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Empirical dependences of the standard enthalpy of formation for related inorganic compounds enhancing glass formers[1]

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Abstract

For the double oxides and other related double $A_xB_yC_z$ compounds in the system AC–BC, linear correlations have been observed between standard enthalpies of formation of the double compounds $A_xB_yC_z$ from the component compounds AC and BC ($\Delta H^0_{\mathrm{f,cc}}$ in kJ (g-atom)$^{-1}$ and values of the sum of the molar fraction enthalpies of the component compounds AC and BC ($\Delta \bar{H}^0_{\mathrm{f}} = x_{\mathrm{AC}}\Delta H^0_{\mathrm{f}}(\mathrm{BC})$, in kJ (g-atom)$^{-1}$. In general, the dependence of $H^0_{\mathrm{f,cc}} = f(\Delta \bar{H}^0_{\mathrm{f}})$ has a minimum, its branches being described with the help of linear equations (the average deviation from the known $\Delta H^0_{\mathrm{f,cc}}$ values was less than ± 4.7% for 121 double compounds in 34 systems). A conclusion has been drawn that these regularities (linear approximation rule — LAR) are characteristic for different types of inorganic double compound.

Keywords: Double compounds; Double oxides; Enthalpy; Pseudobinary systems; System AC–BC

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1. Introduction

Several methods of calculation have been proposed for the determination of standard enthalpies of complex compounds [1–8]. These methods are usually based on certain regularities assuming relative and/or similar substances.

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[1] Dedicated to Professor Hiroshi Suga.

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In this report we present some empirical dependences for standard enthalpies of formation of double oxides and other double compounds from the component compounds ($\Delta H^0_{f,cc}$, in kJ (g-atom)$^{-1}$ as well as some relationships between the $\Delta H^0_{f,cc}$ values and values of the standard enthalpies of formation of the component compounds (ΔH^0_f, in kJ (g-atom)$^{-1}$. The information has been collected from the analysis of 34 pseudobinary systems, i.e. oxide–oxide (26), compound–H_2O (5), halide–halide (1) and halide–NH_3 (2).

2. Method of investigation: oxide–oxide system as an example

For double oxides $A_xB_yO_z$ in the system AO–BO we have investigated the dependence

$$\Delta H^0_{f,cc}(A_xB_yO_z) = f(\Delta \bar{H}^0_f) \tag{1}$$

where $\Delta H^0_{f,cc}(A_xB_yO_z)$ is a standard enthalpy of formation of the double oxide $A_xB_yO_z$ from the component oxides AO and BO and $\Delta \bar{H}^0_f$ represents the sum of molar fraction enthalpies of the component oxides AO and BO according to the following relationship.

$$\Delta \bar{H}^0_f = x_{AO}\Delta H^0_f(AO) + x_{BO}\Delta H^0_f(BO) \tag{2}$$

$\Delta H^0_f(AO)$ and $\Delta H^0_f(BO)$ are the standard enthalpies of formation of the component oxides from the elements and x_{AO} and x_{BO} are the molar fractions of the component oxides in the double oxide $A_xB_yO_z$ with a given composition. Throughout the paper all enthalpy values are expressed in kJ (g-atom)$^{-1}$ of the relevant oxide at a temperature of 298.15 K. $\Delta H^0_{f,cc}(A_xB_yO_z)$ is given in relation to the standard enthalpy of formation of double oxide $A_xB_yO_z$ from the elements ($\Delta H^0_{f,el}(A_xB_yO_z)$) by the following equation

$$\Delta H^0_{f,cc} = \Delta H^0_{f,el} - \Delta H^0_f \tag{3}$$

For determination of the shape of the dependence given in Eq. (1) we constructed graphs of $\Delta H^0_{f,cc}(A_xB_yO_z)$ vs. $\Delta \bar{H}^0_f = f(\Delta H^0_f(AO), \Delta H^0_f(BO))$ for each system under investigation. It is worth noting that $|\Delta H^0_f(AO)| > |\Delta H^0_f(BO)|$ in all cases. The characteristic groups of dependences Eq. (1) are shown in Fig. 1. As it can be seen from this figure, te dependence Eq. (1) exhibits a minimum and its branches can be approximated by linear equations of the form

$$\Delta H^0_{f,cc} = A + B\Delta \bar{H}^0_f \tag{4}$$

For calculation of the constants *A* and *B* linear regression analysis was used with constraints of the following type

$$\Delta H^0_{f,cc} = 0 \quad \text{if} \quad x_{AO} = 1 \quad \text{or} \quad x_{BO} = 1 \tag{5}$$

3. Results and discussion

Calculated results are given in Table 1 for all 34 systems. All enthalpy values for the simple and double compounds necessary for the calculations were compiled from Refs.

