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Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Heat capacities of molten salts with polyatomic anions

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ARTICLE INFO

Article history: Received 15 February 2009 Received in revised form 5 May 2009 Accepted 5 June 2009 Available online 16 June 2009

Keywords: Molten salts Molar heat capacities Packing fraction

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, $y = \pi N_A v d_{C-A}^3/6V$. Here N_A is Avogadro's number, v 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.

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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 quasilattice 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:

$$C_V = C_P - \frac{T V \alpha_P^2}{\kappa_T} \tag{1}$$

For the present purpose $T = 1.1T_{\rm m}$, 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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^{0040-6031/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2009.06.003

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 1.1 T_m .

Ind748715909087IAN525112.5112.5112.5112.53333ILCO40112.21788.310.233ILCO99314.2.818117.313.6.325.5ILCO93314.2.818117.313.6.325.5ILCO93312.1.11114.2.718.4.057.3ILCO755200.01114.2.718.4.057.3ILCO93387.11550.18.5.571.5NAN85375.51550.18.5.571.5NAN57.916.71968.3105.98.4.4NANO57.915.6.412144.09.9NANO57.915.6.412144.019.910.5.1NANO57.915.6.412375.510.013.4.2NANO57.915.6.412375.510.013.0.2NANO57.915.6.412317.510.0.210.0.2NANO67.915.6.412317.510.0.210.0.2NANO67.915.6.412317.510.0.210.0.2NANO67.915.6.412417.970.0NANO67.915.6.413.014.2.210.0.2NANO67.915.6.414.6.518.6.610.0.2NANO67.915.6.414.6.	Salt	<i>T</i> _m (K)	C_P^{a} (J K ⁻¹ mol ⁻¹)	Reference	$C_P(i.g.) (J K^{-1} mol^{-1})$	$C_V (J K^{-1} mol^{-1})$	$\Delta C_P (J K^{-1} mol^{-1})$
Linkb,S25112.516184.391.228.2LiClO,50916.115107.415.833.3LiClO,50916.115107.415.833.6Li,CO,93914.2.818107.3136.325.5Li,SO,11320.7011145.7184.365.5Li,NOA,97421.5111145.7184.565.5Li,NOA,97421.511550.185.093.1NAOH93387.11550.185.575.5NAOK85716.51553.625.9NANO,579136.82086.8106.984.4NANO,579136.8121176.647.047.0NANO,573142.1121176.647.047.0NANO,573142.1121176.647.047.0NANO,573142.1121176.647.047.0NANO,573142.1121176.647.047.0NANO,573142.1121176.5186.659.6NANO,574142.1131145.5186.659.6NANO,573242.2131145.5186.659.6NANO,574126.3185.063.659.6NANO,574126.3185.063.659.6NANO,57324.213 <td< td=""><td>Lioh</td><td>744</td><td>87.1</td><td>[15]</td><td>50.4</td><td></td><td>36.7</td></td<>	Lioh	744	87.1	[15]	50.4		36.7
Liclo401122178833333LiCo509161.115107.415.6.35.3.8Li,Co933142.818117.3136.325.5Li,Co75.5200.011142.7184.057.3Li,Co75.5200.011142.7184.057.3Li,Co75.5200.011142.7184.057.3NAO913213.11553.625.9NANO57.716.71968.3106.948.4NANO57.9136.821.194.039.9NANO57.9136.821.194.039.9NANO57.9165.415.117.519.0NAREA67.9165.417.518.60.0NARO53.1142.312.117.519.0NARO53.1142.317.518.062.2NARO11145.5186.062.219.1NARO13.414.217.078.879.5NARO10.015.414.417.078.6NARO10.224.211145.5186.062.1NARO962215.114.415.016.139.0NARO962215.114.516.019.019.0NARO962215.114.516.130.010.1NARO962215.116.516.1	LiNO3	525	112.5	[16]	84.3	101.2	28.2
LiClo,599161.1151107.4155.853.853.8Li,So,130207.91.1145.0157.262.9Li,Co,755200.01.1142.7184.063.5Li,Mo,97.4215.11.1145.7184.363.5Li,Mo,101.3255.01553.653.851.9NaNO537105.71968.30.648.4NaNO,577105.71968.3115.120.9NaRO,533133.9121.994.099.913.4NaNO,579136.8121.994.099.9NaRG,679154.415117.547.9NaRG,601154.8123.1122.2126.413.0NaRGO,531142.3123<122.2	LiClO ₃	401	122.2	[17]	88.3		33.9
