

Partial Molal Volumes of MgCl_2 , CaCl_2 , SrCl_2 , and BaCl_2 in Aqueous Solution to 200°

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From precise density measurements to 200° on aqueous solutions of magnesium, calcium, strontium, and barium chlorides, the partial molal volumes of the salts, ϕ° were calculated. The values of ϕ° pass through a maximum at temperatures ranging from about 30° for MgCl_2 to 60° for SrCl_2 and BaCl_2 . A useful correlation of electrostriction-volume loss V^e for both the alkali and alkaline earth ion series is given by a new empirical equation $V^e = A'z^{3/2}/\bar{r}$, where $\bar{r} = 1.38 + \text{ion radius}$. Values of A' are reported for the temperature range $25\text{--}200^\circ$, and should prove useful in estimating the partial molal volume of other uni- and bi-valent spherical ions.

THE partial molal volumes of alkali chlorides were recently reported,¹ derived from precise density measurements of salt solutions to 200° . We now present similar information for the alkaline earth chlorides. The relationship of ion size and charge to the temperature-dependence of the molal volume of spherical ions is examined in terms of the electrostriction-volume loss associated with individual ions.

EXPERIMENTAL

The equipment and method of interpretation of the density results were as described.¹ All densities and molal volume calculations are given for a total pressure of 20 atm. The experiments determined the density change of solutions between 50° and a higher temperature with significance in the fifth decimal place, so that to make full use of the experimental precision, reference densities to five decimal

places at 50° were required. As for alkaline earth chlorides densities at 50° were available² only to four decimal places, an arbitrary zero was added as the fifth decimal place to the published figures² for 50° to create the reference baseline. The five-decimal-place high-temperature densities shown in Figure 1 are relative to the density values at 50° so derived. Apparent molal volumes calculated from the densities at 50° in Table I give close to linear graphs of ϕ versus $m^{1/2}$.

A systematic change of unity in the fourth decimal place for the densities at 50° for a salt would cause the extrapolated 50° limiting partial molal volume, ϕ° , to be changed by 1 to 1.5 c.c./mole. A systematic change of similar value in ϕ° would be caused at all the higher temperatures, but this is not important when it is the great variations in ϕ° with temperature that are of primary interest.

¹ A. J. Ellis, *J. Chem. Soc. (A)*, 1966, 1579.

² International Critical Tables, 1928, vol. 3, McGraw-Hill Book Co., New York.

TABLE 1

Densities (g./c.c.) of salt solutions of molality m , at temperatures up to 200°, and at a constant total pressure of 20 atm. The fifth figure following the decimal point has relative significance only to the arbitrarily selected figure shown in this position for the results at 50°

Temp.	Molality	50°	75°	100°	125°	150°	175°	200°
MgCl ₂	1	1.06072	1.04846	1.03385	1.01724	0.99852	0.97791	0.95543
	0.5	1.02614	1.01344	0.99797	0.98017	0.95988	0.93735	0.91260
	0.2	1.00417	0.99120	0.97516	0.95657	0.93527	0.91148	0.88499
	0.1	0.99662	0.98351	0.96724	0.94832	0.92664	0.90233	0.87530
CaCl ₂	1	1.07252	1.05939	1.04397	1.02672	1.00703	0.98554	0.96201
	0.5	1.03221	1.01909	1.00324	0.98511	0.96457	0.94204	0.91660
	0.2	1.00675	0.99358	0.97739	0.95868	0.93719	0.91326	0.88670
	0.1	0.99796	0.98479	0.96844	0.94949	0.92776	0.90320	0.87613
SrCl ₂	0.05	0.99348	0.98027	0.96385	0.94478	0.92280	0.89810	0.87070
	1	1.11863	1.10456	1.08818	1.06980	1.04919	1.02662	1.00182
	0.5	1.05535	1.04173	1.02540	1.00670	0.98555	0.96204	0.93620
	0.2	1.01596	1.00258	0.98618	0.96720	0.94556	0.92134	0.89458
BaCl ₂	0.1	1.00253	0.98924	0.97279	0.95371	0.93188	0.90731	0.88010
	1	1.15782	1.14305	1.12593	1.10676	1.08528	1.06167	1.03589
	0.5	1.07531	1.06130	1.04459	1.02543	1.00385	0.97978	0.95335
	0.2	1.02405	1.01053	0.99396	0.97483	0.95297	0.92854	0.90147
	0.1	1.00661	0.99322	0.97671	0.95761	0.93556	0.91091	0.88361

