Estimation of Standard Heat of Formation of Alloys and Covalent Compounds by a Group Contribution Method[1]

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ABSTRACT

Group contribution equations are proposed for estimating standard heat of formation $\triangle H^{\circ}_{f,298}$ of solid compounds, which are divided into two categories: alloys and covalent compounds. A differenet correlation was developed for each category, in which the elements are considered as the basic functional groups. The group contribution parameters of 64 groups were obtained by correlating the experimental $\triangle H^{\circ}_{f,298}$ data of 500 compounds. The overall average errors are less than 9.0% for alloys and 12% for covalent compounds. Furthermore, standard heat of formation $\triangle H^{\circ}_{f,298}$ of 11 solid compounds, whose experimental data were not used in correlating the models, were predicted by the proposed models with satisfactory results.

Keywords: group-contribution method; standard heat of formation; alloys; covalent compounds.

1. INTRODUCTION

Standard heat of formation $\triangle H^{\circ}_{f,298}$ of a compound is an important thermodynamic property and is one of the basic physical properties required in industrial process calculation, analysis and design. Experimental data are available for many common compounds, however, there are a very large number of compounds for which data are not available. Therefore, it is necessary to develop an accurate method for estimating standard heat of formation.

Group contribution methods have been well developed for estimating a wide variety of physical properties such as standard heat of formation, standard Gibbs free energy of formation, heat capacity, liquid molar volume at normal boiling point and so on, for organic compounds with great generality and reasonable accuracy. These methods are documented in detail by Reid et al. [1,2]. However, there are very few reports on estimating the thermodynamic properties of solid inorganic compounds using group contribution method. Mostafa et al. [3,4] proposed a group contribution method for estimating standard heat and Gibbs free energy of formation as well as heat capacity of solid inorganic salts. In Mostafa's method, the equation for estimating standard heat of formation of solids is the same as the Benson equation for estimating standard heat of formation of organic compounds [5]. Solid inorganic salts are considered to be composed of cations, anions and ligands.

Since alloys and covalent compounds cannot be divided into cations and anions as with solid inorganic salts, it is not feasible to directly use the Mostafa equation to estimate standard heat of formation of these compounds. Our search in the literature did not find any group contribution methods that are applicable to these classes of

compounds.

In this investigation, the group contribution equations were developed for estimating standard heat of formation of alloys and covalent compounds.

2. THE NEW GROUP CONTRIBUTION EQUATIONS

As mentioned above, alloys and covalent compounds cannot be divided into cations and anions whose number of electric charge is integer. In this work, the elements that make up the alloys and covalent compounds are considered the basic functional groups. Therefore, the knowledge of physical properties of the elements such as the absolute entropy of an element at $298K$ and $0.1MPa$ can be used in estimating the compound properties.

The compounds studied in this work were solid inorganic compounds classified into two categories: alloys composed entirely of metallic elements, and covalent compounds composed of metallic and nonmetallic elements. A different correlation was developed for each category.

2.1. Alloys

In this investigation, the solid compound was treated as an assumed solid solution or mixture of elements, and its standard heat of formation was considered as an assumed heat of mixing. Therefore, the concept of mixing rule used for mixtures can be introduced. According to the basic thermodynamic relation the standard heat of formation of a compound can be expressed by the following equation:

$$\triangle H^{\circ}_{f,298} = \triangle G^{\circ}_{f,298} + T^{\circ} \triangle S^{\circ}_{f,298} \tag{1}$$

where

$$\triangle G^{\circ}_{f,298} = G^{\circ} - \sum_i n_i G^{\circ}_i \tag{2}$$

$$\triangle S^{\circ}_{f,298} = S^{\circ} - \sum_i n_i S^{\circ}_i \tag{3}$$

$T^{\circ} = 298.15K$, G°_i and S°_i are Gibbs free energy and entropy of element i , G° and S° are Gibbs free energy and entropy of a compound at the standard state, respectively. n_i is number of occurences of element i. Substituting Eqs. (2) and (3) into Eq. (1) the following equation is obtained:

$$\triangle H^{\circ}_{f,298} = H^{\circ} - \sum_i n_i G^{\circ}_i - T^{\circ} \sum_i n_i S^{\circ}_i \tag{4}$$

H° is the enthalpy of a compound at the standard state. The entropy of an element S°_i is usually available. In this work, the enthalpy of a compound at the standard state H° and Gibbs free energy of an element G°_i were calculated by group contribution method.