LisOq9814.281817.3136.325.5LisOq75.5200.01145.0187.262.9LisOq75.5200.01142.7184.057.3LisOq974215.11145.7184.062.5LisOq974215.115145.9185.051.1NACH83375.51853.625.925.1NACO537116.61968.3106.948.3NACO537116.51968.3106.948.9NACO537165.41517.547.9NARO53819.611.444.077.9NARO531142.312.117.677.9NARO531142.312.117.670.3NARO531142.313.012.278.8NARO17.319.519.217.870.3NASO17.213145.5187.066.2NASO96721.511145.3186.659.6NASO96721.511145.5187.078.8NASO96721.611145.5187.078.6NASAF12.0276.1131550.177.1NASAF12.0276.11527.078.673.1NASAF12.027.113.013.014.113.0NASAF12.014<	LiClO ₄	509	161.1	[15]	107.4	155.8	53.8
Lis.Sol, Lis.Col, TyS200.145.0187.262.9Lis.Mod, Lis.Mod, NOM735200.01142.7184.06.5.7Lis.Mod, NOM93887.115145.9185.093.1NACH S3387.11550.183.571.1NACN NOM57917.01086.8115.140.9NACN NOCO573138.80086.8115.140.9NACO NOCO533139.921.994.099.9NAEFA NACO679165.41517.572.0NAEFA NACO679165.41517.2178.973.1NAECO NAEFA679165.41519.2178.973.2NAECO NAEFA611154.82312.216.673.0NAECO NAEFA61215.119.2178.973.573.0NAECO NAEFA61215.1145.5186.062.2NASO NAEFA17.214.61550.134.417.0NASO NAEFA17.214.61550.134.117.2NASO NAFA17.214.61550.134.117.2NASO NAFA17.214.61550.134.117.2NASO NAFA17.214.61550.134.117.2NASO NASO14.21414.515.316.134.117.2 <td>Li₂CO₃</td> <td>993</td> <td>142.8</td> <td>[18]</td> <td>117.3</td> <td>136.3</td> <td>25.5</td>	Li ₂ CO ₃	993	142.8	[18]	117.3	136.3	25.5
ib.Cron, ityMod, 	Li ₂ SO ₄	1130	207.9	[1]	145.0	187.2	62.9
Linkoo, 10310310310419310519451943105503NaOH59371.1553.653.653.653.653.653.6NANO,537116.71966.3106.948.450.053.6	Li ₂ CrO ₄	755	200.0	[1]	142.7	184.0	57.3
j.k.Wo,103205.015145.9185.0185.053.1NaCN53379.51550.135.625.9NaNO,577116.71968.3106.948.4NACO,533133.92194.039.9NaFS,67.9165.415117.515.0NaHSO,531142.322115.615.0NaHSO,531142.32375.167.0NaHCO,601154.813119.2178.970.3NaHCO,601154.811145.3185.068.2NaCO,601154.811145.5187.270.3NaCO,601154.811145.5187.270.8NaSO,115204.211145.5187.270.8NaSO,67.721.6.111145.5187.270.8NaSA,110145.5187.270.870.8NaSA,112121.123.023.023.023.0NaSA,112145.5187.270.873.070.8NaSA,112145.5187.270.873.070.8NaSA,113145.5187.270.873.073.0NaSA,114145.5187.270.873.073.0NaSA,114145.5187.273.073.073.0NaSA,114147.7173.573	Li ₂ MoO ₄	974	215.1	[1]	145.7	194.3	69.5
NoNSolS71I5S0.183.5S71NANCA83579.515.533.625.9NANCA579136.82068.3106.948.4NANCA579136.82068.3105.950.9NARGA579135.92068.815.150.9NARGA679165.423175.147.970.3NARCO531142.32373.170.370.3NARCO531142.315112.2126.432.6NARCO112185.5119.217.670.370.3NayCO112185.5111145.5186.666.2NayCO10721.511145.5186.666.2NayMO496721.511145.5186.666.2NayMO496721.511145.5186.665.6NayMO496721.511145.5186.665.6NayMO496721.511145.518.665.6NayMAF17.923.670.670.272.673.6NayMAF12.924.821.023.670.870.2NayAF12.024.821.023.670.870.2NayAF12.01340.972.453.670.8NayAF12.014.1145.970.870.370.3KOH63712.1 <td< td=""><td>Li₂WO₄</td><td>1013</td><td>205.0</td><td>[15]</td><td>145.9</td><td>185.0</td><td>59.1</td></td<>	Li ₂ WO ₄	1013	205.0	[15]	145.9	185.0	59.1
NACN NANOS7519593.625.925.9NANO577136.81966.3115.150.0NACO533133.92194.086.8115.150.0NAER679165.415117.547.947.9NABSO455124.11122115.0120.0120.0NAHCO531142.32377.162.0120.0NAMCO601154.823122.0126.435.0NaSOA113185.011146.3185.066.2NaSOA115204.211146.3185.066.2NaSOA962215.111145.5187.270.8NaSOA967216.311145.5187.270.8NaSAR120276.115204.270.870.5NaSAR120276.115201.0345.471.5NaSAR127.936.21550.133.031.1NaSAR127.936.21550.131.130.0NaSAR127.936.21550.131.130.0NaSAR127.936.21550.131.131.1NASAR127.936.21550.131.130.0NASAR127.936.21550.131.131.1NASAR127.936.21550.131.131.1NASAR1	NaOH	593	87.1	[15]	50.1	83.5	37.1
NANO575116.71966.3106.948.4NANO579136.82066.3115.139.0NACO53313.92194.039.0NAFA67916.41517.519.0NAFO53114.213.613.013.0NAFO53114.2237.512.012.0NARO60115.42312.212.612.0NayOO11218.91519.2178.958.2NayOO10022.511145.5186.659.6NayOO6721.511145.5186.659.6NayOO96721.51519.519.27.6NayOO96721.51519.67.57.6NayOO96721.61510.17.67.5NayAFA17.939.61550.17.17.5NayAFA17.939.61550.17.17.5KNA857.31567.57.119.019.0KNA857.31514.912.413.0KNA87.119.019.080.017.418.019.0KSO67.114.014.017.417.510.3KNA87.119.014.017.417.510.3KOH63.119.014.017.417.510.3	NaCN	835	79.5	[15]	53.6		25.9