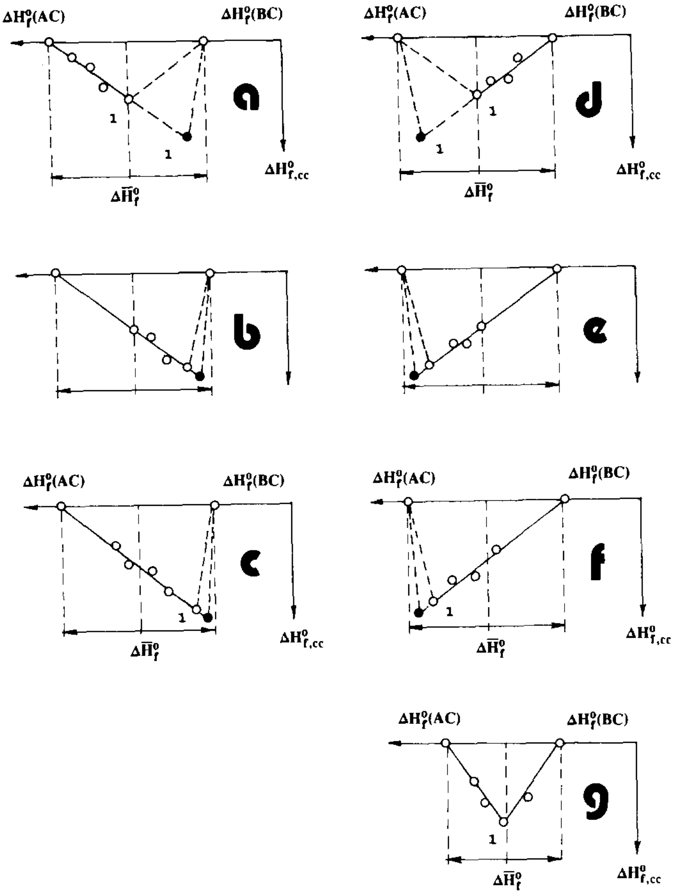

Fig. 1. Characteristic plots for the individual groups of compounds (groups a-g in Table 1: the left-sided example: a (B_2O_3-Na_2O), b (V_2O_5-Na_5O) and c (UO_3-Li_2O) types; right-sided examples: d (SiO_2-PbO), e (SrO-V_2O_5) and f (CaO-B_2O_3) types; symmetric example: g (TiO_2-MgO) type. The solid and dashed lines represent known and estimated data respectively, points designated "1" show existing and estimated minimum values. The cases a and d can be determined only after adding further data.

[5 and 9-17]. The average deviation between experimental values of $\Delta H^0_{\mathrm{f,cc}}$ and the values calculated according to the Eq. (4) (with constants A and B presented in Table 1) was less then $\pm$ 4.7% for all the 121 double compounds accountered in the 34 systems in question.

In the "left-sided" systems (Fig. 1, groups b and c) the minimum of $\Delta H^0_{\mathrm{f,cc}}$ is shifted to the higher concentrations of BC in the complex compounds; in the "right-sided" systems (Fig. 1, groups e and f) it is shifted to the higher concentrations of AC in the complex compounds. In the "symmetric" systems (Fig. 1, group g) the minimum of $\Delta H^0_{\mathrm{f,cc}}$ is observed for equimolar compositions ($x_{\mathrm{AC}} = x_{\mathrm{BC}}$). Because of a lack of complete information about the $\Delta H^0_{\mathrm{f,cc}}$ values for groups a and d it is not possible to

