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Heat capacities of molten salts with polyatomic anions

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ABSTRACT

The molar heat capacities at constant pressure, C_P, of molten salts with polyatomic anions, obtained from the literature, are examined. As a rule, the C_P values are independent of the temperature T, but the molar heat capacities at constant volume, C_V, derived from them, depend on T. The latter were obtained, as far as the required density, expansibility and compressibility data are available, for $1.1T_m$, presumed to be the corresponding state, T_m being the melting temperature. Their ratio $\gamma = C_P/C_V$ is linear with the cation–anion distance in the molten salt, d_{C-A}. The communal, quasi-lattice, heat capacity $\Delta C_P = C_P - C_P$(i.g.) is obtained by subtraction of the sum of published ideal gas heat capacities of the constituent ions at $1.1T_m$, C_P(i.g.). This communal heat capacity ΔC_P is proportional to the packing fraction of the ions in the melt, $y = \pi N_A \nu d_{C-A}{}^3/6V$. Here N_A is Avogadro's number, ν the number of ions per formula unit, and V the molar volume at $1.1T_m$. Some models for the heat capacities of molten salts are shown not to be well applicable to the set of salts discussed here, but no alternative could be suggested.

1. Introduction

Little systematic information is available concerning the heat capacities of molten salts (with univalent cations) having polyatomic anions. Practically only the work of Denielou et al. [1] has comparisons of data for several such salts. These have the general formula M_2XO_4 (M = Li, Na, K, Rb, and Cs; X = S, Cr, Mo, and W). The heat capacity of molten salts with polyatomic anions, in distinction from molten salts having only monatomic ions, involves the excitation of vibrational and rotational modes in addition to the ionic translational and the communal modes noted for the latter kind of salts. The communal mode is characteristic of the quasi-lattice of the molten salt and may be modeled according to several approaches [2].

It is the purpose of this paper to present the relevant data for the molar heat capacity of salts with polyatomic anions at constant pressure, C_P (practically temperature independent) and at constant volume, C_V, the latter at $1.1T_m$. This temperature, where T_m is the melting temperature, may be assumed to constitute a corresponding state for these molten salts [3,4].

The difference ΔC_P between C_P and the sum of the molar ionic heat capacities of the constituent ions in the ideal gas state, C_P(i.g.), obtained from Loewenschuss and Marcus [5], represents the communal, quasi-lattice, heat capacity of the molten salt. This can be correlated with the sizes of the constituent ions in various manners, as is discussed in this paper.

2. Results

A survey of the relevant literature resulted in the C_P data shown in Table 1. In many cases the item shown is the only one available, whereas in some other cases the value shown is selected on the basis of its being compatible with the general trends exhibited by the data on the whole. As a rule, the C_P values of molten salts are independent of the temperature within the error limits of their determination [2]. Some reported C_P values are obviously incorrect, in comparison with values for similar salts and the reported values are placed in Table 1 in brackets.

The values of the sums of the ideal gas heat capacities of the constituent ions, C_P(i.g.) also shown in Table 1, are mildly temperature dependent on the other hand, because of the excitation of vibrational and rotational modes of the polyatomic anions. The values at $1.1T_m$ are inter- or extrapolated from the relevant data reported at several temperatures [5]. For $S_2O_7{}^{2-}$ there were no calculated data available, so the values for $S_2O_6{}^{2-}$ were used instead, since these (rather than those for $S_2O_8{}^{2-}$ and $Cr_2O_7{}^{2-}$) yield reasonable values for ΔC_P, but, of course, their reliability is low.

The values of C_V have not been determined directly but have to be calculated from those of C_P by means of the thermodynamic expression:

$$C_V = C_P - \frac{TV\alpha_P{}^2}{\kappa_T} \qquad (1)$$

For the present purpose $T = 1.1T_m$, and the other quantities pertain to this temperature: V is the molar volume, α_P is the isobaric expansibility, and κ_T is the isothermal compressibility of the molten salt. The values of κ_T are known for very few molten salts with

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Table 1

The temperatures of fusion, T_m, heat capacities at constant pressure, C_P, the ideal gas heat capacities, C_P(i.g.), the heat capacities at constant volume, C_V, and the communal heat capacities, ΔC_P, of molten salts with polyatomic anions, the latter three quantities at $1.1T_m$.