NANO,57918.819.86.811.5.50.0NAGD,53313.92196.047.9NAEK,67.916.5.41517.547.9NAEKO,53112.375.167.2NAMCO,601154.82312.2126.435.6NaCO,601154.82312.2178.970.3NaSO,113199.511146.3185.066.2NaSO,115204.211145.5187.270.8NaSO,96721.5.11145.5187.270.8NaSO,67424.824.122.170.870.8NaSO,67424.824.122.170.870.8NaSO,67424.824.122.170.870.5NaSO,67424.824.122.170.870.5NaSO,67424.824.121.123.170.8NaSO,67424.81550.121.370.1NaSAF,12035.417.175.273.175.2NaSAF,1201550.121.321.321.3KNA,6721550.121.370.111.9KNA,6721567.370.070.370.3KNA,6741550.270.370.370.3KNA,68380.71550.270.315.2 <td>NaNO₂</td> <td>557</td> <td>116.7</td> <td>[19]</td> <td>68.3</td> <td>106.9</td> <td>48.4</td>	NaNO ₂	557	116.7	[19]	68.3	106.9	48.4
NaClo,533133.92194.039.9NaFSa679165.4115175.479.NaFSo,455246.1122115.6130.51NaHCO,531142.32375.1672NaHCO,601154.823122.2176.9070.3NayCO,1123180.5115192.2178.9070.3NayCO,1155204.211146.4177.058.8NayCO,1070212.511146.5186.659.6NayCO,674244.8241221.223.670.8NaySuG,674244.8151250.0345.475.2NaySuG,674244.8151250.0345.475.2NaySuG,677141.01988.014.230.0NayAF,112076.11550.121.3KNA,607141.01988.014.230.0KNA,607141.01988.014.230.0KNA,607140.01567.271.1KNA,607140.01988.014.230.0KNA,607140.01988.014.230.0KNA,607140.01988.017.270.3KNA,607140.01988.017.270.0KNA,607140.01988.017.270.0 <tr< td=""><td>NaNO3</td><td>579</td><td>136.8</td><td>[20]</td><td>86.8</td><td>115.1</td><td>50.0</td></tr<>	NaNO3	579	136.8	[20]	86.8	115.1	50.0
NaBFq6'915.41517.547.9NAHSO,455142.32375.167.2NAHCO,601154.82322.2126.432.6NayCO,112189.515119.2178.970.3NaySO,1123189.515119.2178.970.3NaySO,1123122.511146.3185.066.2NayMOQ,962215.111145.5187.270.8NayMOQ,967216.311145.5187.270.8NayMOQ,967216.311145.5187.270.8NaySO,674244.82422.170.875.2NayMO,96726.31550.130.130.1NayAFF,127.936.21550.131.117.2KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.131.1KIN89573.31550.131.1	NaClO ₃	533	133.9	[21]	94.0		39.9
NAHSQ, NAHCQ, S11124611121115.6130.1NAHCQ, S0153114.2323175.167.2NAMCQ, NayCQ,11314.8412.217.8.970.3NayCQ, NayCQ,112318.9.017.988.8.070.3NayCQ, NayCQ,107021.2.51114.5.4177.088.8NayCQ, NayCQ,107021.2.51114.5.5186.659.6NayMQ, NaySQ,67424.4.824121.223.670.8NayKR, NaySQ,112027.6.11114.5.5187.270.8NayKR, NaySQ,67424.4.824121.223.670.8NayKR, NayKR,112027.6.111.550.121.330.0KN NayKR,83383.115150.121.330.0KN, KSA, KSA,843167.215112.1.140.1KN, KSA, KSA,140.215167.531.073.1KRF, KSA, KSA,183.818112.0.117.2.463.8KRF, KSA, KSA,134.1145.9163.143.1169.2KRSA, KSA, KSA,141.9143.917.343.373.1KRSA, KSA, KSA,141.9144.917.373.3151KRSA, KSA, KSA,144.917.315.944.3151.9KRSA, KSA, KSA,144.917.315.944.3 <t< td=""><td>NaBF₄</td><td>679</td><td>165.4</td><td>[15]</td><td>117.5</td><td></td><td>47.9</td></t<>	NaBF ₄	679	165.4	[15]	117.5		47.9
NAHCQ2 531 142.3 123 75.1 601 54.8 NAMCQ2 601 154.8 123 122.2 126.4 32.6 NayCQ3 1123 189.5 115 119.2 178.9 70.3 NayCQ3 1070 212.5 11 146.3 185.0 66.2 NayMQ4 967 216.3 11 145.5 187.2 70.8 NayMQ4 967 216.3 11 145.5 187.2 70.8 NayMQ4 967 216.3 11 145.5 187.2 70.8 NaySyG7 674 244.8 124 221.2 70.8 70.8 NaySyG7 674 244.8 124 221.2 70.8 70.8 NaySyG7 674 244.8 155 50.1 70.8 70.8 KOH 633 83.1 155 54.0 71.8 71.8 KNS0 607 141.0 191 88.0 114.2 53.0 KKS4 843 167.2 15 67.0 71.1 169.2 KS04 1341 262.0 11 147.7 173.5 63.8 KyC04 189 <t< td=""><td>NaHSO₄</td><td>455</td><td>[246.1]</td><td>[22]</td><td>115.6</td><td></td><td>[130.5]</td></t<>	NaHSO ₄	455	[246.1]	[22]	115.6		[130.5]
NAMCO NaCO 1123154.8123122.2126.432.6NaCO NaCO1123185.515119.217.6082.8NaCOA1070212.511145.4177.058.8Na2COA1070212.511145.5186.639.6Na2MOA962215.111145.5186.639.6Na2MOA967216.311145.5186.639.6Na2SO674244.824121.223.6Na3MF61120276.11596.575.030.0Na3MF61279396.21550.130.030.0KN89575.31554.021.330.0KNS607141.01988.0114.233.0KMF2512104.61567.537.111.9KMF348.3167.217.1172.463.830.0KHF2512104.61567.537.111.9KKO117413.818120.1172.463.8KSO41341242.211147.7173.510.3KSO41341242.211147.7173.513.5KSO41341242.215524.245.733.6KSO413927.115148.915.915.9KSO413927.115149.817.373.3KSO4139	NaHCO ₂	531	142.3	[23]	75.1		67.2