Table 1
Input data and the constants of Eq. (4) for various pseudobinary systems

System AC–BC and double compounds	$\Delta \bar{H}_f^0$/(kJ g-atom)$^{-1}$	$\Delta H^0_{f,cc}$/(kJ (g-atom)$^{-1}$		$\Delta H^0_{f,cc} = A + B\Delta \bar{H}^0_f$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	*A*	*B*	
Group "a"						
SiO_2-Rb_2O [9]						
1. SiO_2	−303.30	0	0	−155.555	−0.513	0
2. Rb_2SiO_3	−208.20	−46.50	−48.40	(points 1–4)		−4.9
3. $Rb_2Si_2O_5$	−239.90	−34.10	−32.50			+4.7
4. $Rb_2Si_4O_9$	−265.20	−22.10	−19.50			+11.6
5. Rb_2O	−113.00	0	–			–
B_2O_3-Na_2O [9]						
1. B_2O_3	−254.60	0	0	−164.050	−0.644	0
2. $NaBO_2$	−196.35	−33.40	−37.50	(points 1–4)		−12.3
3. $Na_2B_4O_7$	−215.80	−25.50	−25.00			+2.0
4. $Na_2B_6O_{10}$	−225.50	−20.60	−18.80			+8.9
5. Na_2O	−138.10	0	–			–
TiO_2-Na_2O [9]						
1. TiO_2	−314.07	0	0	−139. 700	−0.644	0
2. Na_2TiO_3	−226.09	−39.13	−39.13	(points 1–4)		0
3. $Na_2Ti_2O_5$	−255.10	−26.80	−26.05			+2.7
4. $Na_2Ti_3O_7$	−270.10	−20.70	−19.60			+5.6
5. Na_2O	−138.10	0	–			–
SiO_2-K_2O [9]						
1. SiO_2	−303.30	0	0	−163.848	−0.540	0
2. $K_2Si_4O_9$	−266.70	−21.00	−19.8	(points 1–4)		+5.9
3. $K_2Si_2O_5$	−242.20	−36.00	−32.9			+8.6
4. K_2SiO_3	−211.90	−46.10	−49.4			−7.4
5. K_2O	−120.50	0	–			–
KCl-$AlCl_3$ [9]						
1. KCl	−218.40	0	0	−108.582	−0.497	0
2. $KCl \cdot AlC_3$	−197.20	−8.73	−10.50	(points 1–4)		−20.3
3. $3KCl \cdot AlCl_3$	−207.80	−8.71	−5.30			+20.9
4. $3KCl \cdot 2AlCl_3$	−201.40	−8.44	−8.44			0
5. $AlCl_3$	−176.00	0	–			–
Group "b"						
V_2O_5-Na_2O [9]						
1. V_2O_5	−221.50	0	0	−163.854	−0.740	0
2. $NaVO_3$	−179.80	−32.70	−30.90	(points 1–4)		+5.5
3. $Na_4V_2O_7$	−165.90	−41.50	−41.20			+0.7
4. $Na_6V_2O_8$	−159.00	−45.20	−46.30			−2.4
5. Na_2O	−138.10	0	–			–
$BaCl_2$-H_2O [9]						
1. $BaCl_2$	−286.20	0	0	−7.937	−0.028	0
2. $BaCl_2 \cdot H_2O$	−180.70	−2.70	−2.6	(points 1–3)		−1.9

Table 1. (Continued)

