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SOME REGULARITIES OF STANDARD ENTHALPIES OF FORMATION (SEF) FOR RELATIVE INORGANIC COMPOUNDS

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Abstract

The empirical regularities of the SEF for relative inorganic substances in binary and quasibinary systems (energetic and dimensional rules of linear approximation – ELAR and DLAR) are described.

Keywords: complex oxide, intermetallid, regularity, standard enthalpy of formation (SEF)

Introduction

For different thermodynamic investigations, and especially for thermodynamic simulations [1, 2], it is necessary to know the main thermochemical properties of inorganic substances, including the SEF. The operative methods of calculation of properties are currently very popular [3, 4].

The goals of this work are: (i) with the help of analysis of known reference thermochemical data, to establish regularities of the changes in the SEF for relative inorganic compounds, and (ii) to use them to correct known and to estimate unknown SEF.

Investigation methods

The procedures were described in detail in Refs [5–8]. In the present article, we illustrate only the principles of the methods used on the examples of complex relative oxides and double intermetallides.

The system A_lO_m–B_pO_q. For the complex oxides $A_xB_yO_z$, the SEF are presented in the form

$$H^{\circ}_{at}(F)_j = \Delta H^{\circ}_{298}(ox)_j / n_j,\ kJ\ (\text{g-atom})^{-1} \qquad (1)$$

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where ΔH^o_{298} (ox)$_j$ and n_j are the SEF of complex oxide j from a simple one, and the number of atoms in a molecule of complex oxide j, respectively. It is clear that, for simple oxides, $H^o_{at}(F)$ is equal to 0.

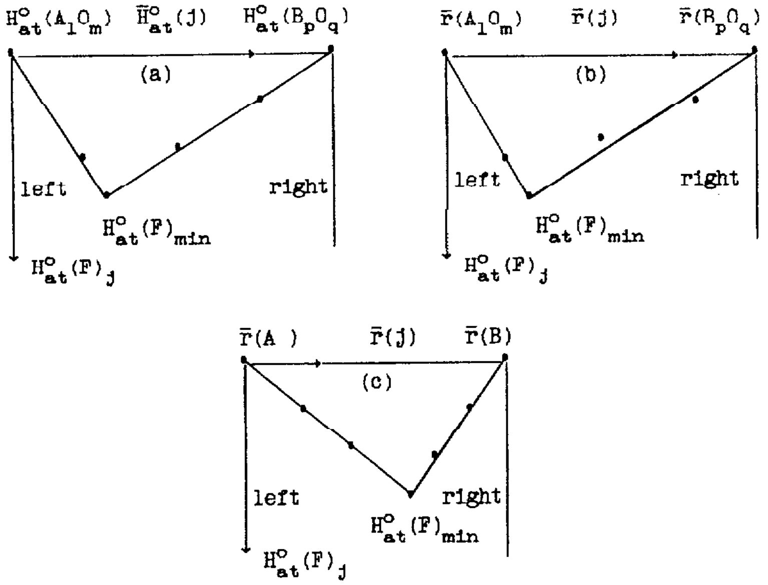

Fig. 1 Schemes of graphical analysis of $H^o_{at}(F)_j$ changes for relative substances, (a) and (b): for the system A_lO_m–B_pO_q ; Eqs (2) and (3), respectively, (c): for system A–B; Eq. (11)

By means of graphical analysis, we investigated the following dependences:

$$H^o_{at}(F)_j = f[\bar{H}^o_{at}(j),\ H^o_{at}(A_lO_m),\ H^o_{at}(B_pO_q)] \tag{2}$$

$$H^o_{at}(F)_j = f[\bar{r}(j),\ \bar{r}(A_lO_m),\ \bar{r}(B_pO_q)] \tag{3}$$

where

$$\bar{H}^o_{at}(j) = [x(A_lO_m)\cdot\Delta H^o_{298}(A_lO_m) + x(B_pO_q)\cdot\Delta H^o_{298}(B_pO_q)]\ /\ n_j,\ \text{kJ (g-atom)}^{-1} \tag{4}$$

$$H^o_{at}(A_lO_m) = \Delta H^o_{298}(A_lO_m)\ /\ (l + m),\ \text{kJ (g-atom)}^{-1} \tag{5}$$

$$H^o_{at}(B_pO_q) = \Delta H^o_{298}(B_pO_q)\ /\ (p + q),\ \text{kJ (g-atom)}^{-1} \tag{6}$$

$$\bar{r}(j) = \left(\frac{x}{x+y+z}\right)r_A + \left(\frac{y}{x+y+z}\right)r_B + \left(\frac{z}{x+y+z}\right)r_O,\ \text{nm} \tag{7}$$

$$\bar{r}(A_lO_m) - \left(\frac{l}{l+m}\right)r_A + \left(\frac{m}{l+m}\right)r_O,\ \text{nm} \tag{8}$$

$$\bar{r}(B_pO_q)=\left(\frac{p}{p+q}\right)r_B+\left(\frac{q}{p+q}\right)r_O,\ \text{nm} \qquad (9)$$

The conditional dimensions of molecules of complex oxides, (7), and simple oxides, (8) and (9), were calculated with use of the ionic radii of elements A, B and O for a coordination number of 6 [9].

Equation (4) can be interpreted as the SEF of the hypothetical ideal solid solution, where $x(i)$ is the mole fraction of simple oxide i in complex oxide j.

In a common case, the dependences (2) and (3) have a minimum ($H^{o}_{at}(F)_{min}$ values), and between H^{o}_{at} (A_lO_m) (or $\bar{r}$ (A_lO_m)) and H^{o}_{at} $(F)_{min}$, and between H^{o}_{at} $(F)_{min}$ and H^{o}_{at} (B_pO_q) (or $\bar{r}$ (B_pO_q)), they can be described by linear regression equations (Fig. 1). For some systems, only the left or right dependences (2) and (3) can exist.