RESULTS

Table 1 summarises the densities obtained by experiment, based on the values shown for 50°. The apparent molal volume ϕ was calculated from these results for the salts at each concentration and temperature by the equation

$$\phi = (V - n_1 V_w^\circ) / n_2 \quad (1)$$

V is the volume of the system, V_w° the molar volume of water, and n_1 and n_2 are the number of moles of water and of salt, respectively. Values of ϕ for the four salts are plotted as a function of the square-root of molality, $m^{1/2}$, in Figures 1—4.

By extrapolation of ϕ values to zero salt concentration, limiting partial molal volumes ϕ° at each temperature were obtained (Table 2). The Table also gives ϕ° values for

TABLE 2

Values of the limiting partial molal volume ϕ° for the alkaline earth chlorides

Temp.	25°	50°	75°	100°	125°	150°	175°	200°
MgCl ₂	15.6	15.1	13.1	8.6	2.2	-6.6	-20.0	-36.0
CaCl ₂	17.0	17.6	15.7	12.0	4.5	-3.3	-13.0	-29.7
SrCl ₂	17.0	19.0	18.0	14.6	8.4	0.0	-11.5	-28.0
BaCl ₂	25.9	27.8	27.1	23.9	17.7	10.5	-1.0	-16.0

25° derived from the published densities. Whereas straight-line graphs gave a satisfactory interpretation of the ϕ versus $m^{1/2}$ relationships for alkali chlorides,¹ lines with a slight curvature which increased with temperature were necessary to join the experimental points for the alkaline earth chlorides.

The error in ϕ° resulting from the uncertainty in free-hand extrapolation increases with temperature and by 200° the ϕ° values could possibly be in error by up to 2—3 c.c./mole. The slopes of the plots of ϕ versus $m^{1/2}$ are very similar at each temperature for all of the alkaline earth chlorides, and much greater than for the alkali chloride series.

DISCUSSION

Trends with temperature in the limiting partial molal of the alkali and alkaline earth chlorides are plotted in Figure 5 as a function of the specific volume of water.¹

¹ E-an Zen, *Geochim. Cosmoch. Acta*, 1957, **12**, 103.

For strontium and barium chlorides a maximum occurs in ϕ° at about 60° as for sodium, potassium, and caesium chlorides. Calcium chloride has a maximum ϕ° value

