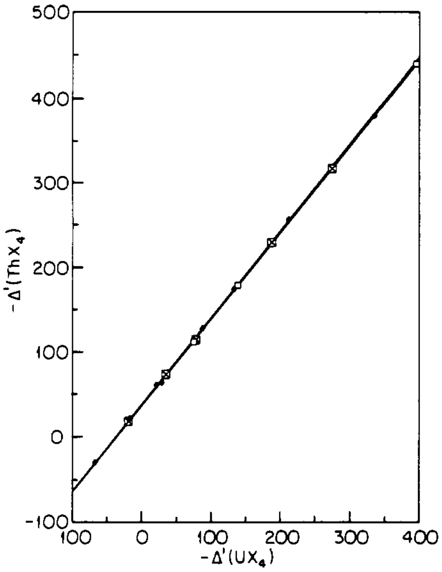

Figure 7. Relationship between $\Delta'(UX_4)$ and $\Delta'(ThX_4)$.

the univalent ions this would have the effect of reducing their *a* values by a factor of $1.2744a_{Li}$. This is a great help in making extrapolations to fluorides or iodides. A similar result would be obtained for the divalent metals by referencing $\Delta(M)$ values to Be, the element with the largest *a* value.

Registry No. $CeBr_3$, 14457-87-5; $TbBr_3$, 14456-47-4; $HoBr_3$, 13825-76-8; $TmBr_3$, 14456-51-0; $YbBr_3$, 13759-89-2; $CrBr_3$, 10031-25-1; $HfBr_4$, 13777-22-5; CuI_2, 13767-71-0; UO_2I_2, 13520-82-6; AuI_3, 13453-24-2; ScI_3, 14474-33-0; TbI_3, 13813-40-6; YbI_3, 13813-44-0; TlI_3, 13783-08-9; MnI_2, 7790-33-2; ZrI_4, 13986-26-0; MoI_2, 14055-74-4; MoI_4, 14055-76-6; TeI_4, 7790-48-9; PtI, 13779-77-6; PtI_2, 7790-39-8; PtI_3, 68220-29-1; MoF_2, 20205-60-1; ReI_3, 15622-42-1; WI_5, 13782-91-7; TaI_5, 14693-81-3; HfI_4, 13777-23-6; PaI_5, 17497-66-4; UI_5, 13775-20-7.

Literature Cited

(1) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1987**, *91*, 3631.
(2) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Ref. Data* **1982**, *11* (Suppl. No. 2).
(3) Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry*, 5th ed.; Pergamon: Oxford, 1979.
(4) The Estimation of the Enthalpy of Formation of Solid Salts. In *From Atoms to Polymers*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1989; Chapter 10.
(5) Smith, D. W. *J. Chem. Educ.* **1986**, *64*, 228.
(6) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem. Ref. Data* **1987**, *16*, 467.
(7) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; International Union of Pure and Applied Chemistry; M. Dekker: New York, 1985.
(8) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1987**, *91*, 5998.
(9) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1985**, *89*, 3417.

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Solubility of Four Amino Acids in Water and of Four Pairs of Amino Acids in Their Water Solutions

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Solubility is measured for L-serine, D-serine, DL-proline, and DL-arginine in water at 25–60 °C. The solubility of an amino acid A in a water solution of amino acid B, and the solubility of B in a solution of A, has been determined in the same temperature range for four pairs of A and B: L-glutamic acid + glycine, L-glutamic acid + L-aspartic acid, L-glutamic acid + L-serine, and L-aspartic acid + L-serine. The eutectic compositions of the water solution of the four pairs of amino acids are reported.

Introduction

Amino acids are valuable chemical substances that are the basic building blocks of all forms of life. For use in industrial processes and scientific laboratories and as food additives, amino acids have to be separated and purified from mixtures that are obtained from protein hydrolysis or an industrial synthetic process. Fractional precipitation and crystallization are suitable for separation of amino acids while other separation methods such as chromatography are also practiced. All separation methods stand to benefit from understanding of the solution and solubility behavior which is basic to the design of separation and purification processes.

The solubility data of some amino acids in water are tabulated in *CRC Handbook of Chemistry and Physics* (*1*) and Fasman's *Handbook of Biochemistry and Molecular Biology* (*2*) while the solubility data of L-threonine, L-cysteine, L-asparagine, L-glutamine, L-lysine, L-arginine, L-histidine, DL-proline, DL-tryptophan, DL-thrionine, DL-cysteine, DL-glutamine, DL-asparagine, DL-lysine, DL-arginine, and DL-histidine in water are still not found. The solubility data of an amino acid in a solution of other amino acids are scarce. Cohn and co-workers (*3*) reported the solubility of asparagine or cystine in solutions of alanine, glycine, or α-aminobutyric acid. Sexton and Dunn (*4*) reported that of glutamic acid or norvaline in glycine solution.

In this work, we experimentally determine the solubility in water for four amino acids and the solubility of each of a pair of amino acids in their solutions for four pairs. We use the dry weight method for the determination.

Dry Weight Method

By the dry weight method, the solubility of a substance is determined by evaporating to dryness a saturated solution of the substance. The weight of the dissolved solute is obtained from the dried sample. The weight of the saturated solution having been determined prior to evaporation of the solution, the amount of solvent is obtained by difference.

The dry weight method has been used for the determination of the solubility of a single amino acid in water (*5*, *6*). In this work the method is adopted for this purpose and is extended to the determination of the solubility of an amino acid A in a mixed solution of amino acids A and B. For the latter purpose, a known unsaturated solution of B is brought in contact with solute A. Upon being saturated with A, the concentration of the total dissolved solutes A and B are determined by evaporating a sample of the solution to dryness. The solubility of A

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