System AC–BC and double compounds	$\Delta\bar{H}^0_f$/(kJ g-atom)$^{-1}$	$\Delta H^0_{f,cc}$/(kJ (g-atom)$^{-1}$		$\Delta H^0_{f,cc} = A + B\Delta\bar{H}^0_f$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	A	B	
3. $BaCl_2 \cdot 2H_2O$	−158.90	−3.30	−3.50			−6.1
4. H_2O	−92.28	0	–			–
$KAl(SO_4)_2$–H_2O [9]						
1. $KAl(SO_4)_2$	−205.85	0	0	−6.604	−0.032	0
2. $KAl(SO_4)_2 \cdot 3H_2O$	−122.93	−2.54	−2.66	(points 1–3)		−4.6
3. $Kal(SO_4)_2 \cdot 12H_2O$	−103.80	−3.37	−3.30			−2.8
4. H_2O	−92.28	0	–			–
$BeSO_4$–H_2O [9]						
1. $BeSO_4$	−200.87	0	0	−10.428	−0.052	0
2. $BeSO_4 \cdot 2H_2O$	−130.40	−3.86	−3.66	(points 1–3)		+5.2
3. $BeSO_4 \cdot 4H_2O$	−116.40	−4.18	−4.39			−4.9
4. H_2O	−92.28	0	–			–
ZrO_2–BaO [5, 9, 11, 13]						
1. $ZreO_2$	−366.85	0	0	−204.296	−0.557	0
2. $BaZrO_3$	−321.80	−25.09	−25.09	(points 1–4)		0
3. $Ba_3Zr_2O_7$	−312.80	−31.15	−30.97			+0.6
4. Ba_2ZrO_4	−306.75	−31.87	−33.47			−5.0
5. BaO	−276.75	0	–			–
$Ca(NO_3)_2$–H_2O [9]						
1. $Ca(NO_3)_2$	−104.30	0	0	−26.228	−0.252	0
2. $Ca(NO_3)_2 \cdot 2H_2O$	−96.30	−2.05	−2.01	(points 1–4)		+1.9
3. $Ca(NO_3)_2 \cdot 3H_2O$	−95.30	−2.34	−2.26			−3.6
4. $Ca(NO_3)_2 \cdot 4H_2O$	−94.70	−2.41	−2.41			0
5. H_2O	−92.28	0	–			–
Group "c"						
SiO_2–BaO [9] [a]						
1. SiO_2	−303.30	0	0	−759.680	−2.505	0
2. $BaSiO_3$	−289.90	−32.05	−33.60	(points 1–3, 5, 6)		−4.7
3. $BaSi_2O_5$	−294.40	−21.87	−22.30			−1.8
4. Ba_2SiO_4	−285.50	−38.71	−35.40	1125.836	4.067	+8.6
5. $Ba_2Si_3O_8$	−292.60	−26.79	−26.80	(points 4, 6, 7)		0
6. $(Ba_8Si_5O_{18})$	−286.90	−41.08	−41.08			0
7. BaO	−276.60	0	0			0
P_2O_5–Na_2O [9]						
1. P_2O_5	−213.14	0	0	−284.180	−1.333	0
2. Na_3PO_4	−156.86	−68.76	−68.90	(points 1–4)		+1.0
3. $Na_4P_2O_7$	−163.09	−66.74	−66.72			0
4. $Na_5P_3O_{10}$	−166.24	−62.83	−75.04			−19.4
5. Na_2O	−138.1	0	–			–
SiO_2–Na_2O [9]						
1. SiO_2	−303.30	0	0	−141.277	−0.466	0

Table 1. (Continued)