Nay, Co, Nay, Co, Na	NaMeCO ₂	601	154.8	[23]	122.2	126.4	32.6
Na_5C0, N	Na ₂ CO ₃	1123	189.5	[15]	119.2	178.9	70.3
N=CrOq NayMOQ NayMOQ NayMOQ NayMOQ Solution122.511146.3185.066.2NayMOQ NayMOQ Solution967216.311145.5186.659.6NaySolot NaySife T12076.112121.223.623.6NaySife NayMife NaySife T279396.215221.0345.4175.2NayAffe NoyMife NayAffe77.31550.130.030.0KN Noy No	Na ₂ SO ₄	1155	204.2	[1]	145.4	177.0	58.8
No.body NayWo4962215.11145.5186.659.6NayWo4967216.311145.5187.270.8NaySy07674244.8224221.223.6NayAF61120276.115196.575.0NayAF61279396.215221.0345.475.2KOH63383.11554.021.3KNO89575.31554.021.3KNO3607141.01988.0114.253.0KHF251.2104.61567.561.161.1KS04481127.215121.161.163.8KS051341204.211149.9172.463.8KyC0413928.011147.7173.570.3KyC04189218.011147.7173.570.3KyC04189218.011147.7173.570.3KyC04189218.011147.7173.570.3KyS056326724222.44515RbOH65883.71550.215.315RbOY0583102.913148.2165.965.6RbS50770827.221.811148.2165.965.6RbS50770827.221.811148.2165.965.6RbS50770813.615 <t< td=""><td>Na₂CrO₄</td><td>1070</td><td>212.5</td><td>[1]</td><td>146.3</td><td>185.0</td><td>66.2</td></t<>	Na ₂ CrO ₄	1070	212.5	[1]	146.3	185.0	66.2
Na Na Na Na Na Na SpC674216.311145.5187.270.8Na Na SpC674244.8241221.223.6Na Na Na Na Na NA <b< td=""><td>Na_2MoO_4</td><td>962</td><td>215.1</td><td>[1]</td><td>145.5</td><td>186.6</td><td>59.6</td></b<>	Na_2MoO_4	962	215.1	[1]	145.5	186.6	59.6
Na 5,00,674244.8241221.223.6Na 5,81%1120276.1151196.579.6Na 5,81%1279396.2151221.0345.4175.2K0H63383.115150.130.0121.3KNo89575.315154.021.350.0KHF2512104.615167.537.1161.0KB74843167.2151121.163.863.8KKO134204.2151121.177.2463.3K5041341204.2151148.960.360.3K5041341204.2151148.960.360.3K504189218.0111147.777.570.3K6C306762267231.360.3151K504189218.015148.935.370.8K50501741[169.9]27.077.015.915.9RbN665883.71550.235.373.8RbN7583[102.9]27.1148.2165.965.6RbS5070827.221.345.457.3RbS0012513.811148.2166.658.9C52,0016112.516.514.2166.658.9C52,00121151148.2166.658.9C52,0012422.4166.6 <t< td=""><td>Na_2WO_4</td><td>967</td><td>216.3</td><td>[1]</td><td>145.5</td><td>187.2</td><td>70.8</td></t<>	Na_2WO_4	967	216.3	[1]	145.5	187.2	70.8
Na_51F Na_1AlF Na_	$Na_2S_2O_7$	674	244.8	[24]	221.2		23.6
NapAlF6127996215221.0345.4175.2KOH63383.11550.133.0KN3607141.01988.0114.253.0KN5_3607141.01988.0114.253.0KH5_2512104.61567.531.0KB5_4843167.21567.5160.1K15_0411120.1172.463.8K15_01174183.818120.1172.463.8K2C0_11174183.818120.1172.463.8K2C0_412009.215148.971.370.3K2C0_4189218.011147.7173.570.3K2C0_0671145.922.2231.3184.6]K2C0_06722672422.435.5K50_06922671550.233.5RbOH65883.71550.233.5RbS0_1141.1124.712619.594.255.6RbS_0_11361549.8171.357.3Rb2S0_113690.513.215.215.2Rb2S0_112813.650.135.7Rb2S0_11281550.135.7Rb2S0_11281550.135.7Rb2S0_11281550.135.7Rb2S0_11281550.135.7<	Na ₂ SiF ₆	1120	276.1	[15]	196.5		79.6
KOH 633 83.1 15 50.1 33.0 KCN 895 75.3 15 50.0 21.3 KN3 607 141.0 19 88.0 142. 53.0 KH5 512 104.6 15 67.5 37.1 KB4 84.3 167.2 15 121.1 46.1 KH50, 481 128.0 12 17.8 60.3 K50,4 134 04.2 11 149.9 172.4 63.3 K50,4 140 04.2 11 149.9 172.4 63.3 K50,4 1250 209.2 15 231.3 184.6] 63.4 K50,7 671 145.9 221 232.4 45 K50,7 692 267 24 222.4 45 K50,6 692 267 24 22.4 25.1 R50,7 692 267 26 19.5 54.2 52.1 R50,7 692 207.1 15 50.2 31.5 52.1 R50,7 783 102.91 26 19.5 94.2 52.1 R50,7 786 77.2 15 50.1	Na ₃ AlF ₆	1279	396.2	[15]	221.0	345.4	175.2
KNN 895 75.3 15 54.0 213 KNO3 607 141.0 19 88.0 114.2 53.0 KHF2 512 104.6 15 67.5 71.1 KBK4 843 167.2 15 21.1 46.1 KHS0, 481 [287.0] 22 17.8 [169.2] K2O3 1174 183.8 18 120.1 172.4 63.8 K2C04 130 29.2 15 148.9 63.8 63.8 K2C70 152 29.2 23.3 (18.4) 63.8 63.8 KyQ04 189 28.0 11 44.7 73.5 70.3 18.4) K5_Q7 67.2 267 24 22.4 45 55 77.0 15.9 18.4 10.1 19.8) 19.8	КОН	633	83.1	[15]	50.1		33.0