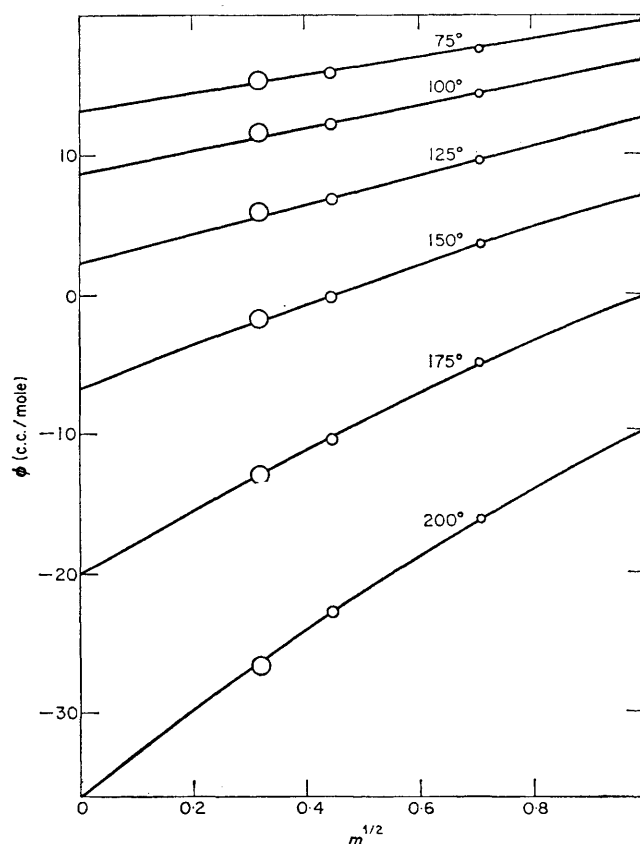


FIGURE 1 The variation of apparent molal volume, ϕ , of magnesium chloride with salt concentration, m

at about 40°, as for lithium chloride, while for MgCl₂ a maximum occurs about 30° (ϕ° for MgCl₂ at 0 and 10° is 12.7 and 14.6, respectively³).

The alkaline earth chlorides show approximately

parallel changes in ϕ° with increasing temperatures above about 75°, a behaviour quite distinct from that for the alkali chlorides (Figure 5).

On the basis of a previous analysis,¹ the average slopes of the graphs at high temperatures can be interpreted to give values of n , the average number of water molecules associated with hydration shells about the dissolved ion of the salts. Values of n between 150 and 200° all fall in the range 20–24 for the alkaline earth chlorides, compared with a range of 9–12 for the alkali

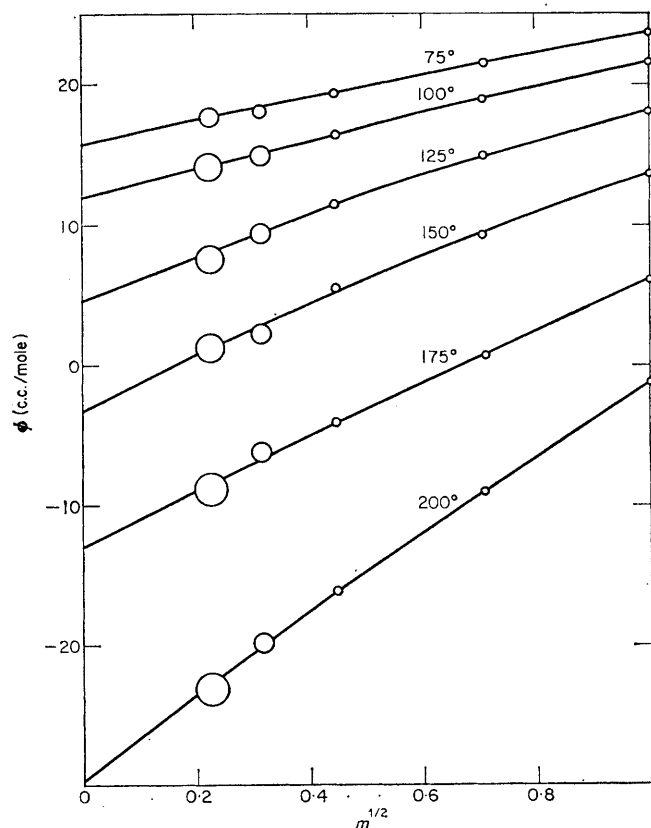


FIGURE 2 The variation of apparent molal volume, ϕ , of calcium chloride with salt concentration, m

chlorides. Whereas the slopes were all similar for the former group at these temperatures, for the latter group n decreased from about 12 to 8 in the series lithium to caesium. There is apparently little relationship between hydration and ion size for the alkaline earth metal ions.