Table 1 Standard enthalpies of some complex oxides, estimated with the help of ELAR and DLAR

Complex oxide	ΔH^{o}_{298}(ox)/kJ mol^{-1}		ΔH^{o}_{298}(ox)/ kJ mol^{-1}
	ELAR	DLAR	
$Na_6Si_2O_7$	−737.6	−696.8	−717.2±19.8
$Na_2Si_4O_9$	−230.6	−228.0	−229.3±1.3
$Na_6Si_8O_{19}$	−567.1	−684.7	−625.9±58.8
$K_2Si_3O_7$	−296.3	−298.8	−297.6±1.25
Ba_3SiO_5	−237.9	−267.0	−252.4±14.6
$Ba_3Si_{15}O_{13}$	−526.1	−503.0	−514.6±11.6
$Ba_2Si_{12}O_{31}$	−733.2	−742.1	−737.6±4.5
$Pb_3Si_2O_7$	−34.8	−33.9	−34.4±1.4
$Pb_{11}Si_3O_{27}$	−63.6	−40.6	−52.1±11.5
$Ca_2B_6O_{11}$	−239.0	−227.4	−233.2±5.8
$Na_2B_8O_{13}$	−345.5	−325.1	−335.3±10.2
$Na_4B_{10}O_{17}$	−665.5	−650.3	−657.6±7.6
NaB_9O_{14}	−179.6	−162.5	−171.0±8.6
$Ca_5Al_6O_{14}$	−66.8	−68.4	−67.6±0.8
$Ca_4Al_6O_{13}$	−70.7	−68.4	−69.2±0.8
$Sr_{16}V_{18}O_{61}$	−2968.3	−2874.4	−2921.4±47.0
$Ca_5Ti_4O_{13}$	−361.5	−356.8	−359.2±2.4
$Na_8Ti_{15}O_{14}$	−975.2	−1025.8	−1000.0±25.3
$Na_2Ti_6O_{13}$	−331.8	−273.9	−302.9±30.0

The systems A–B (intermetallides). The SEF of $A_xB_y(j)$ are presented in the form

$$H^{o}_{at}(F)_j = \Delta H^{o}_{298}(j) / (x+y), \text{ kJ (g-atom)}^{-1} \tag{10}$$

The dependences

$$H^{o}_{at}(F)_j = f[\bar{r}(j), r(A), r(B)] \tag{11}$$

have been investigated graphically.

In Eq. (11),

$$\bar{r}(j) = r_A\left(\frac{x}{x+y}\right) + r_B\left(\frac{y}{x+y}\right), \text{ nm} \tag{12}$$

where r_A and r_B are the atomic radii of elements A and B for a coordination number of 12 [9].

After graphical analysis of dependence (11), we found that the regularities of the changes in the SEF for intermetallides are similar to those discovered earlier for dependence (3) (Fig. 1).

A study of 34 quasibinary systems [5, 6] revealed that the average difference between the values of the SEF calculated according to Eq. (2) and reference data [7–14] was ±5%. For the same systems and literature sources, the average difference of the values calculated with Eq. (3) from the reference data was not more

Table 2 Standard enthalpies of some intermetallides, calculated with the help of DLAR (in kJ (g-atom^{-1})

Compounds	$-\Delta H^{o}_{298}$	Compounds	$-\Delta H^{o}_{298}$	Compounds	$-\Delta H^{o}_{298}$	Compounds	$-\Delta H^{o}_{298}$
Au_9In_4	17.7	Cu_4Al	7.8	Ti_9Al	15.0	Fe_3As_2	49.7
Au_3In_2	22.9	Cu_2Al_3	14.4	Ti_2Al	50.0	$Fe_{12}As_5$	35.4
$Au_{87}In_{13}$	7.6	$FeAl_4$	13.2	Ti_5Al	45.0	Cu_5As_2	25.6
Au_7In	7.2	Fe_2Al_9	12.0	Ti_9Al_{23}	42.0	Cu_6As	12.8
$Au_{39}In_{11}$	12.6	$FeAl_6$	9.4	$Cu_{11}In_9$	0.88	Cu_2As	29.8
Cu_4As	26.25	Pd_5Al_3	74.6	Cu_4In	0.40	Cu_2As_3	35.8
Cr_5As_3	49.4	$PdAl_2$	66.3	$PdIn_3$	63.3	Cu_3As_4	38.3
Cr_4As_3	56.25	$PdAl_3$	49.75	$PtIn_2$	37.1	$CuAs$	44.7
$CrAs_2$	31.6	$Pt_{13}Al_3$	37.6	Pt_3In	27.85	$PdAs$	100.0
Au_3Al	24.4	Rh_4Al_{13}	34.5	Pt_4In_3	47.7	Ti_3As	61.5
Au_5Al	36.6	$RuAl_3$	23.6	$PtIn$	55.7	Ti_5As_3	92.2
Cu_3Al	13	Ru_4Al_{13}	27.5	$TiIn_3$	13.5	Ti_4As_3	105.5

than ±9.0% [7]. For double intermetallides (31 systems), the average difference of the values calculated with Eq. (11) from the reference data [10, 18 and 19] was ±7.2% [8].

Results and discussion

For all systems, the regression coefficients of the left and right dependences (2), (3) and (11) were determined. With the help of these, the SEF of 121 quasibinary compounds [5–7] and 144 intermetallides [8] were revised.

Unknown SEF values for different substances were calculated. Some of these are presented in Tables 1 and 2.

The empirical regularities observed were named the energetic and dimensional rules of linear approximation (ELAR and DLAR).

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