KN0 ₃ 607 14.0 19 88.0 114.2 53.0 KHF ₂ 512 104.6 15 67.5 37.1 KHF ₄ 843 167.2 15 121.1 161.1 KHS0 ₄ 481 [287.0] 122 117.8 163.8 K ₂ CO ₃ 1341 204.2 11 149.9 172.4 63.3 K ₂ CO ₄ 1250 209.2 15 144.9 70.3 60.3 K ₂ CO ₅ 671 [415.9] 25 231.3 184.6] 144.6] K ₂ SO ₇ 672 267 24 224 35.5 15 RbOH 658 83.7 15 50.2 35.3 15.9] 15 Rb ₂ CO ₃ 1124.7 26 19.5 94.2 15.2] 15 16 Rb ₂ CO ₃ 139 207.1 15 50.1 35.3 15 90.5 36.5 Rb ₂ CO ₃ 166 81.6 15 50.1 35.7 35.7 35.7 Rb ₂ CO ₃ 1061	KCN	895	75.3	[15]	54.0		21.3
KHF2 512 104.6 15 67.5 37.1 KBF4 843 167.2 15 121.1 46.1 KHS0, 481 1287.0] 22 117.8 [169.2] K203 1174 183.8 18 120.1 172.4 63.8 K204 1250 209.2 [15] 148.9 60.3 KyW0, 118 218.0 11 47.7 173.5 70.3 KyG70, 671 [415.9] 221 21.3 [18.46] Kyb0, 188 18.1 224 45 35.7 RbN1 658 83.7 [15] 50.2 31.5 RbN2 1339 207.1 [26] 119.5 94.2 [52] Rb2x0, 1329 27.1 [15] 148.8 171.3 57.3 Rb2x0, 1339 207.1 [26] 119.5 94.2 [52] Rb2x0, 125 213.8 [1] 148.2 [66.6 65.6 Rb2x0, 126 118.3 90.5 [32] [32] [32] Cs2C03 1061 [12.5] 26.6 118.3 90.5 [32] Cs2C03	KNO₃	607	141.0	[19]	88.0	114.2	53.0
KBF ₄ 843 167.2 [15] 121.1 [16.2] KHS0 ₄ 481 [287.0] [22] 177.8 [16.2] K2C0 ₃ 174 183.8 [18] 120.1 172.4 63.8 K2C0 ₄ 1341 204.2 [1] 149.9 172.4 63.8 K2C0 ₄ 1250 209.2 [15] 148.9 60.3 KyW0 ₄ 1189 218.0 [1] 147.7 173.5 70.3 KyC0 ₅ 671 [415.9] 25] 231.3 [18.46] 15 KyS2 ₀ 682 267 24] 222.4 45 15 KbDH 658 83.7 [15] 30.2 33.5 15 Rb2 ₂ C0 ₃ 114 [12.9] 29 87.0 77.0 [15.9] Rb2 ₂ C0 ₃ 139 207.1 [15] 149.8 171.3 57.3 Rb2 ₂ C0 ₃ 134 [24.7] 224.5 48.7 35.7 Rb2 ₂ C0 ₃ 166 81.6 15 50.1 31.5 CS0H 616 81.6 15 50.1 31.2 CS2C0 ₃ 166 81.6 15 90.6 53.9	KHF ₂	512	104.6	[15]	67.5		37.1
KHS04481[270][22]117.8[169.2] k_2C0_3 1174183.8[18]120.1172.463.8 k_2S0_4 1250209.2[15]148.960.3 k_3W0_4 189218.0[1]147.7173.570.3 $k_5C_2O_7$ 671[415.9][25]231.3[184.6]K_5S_0692267[24]22.445RbOH65883.7[15]50.233.5RbOJ583[102.9][26]119.594.2[5.2]RbS_2O_31141[124.7][26]119.594.2[5.2]Rb_2SO_4139207.1[15]149.8171.357.3Rb_2SO_4139207.1[51]149.8171.357.3Rb_2SO_4125213.8[1]148.2165.965.6Rb_2SO_7708272.2[24]223.548.731.5CsNO_3680136.0[15]90.645.445.4Cs_2O_31061[121.5]18.390.5[3.2]Cs_2O_4123420.0[1]148.2166.658.9Cs_2NO_412420.011148.2166.663.4Cs_2NO_412420.011148.2166.663.4Cs_2NO_412420.011148.2166.663.4Cs_2NO_4124210.011148.2166.663.4Cs_2NO_4 </td <td>KBF₄</td> <td>843</td> <td>167.2</td> <td>[15]</td> <td>121.1</td> <td></td> <td>46.1</td>	KBF ₄	843	167.2	[15]	121.1		46.1
$k_2 CO_3$ 1174183.818120.1172.463.8 $k_2 CO_3$ 1341204.211149.9172.464.3 $k_2 CTO_4$ 1250209.215148.960.3 $k_2 WO_4$ 1189218.011147.7173.570.3 $k_5 C_2 O_7$ 671[415.9]251231.3[184.6] $k_5 S_2 O_7$ 69226724222.445RbOH65883.71550.233.5RbNO_3583[102.9]27.077.0[15.9] $k_2 CO_3$ 141[124.7]2619.594.25.2]Rb_2 O_3139207.115149.8171.357.3Rb_2 O_3139207.1[15]49.8171.357.3Rb_2 O_316681.6[15]50.131.5CsOH61681.6[15]90.645.4Cs_2 CO_31061[121.5]126118.390.532.1Cs_2 CO_41286207.1[15]148.2166.658.9Cs_2 CO_41284200.0[16]148.2166.662.3Cs_2 CO_41284200.0[16]148.2166.662.3Cs_2 CO_41284200.0[16]148.2166.662.3Cs_2 CO_41284200.0[16]148.2166.663.4Cs_2 CO_41274216.061.863.463.4Cs_2 CO_4 <td>KHSO₄</td> <td>481</td> <td>[287.0]</td> <td>[22]</td> <td>117.8</td> <td></td> <td>[169.2]</td>	KHSO ₄	481	[287.0]	[22]	117.8		[169.2]
$K_5 0_4$ 13412042[1]149.9172.454.3 $K_2 Cr_0$ 1250209.2[15]148.960.3 $K_2 W0_4$ 1189218.0[147.7]173.570.3 $K_2 Cr_2 0_7$ 671[415.9]25]231.3[184.6] $K_5 \Sigma_0 7$ 66226724]222.435 $Rb0H$ 65883.7[15]50.231.3 $Rb0A_3$ 583[102.9]29]87.077.0[15.9] $R_5 Co_3$ 1141[124.7]26]119.594.2[5.2] $Rb_2 No_4$ 125213.8[1]148.2165.965.6 $Rb_2 No_4$ 125213.8[1]148.2165.965.6 $Rb_2 No_4$ 126118.390.5[3.2]32.1 $CsO4$ 126118.390.5[3.2]22.2 $CsC0_3$ 1061[121.5]148.2166.662.3 $Cs_2 Co_4$ 128200.9[1]148.2166.662.3 $Cs_2 No_4$ 120210.0[1]148.1168.666.1 $Cs_2 So_4$ 12724.224.767.467.4 $Cs_2 So_4$ 128130.327.182.027.257.1 $Ray0_3$ 483139.12082.027.257.1 $Ray0_3$ 483130.327.182.027.257.1 $Ray0_3$ 484130.327.182.148.2 $Ray0_3$ 484 <td>K₂CO₃</td> <td>1174</td> <td>183.8</td> <td>[18]</td> <td>120.1</td> <td>172.4</td> <td>63.8</td>	K ₂ CO ₃	1174	183.8	[18]	120.1	172.4	63.8