For binary alloys in which the element ratio is equal to one, the proposed equation for estimating standard heat of formation is as follows:

$$\triangle H^{\circ}_{f,298} = \sum_i x_i \sum_j x_j H^{*}_{ij} - \sum_i n_i G^{*}_i - T^{\circ} \sum_i n_i S^{\circ}_i \tag{5}$$

where

$$H^{*}_{ij} = \begin{cases} \triangle H_i & i = j \\ -\sqrt{|\triangle H_i \triangle H_j|} & i \neq j \end{cases}$$

$$G^{*}_i = \triangle G_i / r_i + r_i \ln(N_{p_i})$$

$$x_i = n_i / \sum_j nj$$

$\triangle H_i$ is the contribution value of element i to H°, $\triangle G_i$ is the contribution value of element i to G_i° , r_i is the covalent radius of element i, N_{p_i} is the periodic number in the periodic table of elements for element i.

For binary alloys with an element ratio not equal to one, the equation for estimating standard heat of formation is as follows:

$$\triangle H_{f,298}^\circ = \sum_i x_i \sum_j x_j H_{ij}^* + \prod_i x_i \alpha_i - \sum_i n_i G_i^* - T^\circ \sum_i n_i S_i^\circ \tag{6}$$

where

$$\alpha_i = C/(r_i N_{p_i} N_{g_i})$$

C is a constant for each group of elements in the periodic table, N_{g_i} is the group number in the periodic table for element i.

2.2 Covalent compounds

Since there is a larger difference between the thermodynamic properties of covalent compounds and those of alloys, the same equations (Eqs. (5) and (6)) give larger correlation errors for covalent compounds than for alloys. In this investigation, the following equation for estimating standard heat of formation of covalent compounds was developed:

$$\triangle H_{f,298}^\circ = \prod_i f_i \triangle H_i - \sum_i n_i G_i^* - T^\circ \sum_i n_i S_i^\circ \tag{7}$$

where

$$f_i = \log[10 n_i + B/\ln(r_i N_{p_i} N_{g_i})] + C \ln(r_i N_{p_i})$$

$G_i^* = \triangle G_i$, and B is a constant for all elements, but C is a constant for each group of elements in the periodic table.

2.3. Evaluation of model parameters

Contribution values of 64 groups and 31 constants in Eqs. (5), (6) and (7) were evaluated by correlating experimental data of standard heat of formation of 500 compounds [6,7]. The Simplex method of Nelder-Mead [8] was used to optimize the following objective function:

$$OF = \sum_{k=1}^{NC} |(\triangle H^{\circ}_{f,298,exp} - \triangle H^{\circ}_{f,298,cal}) / \triangle H^{\circ}_{f,298,exp}|_k \tag{8}$$

For alloys, group-contribution values in Eqs. (5) and (6) are listed in Table 1. Table 2 gives group-contribution values in Eq.(7) for covalent compounds. Entropy S°_i, covalent radius r_i, periodic number N_{p_i} and group number N_{g_i} needed in the calculations for each element i are tabulated in Table 3. The values for constant C in Eqs. (6) and (7) are shown in Table 4. The constant B in Eq. (7) is equal to 1.871657.

3. RESULTS

Experimental data of standard heat of formation for 230 alloys and 270 covalent compounds were correlated by the proposed models and the Mostafa's model, respectively. Results show that the overall average errors of the proposed models are 6.95% for 1 : 1 alloys, 9.00% for other alloys, and 11.45% for covalent compounds. In comparison, the overall average errors of Mostafa's model are 19.4%, 34.9%, 44.26%, respectively. The correlation error of the proposed models is about 1/3 of that of Mostafa's model.

Standard heat of formation of 11 solid compounds, whose experimental data were not used in correlating the models, were predicted by the proposed models with satisfactory results. Table 5 shows the comparison of the predicted results by the proposed models and by the Mostafa's model.