System AC–BC and double compounds	$\Delta\bar{H}^0_f$/(kJ g-atom)$^{-1}$	$\Delta H^0_{f,cc}$/(kJ (g-atom)$^{-1}$		$\Delta H^0_{f,cc} = A + B\Delta\bar{H}^0_f$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	*A*	*B*	
2. Na_4SiO_4	−193.10	−40.90	−40.90	(points 1, 3, 4)		0
3. Na_2SiO_3	−220.20	−38.50	−38.50	102.753	0.744	0
4. $Na_2Si_2O_5$	−248.30	−26.00	−25.90	(points 2, 5)		+1.4
5. Na_2O	−138.10	0	0			0
UO_3–Li_2O [14]						
1. UO_3 [b]	−305.13	0	0	−122.784	−0.402	0
2. $Li_2U_3O_{10}$	−278.68	−11.87	−10.65	(points 1–4)		+10.3
3. Li_2UO_4	−252.22	−21.29	−21.29			0
4. Li_4UO_5	−234.55	−23.33	−28.40			−28.4
5. Li_2O	−199.31	0	–			–
Al_2O_3–Na_2O [9] [c]						
1. Al_2O_3	−333.07	0	0	−81.418	−0.244	0
2. $NaAl_{11}O_{17}$	−317.05	−5.70	−3.92	(points 1–4)		+31.2
3. $NaAl_5O_8$	−300.50	−9.05	−8.07	33.752	0.244	+10.8
4. $NaAlO_2$	−235.60	−23.83	−23.83	(points 4–6)		0
5. Na_5AlO_4	−160.90	−10.81	−5.6	65.452	0.474	+48.2
6. Na_2O	−138.10	0	0	(points 4, 5)		0
$UO_2(NO_3)_2$–H_2O [9]						
1. $UO_2(NO_3)_2$	−122.70	0	0	−20.570	−0.168	0
2. $UO_2(NO_3)_2 \cdot H_2O$	−107.50	−2.06	−2.54	(points 1–4)		−23.3
3. $UO_2(NO_3)_2 \cdot 2H_2O$	−02.30	−3.47	−3.41			+1.6
4. $UO_2(NO_3)_2 \cdot 3H_2O$	−100.00	−3.71	−3.80	76.751	0.832	−2.4
5. $UO_2(NO_3)_2 \cdot 6H_2O$	−96.60	−3.60	−3.60	(points 5, 6)		0
6. H_2O	−92.28	0	0			0
TiO_2–SrO [5]						
1. TiO_2	−314.07	0	0	−934.762	−2.976	0
2. $SrTiO_3$	−305.04	−27.64	−26.89	(points 1, 2, 6)		+2.7
3. Sr_2TiO_4	−302.02	−23.03	−21.45	−21.45		−6.1
4. $Sr_3Ti_2O_7$	−303.23	−25.78	−25.78	1055.530	3.566	0
5. $Sr_4Ti_3O_{10}$	−303.76	−26.69	−27.66	(points 3–7)		−3.6
6. $(Sr_6Ti_5O_{16})$	−304.22	−29.32	−29.32			0
7. SrO	−296.00	0	0			0
ZrO_2-Li_2O [16] [e]						
1. ZrO_2	−366.85	0	0	−31.955	−0.087	0
2. Li_2ZrO_3	−283.08	−7.38	−7.30	(points 1, 2, 5)		+1.2
3. $Li_6Zr_2O_7$	−266.33	−7.48	−8.03			−7.4
4. Li_8ZrO_6	−232.82	−4.49	−4.02	23.877	0.120	+10.9
5. $(Li_{22}Zr_8O_{27})$	−269.85	−8.45	−8.45	(points 3–6)		0
6. Li_2O	−199.31	0	0			0
Group "d"						
SiO_2–PbO [9]						
1. SiO_2	−303.30	0	–	4.075	0.037	–

Table 1. (Continued)

System AC–BC and double compounds	$\Delta \bar{H}_f^0$/(kJ g-atom)$^{-1}$	$\Delta H_{f,cc}^0$/(kJ (g-atom)$^{-1}$		$\Delta H_{f,cc}^0 = A + B\Delta \bar{H}_f^0$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	*A*	*B*	
2. $PbSiO_3$	−206.20	−3.53	−3.63	(points 2–5)		−2.7
3. Pb_2SiO_4	−173.80	−2.42	−2.42			0
4. Pb_4SiO_6	−147.90	−1.69	−1.45			+14.2
5. PbO	−109.10	0	0			0
ZrO_2–SrO [5]						
1. ZrO_2	−366.85	0	–	130.588	0.441	–
2. $SrZrO_3$	−331.43	−14.95	−15.64	(points 2–6)		−4.6
3. $Sr_4Zr_3O_{10}$	−326.40	−13.91	−13.42			+3.5
4. $Sr_3Zr_2O_7$	−324.34	−13.27	−12.510			+5.7
5. Sr_2ZrO_4	−319.59	−11.43	−10.42			+8.9
6. SrO	−296.00	0	0			0
Cs_2O–TeO_2 [15]						
1. Cs_2O	−115.77	0	–	1667.670	15.508	–
2. Cs_2TeO_3	111.40	−54.14	−59.97	(points 2–5)		−10.8
3. $Cs_2Te_2O_5$	−110.11	−40.16	−39.93			+0.6
4. $Cs_2Te_4O_9$	−109.08	−30.55	−24.00			+21.5
5. TeO_2	−107.53	0	0			0
Group "e"						
CaO–V_2O_5 [9]						
1. CaO	−317.55	0	–	76.195	0.344	–
2. CaV_2O_6	−269.53	−15.95	−16.52	(points 2–5)		−3.6
3. CaV_2O_7	−285.56	−23.90	−22.03			+7.7
4. $Ca_3V_2O_8$	−293.54	−24.78	−24.78			0
5. V_2O_5	−221.51	0	0			0
SrO–V_2O_5 [5]						
1. SrO	−296.00	0	–	145.446	0.657	–
2. SrV^2O_6	−258.20	−24.46	−24.46	(points 2–5)		0
3. $Sr_2V_2O_7$	−271.20	−35.64	−32.62			+8.5
4. $Sr_3V_2O_8$	−277.38	−36.16	−36.68			−1.4
5. V_2O_5	−221.51	0	0			0
NH_3(g)–HgI_2 [9]						
1. HN_3(g)	−73.52	0	–	87.505	2.491	–
2. $HgI_2 \cdot 1.333NH_3$	−57.05	−47.05	−54.60	(points 2–5)		−16.1
3. $HgI_2 \cdot 2NH_3$	−60.95	−71.20	−64.32			+9.7
4. $HgI_2 \cdot 6NH_3$	−68.05	−84.08	−82.46			+1.9
5. HgI_2	−35.13	0	0			0
NH_3(l)–HgI_2 [9]						
1. NH_3(l)	−66.00	0	–	110.961	3.159	–
2. $HgI_2 \cdot 1.333NH_3$	−52.76	−63.52	−55.70	(points 2–5)		+12.4

