PREDICTION OF HEAT CAPACITIES OF SOLID BINARY OXIDES FROM GROUP CONTRIBUTION METHOD

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The group contribution method proposed by Golam Mostafa et al. and its use for the prediction of heat capacities of solid binary oxides is discussed. $C_{pm}(298)$ for 113 oxides were predicted and the mean error of 4.3% and the maximum error of 26.3% were found. The proposed temperature dependencies of C_{pm} of the form $C_{pm} = a + bT + c/T^2 + dT^2$ show in some cases unrealistic behavior due to the negative value of the predicted constant d.

Keywords: Heat capacity, Group contribution method, Oxides

INTRODUCTION

The molar heat capacity (C_{pm}) is one of several fundamental thermophysical properties of solids. In order to determine C_{pm} various calorimetric methods have been employed; presently C_{pm} can be measured from very low temperatures (<1 K) up the melting point of a given compound. Calorimetric measurements of C_{pm} have been performed for most binary oxides and the experimental data are currently available in the literature**.** However, for some compounds (e.g. for In_2O, Rb_2O, NdO, SmO, YbO, Tb_2O_3, CrO_2, PdO_2, PtO_2, or RuO_3) these data are still lacking. In order to obtain approximate values of C_{pm} for these substances one of the many empirical estimation methods can be applied. Overviews presenting these estimation methods have been published for instance by Moiseev and Sestak [1] and Spencer [2].

Golam Mostafa et al. have recently proposed a contribution method (GM method) to predict the temperature dependence of C_{pm} of solid inorganic substances [3]. In the GM method, the coefficients in the temperature dependence of C_{pm} in the form

$$C_{pm} = a + b.T + \frac{c}{T^2} + d.T^2 \qquad (1)$$

for a given compound are obtained by the summing ionic contributions of the respective ions forming the compound. These contributions have been evaluated by multiple linear regression method from tabulated data of 664 various substances taken mostly from Knacke et al. [4]. The average error of the prediction (= 3.18%)

and the maximum error (= 13.63%) have been evaluated by comparing the estimated values of $C_{pm}(298)$ and the original data. However, at higher temperatures much larger mean errors were found, and the error of estimation exceeded 50% for some binary oxides.

The aim of the present paper is to verify the suitability of the GM method for the prediction of C_{pm} of solid binary oxides.

RESULTS AND DISCUSSION

Estimation of the heat capacity at temperature of 298.15 K

The $C_{pm}(298)$ values were estimated by the GM method for 113 binary oxides formed by 65 elements and they were compared with selected experimental data. For other oxides no experimental (calorimetric) data exist and/or the ionic contributions have not been evaluated by Golam Mostafa [3]. In the case of oxides with the cation mixed valence state, the cation contributions were calculated as follows: $Me_3O_4 - Me^{2+} + 2\ Me^{3+}$, $Me_3O_5 - 2\ Me^{3+} + Me^{4+}$, $Me_4O_7 - 2\ Me^{3+} + 2\ Me^{4+}$, $Me_5O_9 - 2\ Me^{3+} + 3\ Me^{4+}$, $Me_6O_{11} - 2\ Me^{3+} + 4\ Me^{4+}$, $Me_{10}O_{19} - 2\ Me^{3+} + 8\ Me^{4+}$, $Me_4O_9 - 2\ Me^{4+} + + 2\ Me^{5+}$, $Me_3O_8 - 2\ Me^{5+} + Me^{6+}$. While most of the experimental values were taken from Knacke et al. [4], in some cases recent calorimetric or assessed data were considered. As the GM method is unable to distinguish among various structural modifications data for all phases were taken into account. The results are summarised in table 1. The mean estimation error of 4.3% was found. For 10 oxides the error of the predicted data was higher than 10%.

Table 1. Estimated values of $C_{pm}(298)$ for solid binary oxides according to the method proposed by Golam Mostafa et al. [3] and comparison with experimental data.
(metastable modifications at 298.15 K are printed in italics)