LIST OF SYMBOLS

B	constant in Eq. (7)
C	constant in Eqs. (6) and (7)
G°	Gibbs free energy of a compound at the standard state ($kJ \cdot mol^{-1}$)
G_i°	Gibbs free energy of element i ($kJ \cdot mol^{-1}$)
$\triangle G_i$	contribution value of group i to G_i°
$\triangle G_{f,298}^\circ$	standard Gibbs free energy of formation ($kJ \cdot mol^{-1}$)
H°	enthalpy of a compound at the standard state ($kJ \cdot mol^{-1}$)
H_i°	enthalpy of element i ($kJ \cdot mol^{-1}$)
$\triangle H_i$	contribution value of group i to H°
$\triangle H_{f,298}^\circ$	standard heat of formation ($kJ \cdot mol^{-1}$)
n	number of group
N_{p_i}	periodic number in the periodic table for element i
N_{g_i}	group number in the periodic table for element i
r	covalent radius of an element (Å)
S°	entropy of a compound at the standard state ($kJ \cdot mol^{-1} \cdot K^{-1}$)
S_i°	entropy of element i ($kJ \cdot mol^{-1} \cdot K^{-1}$)
$\triangle S_{f,298}^\circ$	standard entropy of formation ($kJ \cdot mol^{-1} \cdot K^{-1}$)
superscript	
$\circ$	standard state
subscript	
cal	calculated
exp	experimental
$f, 298$	property of formation at $298K$
i, j	group
k	compound

REFERENCES

[1] R.C. Ried, J.M. Prausnitz, and T.K. Sherwood, The Properties of Gases and Liquids. third ed., McGraw-Hill, New York, 1977.

[2] R.C. Ried, J.M. Prausnitz, and B.E. Poling, The Properties of Gases and Liquids. fourth ed., McGraw-Hill, New York, 1987.

[3] A.T.M.G. Mostafa, J.M. Eakman, and S.L. Yarbro, Ind. Eng. Chem. Res., 34 (1995) 4577-4582

[4] A.T.M.G. Mostafa, J.M. Eakman, M.M. Montoya, and S.L. Yarbro, Ind. Eng. Chem. Res., 35 (1996) 343-348

[5] S.W. Benson, F.R. Cruickshank, D.M. Haugen, et al., Chem. Rev., 69 (1969) 279-324.

[6] D.D. Wagman, W.H. Evans, V.B. Parker, et al., J. Phys. Chem. Ref. Data, 11, New York NSRDS, 1982.

[7] I. Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaft mbH, FRG, 1989.

[8] J.A. Nelder and R. Mead, Comput. J., 8 (1965) 308-312

Table 1 Group Contribution Values in Eqs. (5) and (6)

	Eq. (5)		Eq. (6)	
group	$\triangle H$	$\triangle G$	$\triangle H$	$\triangle G$
Al	-2.547775×10	9.485637×10	1.179107×10^2	5.235700×10
Au	-1.883018×10^{-5}	2.334619	-1.864642×10	-3.335688×10
Ba			-3.429983×10^2	1.437883×10
Bi	-4.277584×10^{-3}	-3.474214×10	1.162402×10^2	8.715712×10
Ca	-9.080121×10^{-7}	2.216442×10^2	4.038583×10	1.448583×10^2
Cd	-3.696692	2.616880	-7.527930×10	-3.241828×10
Ce	-6.479415	-1.035324×10	5.442904×10^2	1.036363×10^2
Co	-4.452246	-3.513106	-3.442737×10	-1.223410
Cr			1.109613	-9.363646
Cu	2.751714×10^{-3}	-1.441993×10	-5.613933×10^{-1}	-1.215161×10
Fe	2.084221×10^{-5}	-5.907930×10	-6.496573	-8.072864×10^{-1}
Ga	3.287209	-1.250522×10^2	1.171720×10^2	4.463346×10
Ge	1.251058×10^2	-5.189408×10	-2.277249×10	1.945401×10
Hg	2.329306×10^2	1.455467×10	8.779343	-3.507428×10
In	7.116738	1.312014×10	-1.555072×10^2	-5.265865×10
K	-5.873920	1.054520×10^2	3.481458×10^2	1.054895×10^2
La	-3.559827	-1.098382×10	1.819911×10^2	8.745044×10
Li	-9.809121×10	-3.989451×10^{-1}	-9.645347×10	3.943631×10
Mg	2.694289×10	-1.895389×10	7.071826×10^{-1}	-1.810415×10
Mn	1.523531	1.689250×10	-4.275928	-7.184034

Table 1 (continued)