Salt	T_m (K)	C_P [a] ($J K^{-1} mol^{-1}$)	Reference	C_P(i.g.) ($J K^{-1} mol^{-1}$)	C_V ($J K^{-1} mol^{-1}$)	ΔC_P ($J K^{-1} mol^{-1}$)
LiOH	744	87.1	[15]	50.4		36.7
$LiNO_3$	525	112.5	[16]	84.3	101.2	28.2
$LiClO_3$	401	122.2	[17]	88.3		33.9
$LiClO_4$	509	161.1	[15]	107.4	155.8	53.8
Li_2CO_3	993	142.8	[18]	117.3	136.3	25.5
Li_2SO_4	1130	207.9	[1]	145.0	187.2	62.9
Li_2CrO_4	755	200.0	[1]	142.7	184.0	57.3
Li_2MoO_4	974	215.1	[1]	145.7	194.3	69.5
Li_2WO_4	1013	205.0	[15]	145.9	185.0	59.1
NaOH	593	87.1	[15]	50.1	83.5	37.1
NaCN	835	79.5	[15]	53.6		25.9
$NaNO_2$	557	116.7	[19]	68.3	106.9	48.4
$NaNO_3$	579	136.8	[20]	86.8	115.1	50.0
$NaClO_3$	533	133.9	[21]	94.0		39.9
$NaBF_4$	679	165.4	[15]	117.5		47.9
$NaHSO_4$	455	[246.1]	[22]	115.6		[130.5]
$NaHCO_2$	531	142.3	[23]	75.1		67.2
$NaMeCO_2$	601	154.8	[23]	122.2	126.4	32.6
Na_2CO_3	1123	189.5	[15]	119.2	178.9	70.3
Na_2SO_4	1155	204.2	[1]	145.4	177.0	58.8
Na_2CrO_4	1070	212.5	[1]	146.3	185.0	66.2
Na_2MoO_4	962	215.1	[1]	145.5	186.6	59.6
Na_2WO_4	967	216.3	[1]	145.5	187.2	70.8
$Na_2S_2O_7$	674	244.8	[24]	221.2		23.6
Na_2SiF_6	1120	276.1	[15]	196.5		79.6
Na_3AlF_6	1279	396.2	[15]	221.0	345.4	175.2
KOH	633	83.1	[15]	50.1		33.0
KCN	895	75.3	[15]	54.0		21.3
KNO_3	607	141.0	[19]	88.0	114.2	53.0
KHF_2	512	104.6	[15]	67.5		37.1
KBF_4	843	167.2	[15]	121.1		46.1
$KHSO_4$	481	[287.0]	[22]	117.8		[169.2]
K_2CO_3	1174	183.8	[18]	120.1	172.4	63.8
K_2SO_4	1341	204.2	[1]	149.9	172.4	54.3
K_2CrO_4	1250	209.2	[15]	148.9		60.3
K_2WO_4	1189	218.0	[1]	147.7	173.5	70.3
$K_2Cr_2O_7$	671	[415.9]	[25]	231.3		[184.6]
$K_2S_2O_7$	692	267	[24]	222.4		45
RbOH	658	83.7	[15]	50.2		33.5
$RbNO_3$	583	[102.9]	[29]	87.0	77.0	[15.9]
Rb_2CO_3	1141	[124.7]	[26]	119.5	94.2	[5.2]
Rb_2SO_4	1339	207.1	[15]	149.8	171.3	57.3
Rb_2WO_4	1225	213.8	[1]	148.2	165.9	65.6
$Rb_2S_2O_7$	708	272.2	[24]	223.5		48.7
CsOH	616	81.6	[15]	50.1		31.5
$CsNO_3$	680	136.0	[15]	90.6		45.4
Cs_2CO_3	1061	[121.5]	[26]	118.3	90.5	[3.2]
Cs_2SO_4	1286	207.1	[15]	148.2	166.6	58.9
Cs_2CrO_4	1234	210.9	[1]	148.6	164.6	62.3
Cs_2MoO_4	1220	210.0	[1]	148.2	166.0	61.8
Cs_2WO_4	1217	214.2	[1]	148.1	168.6	66.1
$Cs_2S_2O_7$	728	292.3	[24]	224.7		67.6
$AgNO_3$	483	139.1	[20]	82.0	127.2	57.1
Ag_2SO_4	937	205.0	[15]	142.1	182.5	62.9
$TlNO_3$	484	130.3	[27]	82.1		48.2
Tl_2SO_4	905	205.0	[15]	141.6		63.4
NH_4NO_3	443	161.1	[28]	102.0		59.1

[a] Values in [ ] are judged to be probably incorrect.

polyatomic anions and the non-available ones have to be estimated from the adiabatic compressibility $\kappa_S = 1/u^2\rho$, obtained in turn from ultrasound velocity u and the density ρ. The product $\rho V = M$, the molar mass of the salt, so that the second expression on the right hand side of Eq. (2) results:

$$C_V = C_P\left[1-\left(1+\frac{C_P\kappa_S}{\alpha_P{}^2VT}\right)^{-1}\right] = C_P\left[1-\left(1+\frac{C_P}{u^2\alpha_P{}^2MT}\right)^{-1}\right] \quad (2)$$

Alternatively, κ_T may be estimated from the surface tension via an empirical correlation due to Mayer [6]. As is seen in Table 1, values of C_V could be calculated for only one half of the salts for which C_P is known.