Oxide	Phase	C_{pm}(298 K) -GM	C_{pm}(298 K) -exp	Ref.	δC_{pm} (%)	Oxide	Phase	C_{pm}(298 K) -GM	C_{pm}(298 K) -exp	Ref.	δC_{pm} (%)
Ag_2O	sol	70.27	66.32	4	5.95	PbO_2	sol	60.99	60.99	4	0.00
Al_2O_3	corundum	77.58	79.04	5	-1.85	PdO	sol	43.57	40.29	18	8.14
As_2O_3	claudetite	95.92	96.98	4	-1.09	Pr_6O_{11}	sol-A	399.38	381.48	4	4.69
As_2O_3	*arsenolite*	95.92	95.65	4	0.29	Pr_2O_3	sol	107.67	116.63	4	-7.68
As_2O_5	sol	123.98	116.56	4	6.37	Pu_2O_3	sol	126.31	116.98	19	7.98
B_2O_3	sol	58.67	62.98	4	-6.84	PuO_2	sol	65.93	66.25	4	-0.48
BaO	sol	46.23	47.06	6	-1.76	Re_2O_7	sol	190.44	166.27	4	14.54
BeO	sol-A	25.03	24.98	4	0.18	ReO_2	sol	56.59	56.60	4	-0.01
Bi_2O_3	sol-A	108.46	112.13	7	-3.27	Rh_2O_3	sol	101.51	89.12	20	13.90
CaO	sol	41.02	42.11	4	-2.60	RuO_2	sol	52.69	56.15	21	-6.16
CdO	sol	44.75	44.16	4	1.32	Sb_2O_3	valentinite	108.13	101.39	4	6.65
Ce_2O_3	sol	108.72	115.00	8	-5.46	Sc_2O_3	sol	93.11	93.94	4	-0.88
CeO_2	sol	61.53	61.53	4	0.01	Se_2O_5	sol	127.38	127.37	4	0.01
Co_3O_4	sol	155.93	123.42	4	26.34	SeO_2	sol	56.23	58.31	4	-3.57
CoO	sol	47.93	55.22	4	-13.19	SeO_3	sol	65.40	77.19	22	-15.27
Cr_2O_3	sol	103.79	114.26	4	-9.16	SiO_2	quartz	44.20	44.42	4	-0.50
Cr_3O_4	sol	142.77	135.64	9	5.26	SiO_2	*tridimite*	44.20	44.71	4	-1.13
CrO_3	sol	73.43	79.12	4	-7.19	SiO_2	*cristobalite*	44.20	44.95	4	-1.66
Cs_2O	sol	78.18	75.90	4	3.00	SiO_2	*coesite*	44.20	45.12	23	-2.03
Cu_2O	sol	59.95	62.47	10	-4.03	Sm_2O_3	cubic	116.04	115.82	4	0.18
CuO	sol	42.92	42.26	10	1.57	Sm_2O_3	*monoclinic*	116.04	114.52	14	1.33
Dy_2O_3	sol-A	113.15	116.26	4	-2.67	SnO	sol	45.24	47.77	4	-5.29
Er_2O_3	sol	128.04	108.49	11	18.01	SnO_2	sol	52.60	52.60	4	0.00
Eu_2O_3	cubic	128.42	127.09	12	1.05	SrO	sol	42.96	45.15	6	-4.84
Eu_2O_3	*monoclinic*	128.42	122.33	12	4.98	Ta_2O_5	sol	139.10	135.75	24	2.47
EuO	sol	48.92	48.73	4	0.39	TeO_2	sol	70.30	63.88	4	10.05
Fe_2O_3	sol-A	106.89	104.77	4	2.02	ThO_2	sol	61.57	61.81	4	-0.40
Fe_3O_4	sol	149.84	151.78	4	-1.27	Ti_2O_3	sol	103.99	101.80	4	2.15
FeO	sol	42.95	47.64	13	-9.84	Ti_3O_5	sol-A	162.13	154.75	4	4.77
Ga_2O_3	sol	95.61	93.86	4	1.86	Ti_4O_7	sol	220.26	208.16	4	5.81
Gd_2O_3	cubic	101.88	105.51	4	-3.43	Ti_5O_9	sol	278.39	275.70	25	0.98
Gd_2O_3	*monoclinic*	101.88	106.63	14	-4.45	Ti_6O_{11}	sol	336.52	334.38	25	0.64
GeO_2	hexagonal	54.24	51.95	4	4.41	$Ti_{10}O_{19}$	sol	569.04	568.20	25	0.15
GeO_2	*tetragonal*	54.24	50.17	14	8.13	TiO	sol-A	43.95	39.96	4	9.98
HfO_2	sol-A	59.65	60.26	4	-1.03	TiO	sol-B	43.95	40.40	26	8.79
HgO	sol	43.88	44.01	15	-0.29	TiO_2	rutile	58.13	55.10	4	5.50
Ho_2O_3	sol	113.46	114.96	4	-1.30	TiO_2	*anatas*	58.13	54.02	4	7.60
In_2O_3	sol	100.59	99.07	16	1.54	Tl_2O	sol	78.16	78.84	4	-0.87
IrO_2	sol	55.59	55.64	4	-0.09	Tl_2O_3	sol	107.61	105.46	4	2.04
K_2O	sol	78.06	84.53	4	-7.66	Tm_2O_3	sol-A	115.00	116.72	4	-1.48
La_2O_3	sol	104.71	108.78	4	-3.74	U_3O_8	sol	224.49	237.23	4	-5.37
Li_2O	sol	57.98	54.25	4	6.87	U_4O_9	sol	264.14	292.14	4	-9.58
Lu_2O_3	sol	101.08	101.76	4	-0.67	UO_2	sol	63.16	63.59	4	-0.68
MgO	sol	36.54	37.26	4	-1.93	UO_3	sol	86.67	81.19	4	6.74
Mn_2O_3	sol	99.78	99.04	4	0.75	V_2O_3	sol	98.29	101.87	4	-3.51
Mn_3O_4	sol-A	142.92	140.53	4	1.70	V_2O_5	sol	127.32	127.37	4	-0.04
MnO	sol	43.14	44.16	17	-2.31	V_3O_5	sol	160.97	159.42	25	0.97
MoO_2	sol	65.00	55.99	4	16.11	V_4O_7	sol	223.66	229.12	25	-2.38
MoO_3	sol	74.84	75.14	4	-0.40	VO	sol	40.92	38.54	4	6.16
Na_2O	sol-A	69.88	68.56	4	1.92	VO_2	sol-A	62.69	56.88	4	10.21
Nb_2O_5	sol	146.30	132.13	4	10.72	WO_2	sol	62.39	56.83	4	9.79
NbO_2	sol-A	59.36	57.69	4	2.89	WO_3	sol-A	77.26	72.80	4	6.12
Nd_2O_3	sol-A	107.18	111.34	4	-3.73	Y_2O_3	sol-A	100.56	102.51	4	-1.91
NiO	sol-A	43.80	44.29	4	-1.12	Yb_2O_3	sol-A	112.26	115.36	4	-2.69
P_2O_5	sol	104.24	105.74	4	-1.42	ZnO	sol	39.97	41.07	4	-2.66
PbO	red	47.48	45.74	4	3.81	ZrO_2	sol-A	56.07	56.21	4	-0.24
PbO	*yellow*	47.48	45.81	14	3.64						