	Eq. (5)		Eq. (6)	
group	$\triangle H$	$\triangle G$	$\triangle H$	$\triangle G$
Mo			3.202029	-3.277570×10
Na	-4.592755×10	-1.502860×10	2.528262×10^{2}	5.452215×10
Nb			1.195689×10	6.791362
Ni	-1.572591×10	-2.894370	-7.419577×10	7.786413
Pb	-9.158692×10	-9.700515×10	2.019791×10	-1.930488×10
Pr	-2.823006×10	-3.481951	-6.319589×10	4.301640×10
Rb	-6.616758	1.434214×10^{2}	3.488986×10	1.089340×10^{2}
Sb	2.564174×10	-1.448817×10	5.538633×10	-5.338176×10^{-1}
Sn	-1.361897×10	-5.761840	1.080848×10^{2}	3.239968×10
Sr	-1.203010×10	3.083991×10^{2}	-1.717431×10^{2}	1.171444×10^{2}
Ta			3.287947×10^{2}	5.088807×10
Th	-1.567242×10^{2}	2.232564×10	1.858117×10^{2}	5.542607×10
Ti	8.724409×10^{-8}	9.281155×10	1.070095×10^{2}	2.631314×10
Tl	3.649051×10^{-7}	-1.383732	-7.878264×10	-3.828927×10
U	-3.095126×10^{-1}	1.468445×10^{2}	1.449111×10^{-1}	1.291050×10
V			-8.418723×10	-5.075184×10
W			1.799521×10^{3}	-5.915926
Y	8.867661×10^{-5}	3.006253×10	1.468791×10^{2}	9.847638×10
Zn	-8.830403	2.587251	-8.586199	1.368690×10

Table 2 Group Contribution Values in Eq. (7)

group	$\triangle H$	$\triangle G$	group	$\triangle H$	$\triangle G$
Al	-7.204662×10	8.390300×10	N	7.768515	-3.760277
Ag	-1.032491×10^3	-2.299243×10	Na	7.707443×10	1.866753×10^2
As	-4.125938	1.316704×10	Nb	-1.148827×10^2	1.146555×10^2
Au	$5.520272D-03$	-9.849081×10	Ni	4.557773×10	3.220369×10
B	2.515328	4.245996×10	O	6.854222	2.698764×10^2
Ba	5.635018	6.967224×10	P	2.704476	7.706615×10
Bi	-1.446955×10^2	-2.554732×10^2	Pb	4.971642×10	-5.679807×10^2
C	1.805951	-1.279682	Pd	1.669596×10^2	2.866064×10
Ca	-1.516622×10^2	-3.506314×10	Pr	-1.493080×10	3.631194×10^2
Cd	-1.150475×10^2	1.923645×10^2	Pt	2.161230×10^2	6.780547×10
Ce	-4.595508×10^2	-6.919374×10	Rb	3.864891×10	7.687927×10
Cl	9.455100	1.405818×10^2	Re	-1.058977×10	5.028698
Co	8.435930	4.203345	S	5.852356	8.513777×10
Cr	2.467709	1.228178×10	Sc	-4.286165×10^3	1.600817×10^3
Cs	1.083060×10^2	1.885612×10^2	Se	3.286687	2.108180×10
Cu	2.010446×10^2	-2.185881×10	Si	3.133557	2.107106×10
F	7.695698	3.511720×10^2	Sn	-9.948965	1.376805×10
Fe	1.052125×10	7.393210	Ta	-4.984421×10	4.072078×10
Ga	-6.179177	1.080938×10^2	Tb	-3.163823×10^2	-8.623455×10
H	-5.498074×10^{-1}	-8.179586×10	Te	-5.819399	3.671637×10
Hf	9.825033	2.098489×10^2	Th	-2.260972×10^2	1.710950×10^2
Ho	2.909510×10^2	1.886210×10	Ti	5.837112	1.257576×10^2
I	8.872796×10^{-1}	7.262360	Tl	-2.978788×10^2	-4.664417×10^2
In	1.389605×10	-2.756333×10	U	-1.246233×10^2	1.086456×10^2
Ir	-1.202410×10^2	5.028018×10	V	-2.290800×10	7.875071×10
K	1.831853×10	4.553135×10	W	4.006844	4.914422
La	1.449894×10^3	1.960074×10^2	Y	8.514982×10^2	2.043639×10^2
Mg	1.000210×10^3	8.402736	Zr	1.492177	1.090187×10^2
Mn	1.075300	2.176377×10	Zn	-6.021647×10	7.395255×10
Mo	1.579494	3.285290×10			