As in the earlier Paper¹ the effect of temperature on ϕ° can be examined in terms of the intrinsic volume, V° , and the electrostriction-volume loss V^e for the ions of the salts. Following Glueckauf,⁴ we can calculate V°

$$\phi = V^\circ - V^e \quad (2)$$

from the ionic radii by taking into account the spacial arrangement of water molecules about the ions. V° changes little with temperature. Temperature effects on partial molal volumes arise principally from changes in V^e , and it is important to see how this changes with

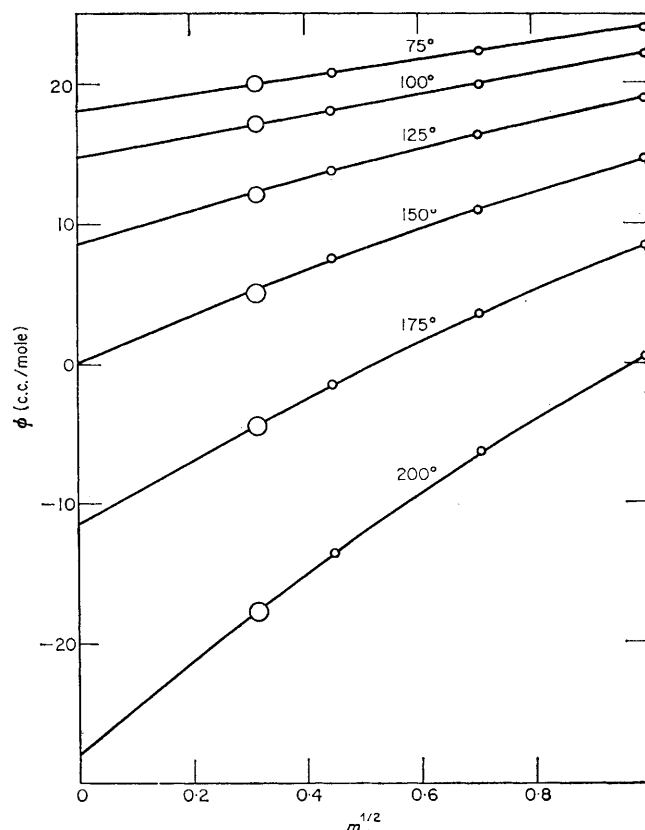


FIGURE 3 The variation of apparent molal volume, ϕ , of strontium chloride with salt concentration, m

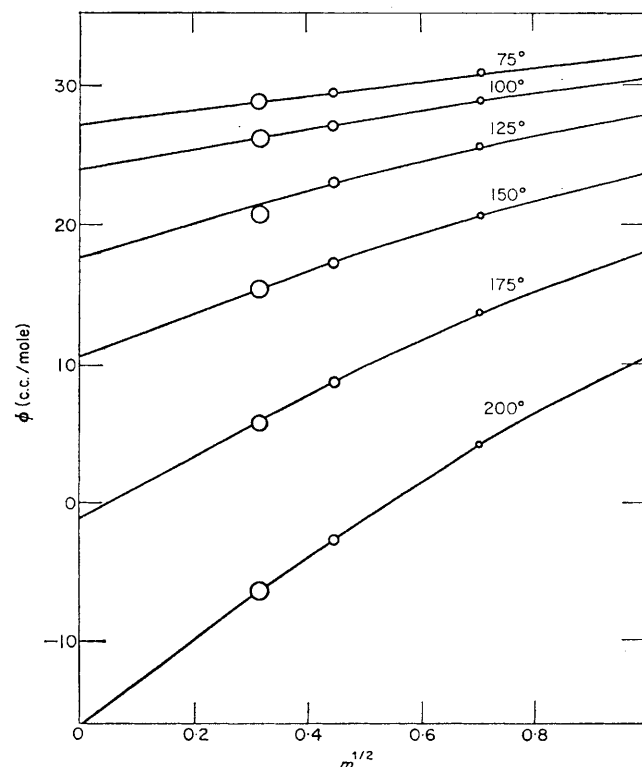


FIGURE 4 The variation of apparent molal volume, ϕ , of barium chloride with salt concentration, m

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ion size and charge for a range of salts. For many spherical univalent ions V^e is inversely proportional⁴ to a modified ionic radius \bar{r} ($\bar{r} = r_o + 1.38 \text{ \AA}$), and Glueckauf⁴ developed the following equation

$$V^e = Az^2/\bar{r} \quad (3)$$

A constant value of A at each temperature adequately expressed¹ the values of V^e for chloride solutions of the