In several instances only the data for a single compound have been used for the evaluation of individual contributions of the cations [3]. For Ce^{4+}, Ir^{4+}, Pb^{4+}, Re^{4+}, and Sn^{4+}, data for relevant oxides have been used therefore are no differences between the experimental and estimated values of $C_{pm}(298)$ for these oxides. It must be noted that the contributions of Pr^{4+}, Tb^{4+}, Tc^{4+} and Tc^{6+} have been obtained from data of the respective oxides PrO_2, TbO_2, TcO_2 and TcO_3. However, the tables [4] for these oxides report values that were formerly estimated and not measured experimentally. Hence much larger mean error than that reported by Golam Mostafa et al. [3] has to be expected when estimating C_{pm} of different substances using the above mentioned cation contributions. In other cases (Mn^{4+}, Nb^{2+}, Os^{4+}, Sb^{4+}, and Sb^{5+}) the ionic contributions have not been derived although experimental heat capacity data just for binary oxides are tabulated [4].

Prediction of the temperature dependence of heat capacity

The coefficients of the equation (1) have been estimated by means of the GM method. For selected oxides the $C_{pm}(T)$ curves are plotted in figure 1. From the shape of the curves it is apparent that the GM method gives physically unrealistic behavior at higher temperatures showing a decrease of C_{pm} with increasing temperature. Within the considered temperature range the overall value of C_{pm} for substances without changes in magnetic ordering consists of two terms: 1) due to the lattice vibrations C_{vib}, and 2) due to the dilatation C_{dil}. According to the Debye model, the C_{vib} approaches a constant value of $3NR$ at high temperatures (where N is the number of atoms in formula unit). The contribution $C_{dil} = TV_m\alpha^2 K_T$ (where V_m is the molar volume, α is the thermal expansion coefficient and K_T the isothermal bulk modulus) generally increases with increasing temperature.