$k_2 cro_4$ 1250209.215148.960.3 $k_2 W0_4$ 1189218.01147.7173.570.3 $k_2 Cr_0 7$ 671[415.9]25231.3[184.6] $k_5 S_0 7$ 69226724222.435.5RbM 6 65883.71550.233.5RbN 3583[102.9]2987.077.0[15.9]Rb_2 CO_31141[124.7]26]119.594.2[5.2]Rb_2 CO_41339207.115149.8171.357.3Rb_2 No_4125213.811148.2165.665.6Rb_2 S_0 770827.224]223.548.731.5C SOH61681.61550.131.532.1C SNO_3680136.01590.645.432.1C S_2 Co_412421.91148.2166.658.9C S_2 Co_412421.91148.6164.662.3C S_2 Co_412421.01148.2166.061.8C S_2 MO_4127214.21148.1168.666.1C S_2 Sol_4139.12082.0127.257.1AgN 3483130.32782.148.248.2N 4 MN 3443130.32782.148.2N 4 MN 3443161.128102.059.1	K ₂ SO ₄	1341	204.2	[1]	149.9	172.4	54.3
$K_2 W 0_4$ 1189218.011147.7173.570.3 $K_2 Cr_2 0_7$ 671[415.9][25]231.3[184.6] $K_2 5_0 0_7$ 692267[24]222.453.5RbOH65883.7[15]50.233.5RbN0_3583[102.9][29]87.077.0[15.9] $Rb_2 Co_3$ 1141[124.7][26]119.594.2[5.2] $Rb_2 W 0_4$ 1225213.8[1]148.2165.965.6 $Rb_2 So_4$ 708272.2[24]223.548.731.5 $Cs OH$ 61681.6[15]50.131.5 $Cs N 0_3$ 680136.0[15]90.645.4 $Cs_2 Co_3$ 1061[121.5][26]118.390.5[3.2] $Cs_2 Co_4$ 123420.9[1]148.2166.662.3 $Cs_2 M 0_4$ 1220210.0[1]148.2166.662.3 $Cs_2 So_4$ 1234210.9[1]148.2166.061.8 $Cs_2 So_4$ 1234210.9[21]24.766.161.8 $Cs_2 So_4$ 937205.0[15]142.1182.562.9 $R N 0_3$ 483130.1[20]82.0127.257.1 $R N 0_3$ 484130.3[27]82.148.2 $R N 0_3$ 443161.1[28]102.059.1	K ₂ CrO ₄	1250	209.2	[15]	148.9		60.3
$K_2 Cr_2 O_7$ 671 $[415.9]$ $25]$ 231.3 $[184.6]$ $K_2 S_2 O_7$ 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 $[15.9]$ $Rb_2 CO_3$ 1141 $[124.7]$ $26]$ 119.5 94.2 $[5.2]$ $Rb_2 NO_4$ 1339 207.1 $15]$ 149.8 171.3 57.3 $Rb_2 NO_4$ 1225 213.8 $1]$ 148.2 165.9 65.6 $Rb_2 S_2 O_7$ 708 272.2 $24]$ 223.5 48.7 $CsOH$ 616 81.6 $15]$ 50.1 31.5 $Cs_2 CO_3$ 1061 $[121.5]$ $26]$ 118.3 90.5 $[3.2]$ $Cs_2 CO_3$ 1061 $[121.5]$ 148.2 166.6 58.9 $Cs_2 CO_4$ 1234 210.9 $1]$ 148.6 164.6 62.3 $Cs_2 WO_4$ 127.2 210.0 $[1]$ 148.1 168.6 66.1 $Cs_2 WO_4$ 127.2 205.0 $15]$ 142.1 182.5 62.9 $AgNO_3$ 483 139.1 $20]$ 82.1 48.2 66.4 $M_4 NO_3$ 443 161.1 $28]$ 102.0 59.1	K_2WO_4	1189	218.0	[1]	147.7	173.5	70.3
$K_2 S_2 O_7$ 692 267 24 222.4 35 RbOH 658 83.7 15 50.2 33.5 RbNO_3 583 102.9 29 87.0 77.0 15.9 Rb_2 CO_3 1141 124.7 26 119.5 94.2 $[5.2]$ Rb_2 NO_4 1329 207.1 15 149.8 171.3 573.3 Rb_2 NO_4 1225 213.8 11 148.2 165.9 65.6 Rb_2 S_2 O_7 708 272.2 244 223.5 48.7 CsOH 616 81.6 15 90.6 45.4 Cs_2 CO_3 1061 121.5 26 118.3 90.5 32.5 Cs_2 CO_3 1061 121.5 26 118.3 90.5 32.5 Cs_2 CO_4 1234 210.9 11 148.6 164.6 62.3 Cs_2 WO_4 1272 210.0 11 148.1 166.6 63.8 Cs_2 WO_4 1217 214.2 11 148.1 166.6 62.3 Cs_2 WO_4 1217 214.2 12 21.2 71.1 AgNO_3 483 139.1 20 82.0 127.2 57.1 AgNO_3 484 130.3 27 82.1 82.1 48.2 $11NO_3$ 484 130.3 27 82.1 82.1 83.4 $11N_4N_3$ 443 161.1 28 102.0 59.1	$K_2Cr_2O_7$	671	[415.9]	[25]	231.3		[184.6]
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] 261 119.5 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_2SO ₇ 708 27.2 24 223.5 48.7 31.5 CsOH 616 81.6 [15] 50.1 31.5 31.5 Cs2C0 ₃ 1061 [121.5] [26] 118.3 90.5 [3.2] Cs2C0 ₄ 1286 207.1 [15] 148.2 166.6 58.9 Cs2C0 ₄ 1284 210.9 [1] 148.6 164.6 62.3 Cs2Mo ₄ 120 210.0 [1] 148.2 166.6 66.1 Cs2So ₄ 127 214.2 [1]	$K_2S_2O_7$	692	267	[24]	222.4		45