Table 3 Parameters for elements used in the calculations

group	$S_i^\circ \times 10^3$ $kJ \cdot mol^{-1} \cdot K^{-1}$	r_i Å	N_{p_i}	N_{g_i}	group	$S_i^\circ \times 10^3$ $kJ \cdot mol^{-1} \cdot K^{-1}$	r_i Å	N_{p_i}	N_{g_i}
Al	28.2750	1.180	3	3	Mo	28.5935	1.300	5	6
Ag	42.6768	1.340	5	1	N	95.8045	0.549	2	5
As	35.7063	1.200	4	5	Na	51.4550	1.539	3	1
Au	47.4968	1.340	6	1	Nb	36.4010	1.340	5	5
B	5.8300	0.795	2	3	Ni	29.8738	1.150	4	8
Ba	62.4169	1.980	6	2	O	102.5735	0.604	2	6
Bi	56.7350	1.460	6	5	P	41.0700	0.947	3	5
C	5.7404	0.772	2	4	Pb	64.7851	1.470	6	4
Ca	41.4216	1.740	4	2	Pd	37.8234	1.280	5	8
Cd	51.7979	1.480	5	2	Pr	73.9313	1.650	6	3
Ce	69.4544	1.650	6	3	Pt	41.6308	1.300	6	8
Cl	111.5583	0.994	3	7	Rb	76.7800	2.160	5	1
Co	30.0411	1.160	4	8	Re	36.5263	1.280	6	7
Cr	23.6396	1.180	4	6	S	32.0560	0.944	3	6
Cs	85.1470	2.350	6	1	Sb	45.5219	1.400	5	5
Cu	33.1640	1.170	4	1	Sc	34.6435	1.440	4	3
F	101.3975	0.709	2	7	Se	42.2584	1.076	4	6
Fe	27.2797	1.170	4	8	Si	18.8196	1.126	3	4
Ga	40.8275	1.260	4	3	Sn	51.1954	1.410	5	4
Ge	31.0871	1.220	4	4	Sr	55.6900	1.910	5	2
H	65.3400	0.280	1	7	Ta	41.5053	1.340	6	5
Hf	43.5554	1.440	6	4	Tb	73.3037	1.590	6	3
Hg	75.8978	1.490	6	2	Te	49.4967	1.295	5	6
Ho	75.0191	1.580	6	3	Th	53.3878	1.650	7	3
I	58.0710	1.333	5	7	Ti	30.7590	1.320	4	4
In	57.8229	1.440	5	3	Tl	64.1826	1.480	6	3
Ir	35.5054	1.270	6	8	U	50.2917	1.420	7	3
K	64.6700	1.962	4	1	V	28.9114	1.220	4	5
La	56.9024	1.690	6	3	W	32.6603	1.300	6	6
Li	29.0800	1.336	2	1	Y	44.4341	1.620	5	3
Mg	32.6770	1.360	3	2	Zr	38.8690	1.450	5	4
Mn	32.0076	1.170	4	7	Zn	41.6308	1.250	4	2

Table 4 Constant C in Eqs.(6) and (7)

Group No.	Eq. (6)	Eq. (7)	Group No.	Eq. (6)	Eq. (7)
1A	163.0907	−0.1695938	1B	23.96351	−0.6166086
2A	−235.7235	−0.6813163	2B	−32.28444	−2.1371800
3A	−203.4436	−2.7029500	3B	−24.69000	−0.3644749
4A	251.5809	−1.7504590	4B	−136.2114	−6.9506290
5A	65.57764	−0.9357792	5B	11.53414	−0.4572245
6A		−0.7699247	6B	−565.7197	0.4796362
7A		−1.6300300	7B	−358.3441	−0.8830953
			8B	23.24426	−0.4141101

Table 5 Predicted Results by the Proposed Models

in Comparison with the Mostafa's Model

No.	Compounds	$\triangle H^{\circ}_{f,298,exp}$ $kJ \cdot mol^{-1}$	This Work $\triangle H^{\circ}_{f,298,cal}$ $kJ \cdot mol^{-1}$	This Work error %	Mostafa's Model $\triangle H^{\circ}_{f,298,cal}$ $kJ \cdot mol^{-1}$	Mostafa's Model error %
1	UBi2	−109.00	−136.03	24.7	−165.09	51.4
2	U3Bi4	−385.00	−361.90	5.99	−340.09	11.6
3	MgCu2	−33.560	−33.490	0.20	−10.407	68.9
4	Mg2Cu	−28.620	−29.855	4.31	−10.096	64.7
5	K3Bi	−232.20	−173.14	25.4	−248.74	7.12
6	CaAl4	−213.00	−207.55	2.55	−263.89	23.8
7	Fe0.877S	−105.44	−103.73	1.61	−110.36	4.66
8	Si2Th3	−284.93	−272.26	4.44	−1095.1	284.5
9	Fe0.947O	−266.27	−291.94	9.64	−366.38	37.5
10	NiS0.84	−82.425	−104.46	26.7	−102.76	24.7
11	Co3O4	−910.02	−1169.3	28.4	−1447.1	59.0
	Total			11.3		58.0