The ratios $\gamma = C_P/C_V$ are approximately linear with the mean inter-ionic distances d_{C-A} between the cations C and the anions A. The correlation expression is:

$$\gamma = (0.73 \pm 0.04) + (1.30 \pm 0.13)\cdot(d_{C-A}/\mathrm{nm}) \quad (3)$$

with a standard error of the fit of 0.036 in values of γ ranging from 1.04 to 1.29 for the salts shown. These mean distances were taken as the sums of the reported ionic radii in solid salts [7] (except for $NO_3{}^-$, for which the value 0.219 nm used for molten salts [8] is preferred), because the thermal expansion of the molten salts results mainly in increasing the volumes of the voids rather than in separating cations and anions from contact in the quasi-lattice

[9]. Thus, γ is least in lithium salts with small anions and largest in cesium salts with large anions, independent of the valency of the anions. Expression (3) may be used to obtain approximate values of C_V from those of C_P if the required density, expansibility, and compressibility data are lacking, but the fairly large standard error in the correlation needs to be considered.

Whereas bulk thermodynamic properties of molten salts scale well with the inter-ionic distances, as the theory of corresponding states prescribes, the quasi-lattice heat capacity, $\Delta C_P = C_P - C_P(\text{i.g.})$, does not correlate so well with the inter-ionic distances $d_{\text{C–A}}$. For salts with univalent polyatomic anions ΔC_P increases with $d_{\text{C–A}}$:

$$\Delta C_P/\text{J K}^{-1}\,\text{mol}^{-1} = (24.6 \pm 4.3) + (58.7 \pm 13.5)(d_{\text{C–A}}/\text{nm}) \qquad (4)$$

but there are nearly as many outliers from a linear dependence as there are salts conforming to it. For salts with divalent anions $\Delta C_P \approx 68 \pm 5\,\text{J K}^{-1}\,\text{mol}^{-1}$, without a clear dependence on $d_{\text{C–A}}$. This is contrary to the well established linear dependencies of ΔC_P on $d_{\text{C–A}}$ found for molten salts with monatomic ions only [2]. Some other expression of the dependence of the quasi-lattice heat capacity on the properties of the ions should be used instead. The most immediate function of the sizes of the ions is their packing fraction:

$$y = \frac{\pi N_A \nu d_{\text{C–A}}{}^3}{6V} = 315.3\nu(d_{\text{C–A}}/\text{nm})^3(V/\text{cm}^3\,\text{mol}^{-1})^{-1} \qquad (5)$$

Here ν is the number of ions constituting the salt: 2 for uni-univalent and 3 for uni-divalent salts. The packing fraction accentuates the inter-ionic distance $d_{\text{C–A}}$ by raising it to the third power but moderates this by the bulk molar volume V. The resulting correlation shows the quasi-lattice heat capacity to be proportional to the packing fraction y that varies from 0.236 to 0.630 for the salts considered:

$$\Delta C_P/\text{J K}^{-1}\,\text{mol}^{-1} = (109 \pm 5)y \qquad (6)$$

for 37 salts with a correlation coefficient of 0.947 and a standard error of $6\,\text{J K}^{-1}\,\text{mol}^{-1}$, and irrespective of whether the salts have univalent or divalent anions. Four carbonate salts are outliers: Rb and Cs carbonates have much too small values of ΔC_P, and on the other hand, Na and K carbonates have rather too large values of ΔC_P. The former two salts obviously have too low reported values of C_P, but these were read from small scale plots and are inaccurate. For the latter two salts their too large ΔC_P may be due to an underestimate of the size of the ionic planar trigonal carbonate anion included in y. A further outlier is RbNO_3, having rather too small values of C_P, hence of ΔC_P.

3. Discussion

Hoch and Vernardakis [10] modeled C_P, for some molten metal halides with:

$$C_P = 3R\,f\left(\frac{\theta}{T}\right) + gT + hT^{-2} \qquad (7)$$

Here $f(\theta/T)$ is the Debye function involving the Debye temperature θ, gT is the electronic heat capacity (irrelevant in the present cases of the salts considered), and h is the coefficient of the anharmonic term. For molten salts $1.1T_m$ is generally considerably larger than θ, so that $f(\theta/T) \approx 1$, even for salts with relatively high θ such as LiF and NaF ($\theta = 780$ and 490 K [11]) or for low-melting salts such as LiNO_3 ($\theta = 152$ K [12]). The Debye temperature appears to be the same for crystals and their melts [10] or smaller for the latter [12] and may be estimated from $\theta/\text{K} = 5.4\,\nu/(\langle M\rangle/\text{kg mol}^{-1})\cdot(d_{\text{C–A}}/\text{nm})^3)^{1/2}$, where $\langle M\rangle$ is the mean molar mass of the salt. Hence Eq. (7) reduces to $C_P = 3R + hT^{-2}$, but this is contrary to the observed temperature independence of C_P at least up to $1.1T_m$ and generally considerably beyond and contrary to its magnitude relative to $3R$. This fact obviates the use of expression (7) for the present purposes.