RbNO3583[102.9]2987.077.0[15.9]Rb_CO31141[124.7]26119.594.2[5.2]Rb_SO41339207.115149.8171.3573Rb_SQ041225213.8[15]149.8165.965.6Rb_S2O7708272.2[24]223.548.7CsOH61681.61550.131.5CsNO3680136.0[15]90.645.4Cs2C031061[121.5]26]118.390.5[3.2]Cs2S041286207.115148.2166.658.9Cs2C041234210.9[1]148.6164.662.3Cs2N041217214.2[1]148.1168.666.1Cs2S07728292.3[24]224.767.6AgNO3483139.120]82.0127.257.1Ag2S04937205.015142.1182.562.9TINO3484130.3[27]82.148.2Tl_SO4905205.015141.663.4NH4NO3443161.1[28]102.059.1	RbOH	658	83.7	[15]	50.2		33.5
Rb ₂ CO ₃ 1141 [124.7] [26] 119.5 94.2 [5.2] Rb ₂ SO ₄ 1339 207.1 [15] 149.8 171.3 57.3 Rb ₂ SO ₇ 708 213.8 [1] 148.2 165.9 65.6 Rb ₂ SO ₇ 708 27.2 [24] 223.5 48.7 CsOH 616 81.6 [15] 90.6 45.4 CsNO ₃ 680 136.0 [15] 90.6 45.4 Cs ₂ CO ₃ 1061 [121.5] [26] 118.3 90.5 [3.2] Cs ₂ CO ₃ 1061 [121.5] [26] 118.3 90.5 [3.2] Cs ₂ CO ₃ 1061 [121.5] [26] 118.3 90.5 [3.2] Cs ₂ CO ₄ 1234 210.9 [1] 148.2 166.6 62.3 Cs ₂ WO ₄ 1217 214.2 [1] 148.1 168.6 66.1 Cs ₂ SO ₇ 728 292.3 [24] 224.7 67.6 67.6 AgNO ₃ 483 139.1 [20]	RbNO3	583	[102.9]	[29]	87.0	77.0	[15.9]
Rb2S041339207.1[15]149.8171.357.3Rb2W041225213.8[1]148.2165.965.6Rb2S07708272.2[24]223.548.7CsOH61681.6[15]50.131.5CsN03680136.0[15]90.645.4Cs2C31061[121.5][26]118.390.5[3.2]Cs2S041286207.1[15]148.2166.658.9Cs2CrO41234210.9[1]148.6164.662.3Cs2W041217214.2[1]148.1168.666.1Cs2S07728292.3[24]224.767.6AgN03483139.1[20]82.0127.257.1INO3484130.3[27]82.148.2INO3443161.1[28]102.059.1	Rb ₂ CO ₃	1141	[124.7]	[26]	119.5	94.2	[5.2]
Rb2W041225213.81148.2165.965.6Rb2S207708272.224223.548.7Cs0H61681.61550.131.5CsN03680136.01590.645.4Cs2C031061121.526118.390.5[3.2]Cs2C041286207.115148.2166.658.9Cs2C041234210.91148.6164.662.3Cs2W041220210.01148.2166.061.8Cs2V041217214.21148.1188.666.1Cs2S07728292.324224.767.667.6AgNO3483139.1[20]82.0127.257.1INO3484130.3[27]82.148.263.4INA3443161.1[28]102.059.1	Rb_2SO_4	1339	207.1	[15]	149.8	171.3	57.3
Rb2S2O7708272.224223.548.7CsOH61681.6 $[15]$ 50.131.5CsNO3680136.0 $[15]$ 90.645.4Cs2C031061 $[121.5]$ [26]118.390.5[3.2]Cs2S041286207.1 $[15]$ 148.2166.658.9Cs2C041234210.9 $[1]$ 148.6164.662.3Cs2W041220210.0 $[1]$ 148.1168.666.1Cs2S07728292.3 $[24]$ 224.767.6AgNO3483139.1[20]82.0127.257.1Ag2S04937205.0 $[15]$ 142.1182.562.9TINO3484130.3[27]82.148.2Tl_SO4905205.0 $[15]$ 141.663.4NH4NO3443161.1[28]102.059.1	Rb_2WO_4	1225	213.8	[1]	148.2	165.9	65.6
CsOH61681.6[15]50.131.5CsN03680136.0[15]90.645.4Cs2C031061[121.5][26]118.390.5[3.2]Cs2S041286207.1[15]148.2166.658.9Cs2C041234210.9[1]148.6164.662.3Cs2W04120210.0[1]148.1168.666.1Cs2W041217214.2[1]148.1168.666.1Cs2S07728292.3[24]224.767.6AgN03483139.1[20]82.0127.257.1Ag2S04937205.0[15]142.1182.562.9TIN03484130.3[27]82.148.263.4NH4N03443161.1[28]102.059.1	$Rb_2S_2O_7$	708	272.2	[24]	223.5		48.7
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	CsOH	616	81.6	[15]	50.1		31.5
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	CsNO ₃	680	136.0	[15]	90.6		45.4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cs_2CO_3	1061	[121.5]	[26]	118.3	90.5	[3.2]
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cs ₂ SO ₄	1286	207.1	[15]	148.2	166.6	58.9
	Cs ₂ CrO ₄	1234	210.9	[1]	148.6	164.6	62.3
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cs ₂ MoO ₄	1220	210.0	[1]	148.2	166.0	61.8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cs ₂ WO ₄	1217	214.2	[1]	148.1	168.6	66.1
AgNO3483139.1[20]82.0127.257.1 Ag_2SO_4 937205.0[15]142.1182.562.9TINO3484130.3[27]82.148.2 Tl_2SO_4 905205.0[15]141.663.4 NH_4NO_3 443161.1[28]102.059.1	$Cs_2S_2O_7$	728	292.3	[24]	224.7		67.6
Ag2SU4937205.0[15]142.1182.562.9TINO3484130.3[27]82.148.2 T_2SO_4 905205.0[15]141.663.4 NH_4NO_3 443161.1[28]102.059.1	AgNO ₃	483	139.1	[20]	82.0	127.2	57.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ag ₂ SO ₄	937	205.0	[15]	142.1	182.5	62.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TINO ₃	484	130.3	[27]	82.1		48.2
NH_4NO_3 443 161.1 [28] 102.0 59.1	$\Pi_2 SO_4$	905	205.0	[15]	141.6		63.4
	INH ₄ INU 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:

$$C_V = C_P \left[1 - \left(1 + \frac{C_P \kappa_S}{\alpha_P^2 V T} \right)^{-1} \right] = C_P \left[1 - \left(1 + \frac{C_P}{u^2 \alpha_P^2 M T} \right)^{-1} \right]$$
(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:

$$\gamma = (0.73 \pm 0.04) + (1.30 \pm 0.13) \cdot (d_{C-A}/nm)$$
(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 NO₃⁻, 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, $\Delta C_P = C_P - C_P$ (i.g.), does not correlate so well with the inter-ionic distances d_{C-A} . For salts with univalent polyatomic anions ΔC_P increases with d_{C-A} :

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

but there are nearly as many outliers from a linear dependence as there are salts conforming to it. For salts with divalent anions $\Delta C_P \approx 68 \pm 5 \,\mathrm{J}\,\mathrm{K}^{-1}\,\mathrm{mol}^{-1}$, without a clear dependence on $d_{\mathrm{C-A}}$. This is contrary to the well established linear dependencies of ΔC_P on $d_{\mathrm{C-A}}$ 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:

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

Here ν is the number of ions constituting the salt: 2 for uniunivalent and 3 for uni-divalent salts. The packing fraction accentuates the inter-ionic distance d_{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:

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

for 37 salts with a correlation coefficient of 0.947 and a standard error of 6 J K⁻¹ 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 RbNO₃, 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:

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

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 $1.1T_{\rm m}$ 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 (θ = 780 and 490 K [11]) or for low-melting salts such as LiNO₃ (θ = 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 $\theta/K = 5.4 v/(\langle M \rangle/\text{kg mol}^{-1}) \cdot (d_{C-A}/\text{nm})^3)^{1/2}$, 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 $1.1T_{\rm m}$ 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]:

$$C_P = 5R + 2R[-1 + \alpha_P T f(y)]$$
(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, 5*R*, is $C_P(i.g.)$ 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:

$$u_{\mathsf{C}-\mathsf{A}} = \frac{z_{\mathsf{C}} z_{\mathsf{A}} e^2}{4\pi\varepsilon_0 r} \quad \text{for } r > d_{\mathsf{C}-\mathsf{A}} \quad \text{and} \quad u_{\mathsf{C}-\mathsf{A}} = \infty \quad \text{for } r < d_{\mathsf{C}-\mathsf{A}} \quad (9)$$

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_{C-A} is taken to be independent of the temperature, then the expansion on heating is confined to the increase in the void volume:

$$V_{\rm f} = V - \left(\frac{\nu \pi N_{\rm A}}{6}\right) d_{\rm C-A}^{3} \tag{10}$$

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_{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 $C_P(i.g.)$ temperature dependent [5], $(\partial C_P(i.g.)/\partial T)_P \sim 0.055 \pm 0.01 \text{ J K}^{-2} \text{ mol}^{-1}$ 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 J K⁻¹ 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 $\Delta C_P (\approx C_P^Q \text{ at } 1.1T_m)$ for these salts is $68 \pm 5 \text{ J K}^{-1}$ 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

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

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