Table 1. (Continued)

System AC–BC and double compounds	$\Delta \bar{H}^0_f$/(kJ g-atom)$^{-1}$	$\Delta H^0_{f,cc}$/(kJ (g-atom)$^{-1}$		$\Delta H^0_{f,cc} = A + B\Delta \bar{H}^0_f$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	A	B	
3. $HgI_2 \cdot 2NH_3$	−55.94	−65.73	−65.73			0
4. $HgI_2 \cdot 6NH_3$	−61.60	−77.40	−83.60			−8.0
5. HgI_2	−35.13	0	0			0
Group "f"						
CaO–SiO_2 [9]						
1. CaO	−317.54	0	0	−1095.800	−3.451	0
2. $CaSiO_3$	−310.42	−16.70	−16.40	(points 1, 3–5)		+1.8
3. Ca_2SiO_4	−312.80	−18.90	−16.40			+13.2
4. Ca_3SiO_5	−314.00	−12.70	−12.20	698.584	1.303	+3.9
5. $Ca_3Si_2O_7$	−311.84	−19.70	−19.70	(points 2, 5, 6)		0
6. SiO_2	−303.30	0	0			0
CaO–TiO_2 [9][f]						
1. CaO	−317.54	0	0	−3388.470	−10.671	0
2. $CaTiO_3$	−315.81	−16.66	−16.58	(points 1, 3–5)		+0.5
3. $Ca_3Ti_2O_7$	−316.15	−13.40	−14.80			+9.5
4. $Ca_4Ti_3O_{10}$	−316.05	−17.51	−18.90	3003.402	9.563	−7.4
5. ($Ca_9Ti_8O_{25}$)	−315.90	−17.50	−17.50	(points 2, 5, 6)		0
6. TiO_2	−314.07	0	0			0
MoO_3–K_2O [10][g]						
1. MoO_3	−186.27	0	0	−345.540	−1.855	0
2. K_2MoO_4	−153.39	−56.82	−61.00	(points 1–6)		−7.3
3. $K_2Mo_2O_7$	−164.37	−40.64	−40.64			0
4. $K_2Mo_3O_{10}$	−169.83	−30.50	−30.50	208.158	1.728	0
5. $K_2Mo_4O_{13}$	−173.12	−25.41	−24.40	(points 6, 7)		+4.0
6. $K_2Mo_8O_{25}$	−179.38	−14.34	−12.80			+10.7
7. K_2O	−121.50	0	0			0
SrO–WO_3 [5][h]						
1. SrO	−296.00	0	0	−520.920	−1.760	0
2. $SrWO_4$	−253.36	−41.76	−41.56	(points 1, 3–5)		+0.5
3. Sr_2WO_5	−267.60	−43.93	−49.94			−13.6
4. Sr_3WO_6	−274.68	−40.56	−37.48	205.412	0.975	+7.6
5. ($Sr_9W_5O_{24}$)	−265.60	−53.16	−53.16	(points 2, 5, 6)		0
6. WO_3	−210.72	0	0			0
Al_2O_3–CaO [9]						
1. Al_2O_3	−333.07	0	–	146.094	0.460	–
2. $CaAl_2O_4$	−325.31	−3.69	−3.55	(points 2–7)		+4.0
3. $CaAl_4O_7$	−327.90	−5.00	−4.74			+5.2
4. $Ca_3Al_2O_6$	−321.43	−1.57	−1.76			−12.1
5. $Ca_{16}Al_2O_{19}$	−318.48	−0.53	−0.41			+22.6
6. $Ca_{12}Al_{14}O_{33}$	−323.30	−2.57	−2.62			−2.0
7. CaO	−317.55	0	0			0