Yosim and Owens [4] discussed molten salt properties in terms of a rigid sphere equation of state based essentially on the restricted primitive model expounded by Larsen [13]. These considerations lead to the thermodynamic quantities describing the molten salts. They applied the model, however, only to monatomic ions, such as those of the alkali halides. Larsen's model, furthermore, features the indefinite concept of the permittivity mediating between the interacting ions. The resulting expression for the heat capacity at constant pressure of a symmetrical salt is [4]:

$$C_P = 5R + 2R[-1 + \alpha_P T\,f(y)] \qquad (8)$$

where $f(y) = (1 + y + y^2)/(1 - y)^3$ is a function of the packing fraction. The first term on the right hand side, $5R$, is $C_P(\text{i.g.})$ for the two monatomic ions, so that the second term represents the communal quasi-lattice heat capacity ΔC_P. The electrostatic interactions between the ions are implicitly taken care of by the packing fraction y and the isobaric expansibility α_P. However, the two factors $\alpha_P T$ and $f(y)$ in Eq. (8) do not eliminate between them the temperature dependence, so that Eq. (8) does not represent well the experimentally noted temperature independence of C_P.

The model employed in the present work involves the restricted primitive model, describing the ions as hard spheres of constant radii. However, the scaled particle approach of Yosim and Owens is replaced by the quasi-lattice approach having two intertwined quasi-lattices of cations and anions. Nearest neighbors tend to be of opposite charge and the pair-wise potential in this model is:

$$u_{\text{C–A}} = \frac{z_C z_A e^2}{4\pi\varepsilon_0 r} \quad \text{for } r > d_{\text{C–A}} \quad \text{and} \quad u_{\text{C–A}} = \infty \quad \text{for } r < d_{\text{C–A}} \qquad (9)$$

The coordination number is lower in the melt than in the crystalline solid [9], and this allows for some void volume [1] and for free rotation of the polyatomic anions. If the cation–anion distance $d_{\text{C–A}}$ is taken to be independent of the temperature, then the expansion on heating is confined to the increase in the void volume:

$$V_f = V - \left(\frac{\nu\pi N_A}{6}\right) d_{\text{C–A}}{}^3 \qquad (10)$$

leading to a decrease in the packing fraction y, Eq. (5). A negative value of $(\partial y/\partial T)_P$ of about $-(8 \pm 2) \times 10^{-5}\,\text{K}^{-1}$ was shown by Itami and Shimoji [14] to be required for their expression for the heat capacity at constant volume, C_V, of the alkali halides.

For a series of molten salts with polyatomic anions the empirically found proportionality between ΔC_P and y, Eq. (6), is comprehended in view of the stronger interactions between the ions of opposite charge when their packing is tighter: $u_{\text{C–A}}$ is more negative when the average r is smaller, Eq. (9). The energy supplied to the system on heating goes into increasing the amount of void volume, working against the Coulombic attraction of the ions. Some of the energy, though, goes into the vibrational and rotational degrees of freedom of the polyatomic anions, making $C_P(\text{i.g.})$ temperature dependent [5], $(\partial C_P(\text{i.g.})/\partial T)_P \sim 0.055 \pm 0.01\,\text{J K}^{-2}\,\text{mol}^{-1}$ for polyatomic anions with more than two atoms. In this respect the molten salts discussed here differ from those with monatomic ions only, such as the alkali halides, which were dealt with previously by most authors [4,10,14]. This positive temperature derivative compensates the negative derivative of y, resulting in a temperature independent relationship between ΔC_P and y, as in Eq. (6).

Denielou et al. [1] calculated the configurational heat capacity (at constant volume and at T_m) $C_V{}^Q$ for the alkali metal sulfates, chromates, molybdates, and tungstates and found it to range from 48 to $81\,\text{J K}^{-1}\,\text{mol}^{-1}$. It increases with the size of the anion but decreases with the size of the cation. The latter trend appears to be contrary to the present findings, for which ΔC_P ($\approx C_P{}^Q$ at $1.1T_m$) for these salts is $68 \pm 5\,\text{J K}^{-1}\,\text{mol}^{-1}$ with no clear trend with the ion sizes. The discrepancy may be due to the calculation of $C_P(\text{i.g.})$ at

$1.1T_\mathrm{m}$ rather than at T_m, leading to a larger value, hence to a smaller configurational heat capacity.

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