A decrease of C_{pm} with increasing temperature at higher temperatures occurs usually in cases when the parameter d in equation (1) is negative and relatively large. For the oxygen anion the contribution $d(O^{2-}) = -4.026 \cdot 10^{-6}$ ($J.K^{-3}.mol^{-1}$), which results in a broad maximum at $T = 1547$ K in the temperature dependence of $C_{pm}(O^{2-})$ followed by a gradual decrease. Oxides with a general formula A_mO_n can be categorized into three groups depending on the magnitude of the cation contribution to the parameter d:

I $d(A^{z+}) > 0$ $m.d(A^{z+}) > n.|d(O^{2-})|$
II $d(A^{z+}) > 0$ $m.d(A^{z+}) < n.|d(O^{2-})|$
III $d(A^{z+}) < 0$

Since for all 92 oxides considered the parameters in equation (1) follow: $a > 0$, $b > 0$ or $b < 0$ and are always relatively small in magnitude, and the effect of the third term c/T^2 substantially decreases with increasing temperature, the following points should be noticed:
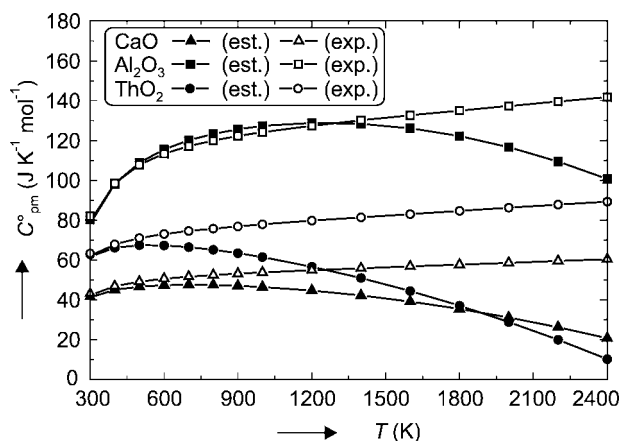

Figure 1. Comparison of experimental heat capacities of solid CaO, Al_2O_3, and ThO_2 with predicted values based on the group contribution method of Golam Mostafa et al. [3].

The temperature dependence of C_{pm} for oxides from the first group does not reveal any maximum for $T > 298.15$ K .

The temperature dependence of C_{pm} for oxides from the second group usually shows a maximum for $T > T_m$ (T_m being the melting point of the oxide of interest).

The temperature dependence of C_{pm} for oxides from the third group shows usually a maximum for $T < T_m$.

From the total number of 129 cations the negative contribution to d parameter occurs in 25 cases: Al^{3+}, B^{3+}, Ca^{2+}, Cm^{3+}, Co^{3+}, Cu^{2+}, Er^{3+}, In^{2+}, Mg^{2+}, Mo^{5+}, Nb^{3+}, Np^{3+}, Np^{4+}, Pu^{4+}, Pu^{6+}, Ru^{3+}, Si^{4+}, Sm^{2+}, Ta^{3+}, Ta^{4+}, Th^{4+}, U^{5+}, U^{6+}, W^{2+} a Yb^{2+}. Hence, the GM method does not provide a reliable prediction of $C_{pm}(T)$ for oxides formed from the above mentioned cations. Considering the fact that $d < 0$ also for most other anions, the same situation (as discussed here) can be anticipated for other compounds as well.

CONCLUSIONS

The ionic contribution method of Golam Mostafa et al. [3] (the GM method) gives reasonable estimates of C_{pm} for solid binary oxides at $T = 298.15$ K. However as discussed in this comment, generalizing the GM method to predict C_{pm} at other temperatures appears to be rather problematic.

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ODHAD TEPELNÝCH KAPACIT BINÁRNÍCH OXIDŮ
V PEVNÉM STAVU POMOCÍ PŘÍSPĚVKOVÉ METODY

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V práci je diskutována odhadová metoda pro predikci molárních tepelných kapacit pevných látek navržená Golamem Mostafou a spol. a její použití pro binární oxidy. Pomocí této metody byly získány hodnoty $C_{pm}(298)$ pro 113 oxidů s průměrnou chybou 4,3% a maximální chybou 26,3%. Získané teplotní závislosti molárních tepelných kapacit ve tvaru $C_{pm} = a + bT + c/T^2 + dT^2$ vykazují v některých případech nerealistický průběh v důsledku predikované záporné hodnoty konstanty d.