Table 1. (Continued)

System AC–BC and double compounds	$\Delta \bar{H}^0_f$/(kJ g-atom)$^{-1}$	$\Delta H^0_{f,cc}$/(kJ (g-atom)$^{-1}$		$\Delta H^0_{f,cc} = A + B\Delta \bar{H}^0_f$/(kJ g-atom)$^{-1}$		%
		Exp.	Calc.	A	B	
CaO–B_2O_3 [9]						
1. CaO	−317.55	0	–	128.870	0.506	–
2. CaB_2O_4	−286.05	−17.59	−15.95	(points 2–6)		+9.3
3. CaB_4O_7	−275.53	−14.97	−10.62			+29.0
4. $Ca_2B_2O_5$	−296.57	−21.27	−21.27			0
5. $Ca_3B_2O_6$	−301.80	−22.82	−23.92			−4.8
6. B_2O_3	−254.55	0	0			0
BaO–WO_3 [5][i]						
1. BaO	−276.80	0	0	−929.989	−3.360	0
2. $BaWO_4$	−243.76	−48.17	−44.47	(points 1, 4, 5)		+7.7
3. Ba_2WO_5	−254.80	−53.60	−59.32			−10.7
4. Ba_3WO_6	−260.28	−52.11	−55.51	283.595	1.346	−6.5
5. $(Ba_5W_2O_{11})$	−257.90	−63.50	−63.50	(points 2, 3, 5, 6)		0
6. WO_3	−210.71	0	0			0
TiO_2–MgO [9]						
Group "g"						
1. TiO_2	−314.07	0	0	−249.450	−0.794	0
2. $MgTiO_3$	−307.46	−5.78	−5.25	(points 1–3)		+9.2
3. $MgTi_2O_5$	−309.67	−2.94	−3.49			−18.8
4. Mg_2TiO_4	−305.25	−2.80	−3.49	238.950	0.794	−24.6
5. MgO	−300.85	0	0	(points 2, 4, 5)		0

[a] The interpretation was made taking into account the phase $Ba_8Si_5O_{18}$ [17].

[b] $\Delta H^0_f(UO_3)$ was taken as the arithmetic mean ΔH^0_f value for known phase modifications, In the same way we determined ΔH^0_f values for other simple compounds with different modification stable under standard conditions.

[c] With the supposition that we analysed the all existing double oxides in the system Al_2O_3–Na_2O, the $\Delta H^0_{f,cc}$ data for Na_5AlO_4 are not completely correct. In this situation the investigating system is symmetric-type. If phase $Na_6Al_4O_9$ exists ($\Delta \bar{H}^0_f = -220$ kJ (g-atom)$^{-1}$ $\Delta H^0_{f,cc} = -32.5$ kJ (g-atom)$^{-1}$ the system is "left-sided".

[d] The interpretation was made taking into account the possible existence of the phase $Sr_6Ti_5O_{16}$ ($\Delta H^0_{f,cc}$ is minimum).

[e] The same as [d] with the phase $Li_{22}Zr_8O_{27}$.

[f] The same as [d] with the phase $Ca_9Ti_8O_{25}$.

[g] The same as [d] with the phase $K_{12}Mo_7O_{27}$.

[h] The same as [d] with the phase $Sr_9{}^{W}{}_5O_{24}$.

[i] The same as [d] with the phase $Ba_5W_2O_{11}$.

clearly classify these systems according to this scheme. For the same reasons we cannot determine the minimum value of $\Delta H^0_{f,cc}$ sufficiently accurately for the majority of the systems in groups b, c, e and f.

By analyzing of the observed regularities it follows that a common linear equation for the branches of the dependence Eq. (4) can be written for all assuming only limited

Table 2
Values of standard enthalpy of formation from component from component oxides for some complex oxides estimated with the help of the equations presented in the text

Double oxides according to Ref. [17]	$\Delta H^0_{\mathrm{f,cc}}$/(kJ mol^{-1})	Double oxides according to Ref. [17]	$\Delta H^0_{\mathrm{f,ee}}$/(kJ mol^{-1})
$Na_6Si_2O_7$	−737.6	$Ca_2B_6O_{11}$	−239.0
$Na_2Si_4O_9$	−230.6	$Na_2B_8O_{13}$	−345.5
$Na_6Si_8O_{19}$	−567.1	$Na_4B_{10}O_{17}$	−665.5
$K_2Si_3O_7$	−296.3	NaB_9O_{14}	−179.6
Ba_3SiO_5	−237.9	$Ca_5Al_6O_{14}$	−66.8
$Ba_3Si_5O_{13}$	−526.1	$Ca_4Al_6O_{13}$	−70.0
$Ba_2Si_{12}O_{31}$	−33.3	$Sr_{61}V_{18}O_{61}$	−2968.3
$Ba_8Si_5O_{18}$	−1273.5	$Ca_5Ti_4O_{13}$	−361.5
$Pb_3Si_2O_7$	−34.8	$Na_8Ti_5O_{14}$	−331.8
$Pb_{11}Si_3O_{27}$	−63.6	$Na_2Ti_6O_{13}$	−975.2

information about the double compounds available: for the "left-sided"

$$\Delta H^0_{\mathrm{f,cc}} = \frac{\Delta H^0_{\mathrm{f,cc}}(\mathrm{i})}{\Delta H^0_{\mathrm{f}}(\mathrm{AC}) - \Delta \bar{H}^0_{\mathrm{f}}(\mathrm{i})}[\Delta H^0_{\mathrm{f}}(\mathrm{AC}) - \Delta \bar{H}^0_{\mathrm{f}}] \tag{6}$$

and for the "right-sided"

$$\Delta H^0_{\mathrm{f,cc}} = \frac{\Delta H^0_{\mathrm{f,cc}}(\mathrm{i})}{\Delta \bar{H}^0_{\mathrm{f}}(\mathrm{i}) - \Delta H^0_{\mathrm{f}}(\mathrm{BC})}[\Delta H^0_{\mathrm{f}} - \Delta H^0_{\mathrm{f}}(\mathrm{BC})] \tag{7}$$

$\Delta H^0_{\mathrm{f,cc}}(\mathrm{i})$ and $\Delta \bar{H}^0_{\mathrm{f}}(\mathrm{i})$ are relevant enthalpy values for a reference double compound *i* for which reliable enthalpy data are available.

If we take the observed regularities as acceptable (we can name them as Linear Approximation Rule-LAR), we can point out some possibilities of its application. For example it is possible to revise the known enthalpy data of double compounds. In particular this revision was performed for some complex compounds in Table 1. It is also possible to estimate unknown $\Delta H^0_{\mathrm{f,cc}}$ values of some double compounds, if the reveant$\Delta \bar{H}^0_{\mathrm{f}}$ is located in the range of know $\Delta H^0_{\mathrm{f,cc}}$ data; such examples are presented in Table 2.

4. Conclusion

On basis of the analysis the 34 inorganic pseudobinary systems the empirical dependences for the standard enthalpies of formation of the double compounds from the component compounds (Linear Approximation Rule) have been proposed. The LAR can be used for revision and correction of known $\Delta H^0_{\mathrm{f,cc}}$ values and for estimation of unknown values, for related double compounds. With the help of LAR the standard enthalpies of formation from component oxides have been calculated for the complementary 20 double oxides. It seems reasonably to assume that the observed regularities are correct and sufficiently reliable for related double compounds in other inorganic systems.

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