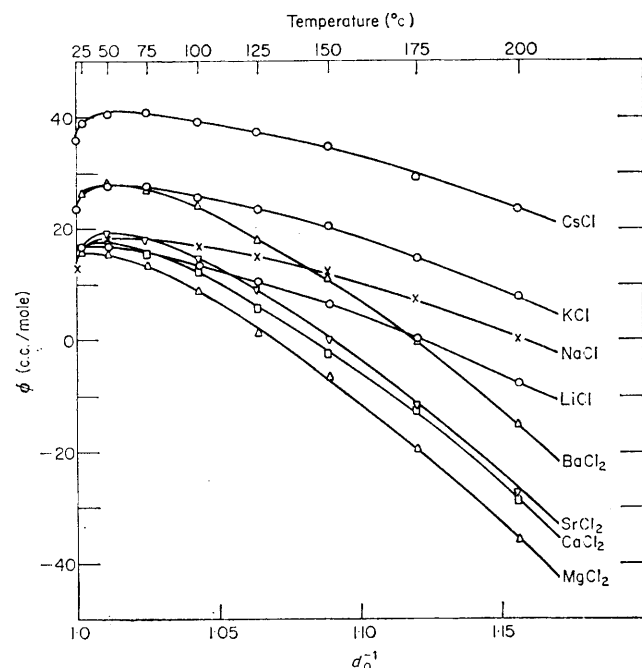


FIGURE 5 The change in limiting partial molal volume, ϕ° , of alkali and alkaline earth chlorides with specific volume of water, d_0^{-1}

larger univalent ions Cs^+ and K^+ up to 200° , and for sodium chloride up to 125 – 150° . Lithium chloride was anomalous.

However, if equation (3) is applied to the alkaline earth chlorides, the calculated mean value of A at a given temperature is considerably lower than that for the alkali chlorides. Glueckauf⁴ pointed out that equation (3) did not apply to ions with $z^{1/2}/\bar{r}$ ratios above about 0.5, and introduced another factor, namely the number of "ice structure" water molecules about ions of high $z^{1/2}/\bar{r}$ ratio.

In the analysis of the present partial molal volume results it was found empirically that equation (4) allowed a correlation of the electrostriction-volume losses for both alkali and alkaline earth chlorides to at least 150° without introducing further factors.

$$V^e = A'z^{3/2}/\bar{r} \quad (4)$$

This modification of equation (3) is in line with a charge-saturation effect about multivalent ions. If the ion charges were fully effective equation (3) rather than equation (4) is predicted by theory.⁴ We cannot suggest a theoretical reason why a $\frac{3}{2}$ power to z should apply.

⁴ E. Glueckauf, *Trans. Faraday Soc.*, 1965, **61**, 914.

The partial molal volume information is analysed below through the use of equation (4), and with the assumption that $A'_{\text{Cs}} = A'_{\text{K}} = A'_{\text{Cl}}$ (see Table 4), i.e., the electrostriction effects of large cations and anions are equal. Table 3 contains the calculated values

TABLE 3

Total intrinsic volume ($V^\circ_{\text{M}^{2+}} + 2V^\circ_{\text{Cl}^-}$) of the ions of the alkali chlorides at various temperatures

Temp.	25°	50°	75°	100°	125°	150°	175°	200°
MgCl_2	70.8	71.7	71.7	73.4	74.4	75.3	77.4	80.5
CaCl_2	75.6	76.6	76.6	78.4	79.5	80.5	82.7	86.1
SrCl_2	78.4	79.3	79.3	81.3	82.4	83.4	85.7	89.2
BaCl_2	83.4	84.7	84.7	86.8	88.0	89.0	91.4	95.2

for the total intrinsic volumes V° of the ions for each alkaline earth salt which were used in conjunction with equation (2).

In Table 4, A' values are summarised for the alkaline earth metal ions, and the alkali ions. By use of a $z^{3/2}$, instead of z^2 term, the agreement between A' values derived from the electrostriction volumes for the larger uni- and bi-valent ions is excellent up to 150° . At higher temperatures the bivalent ions tend towards a

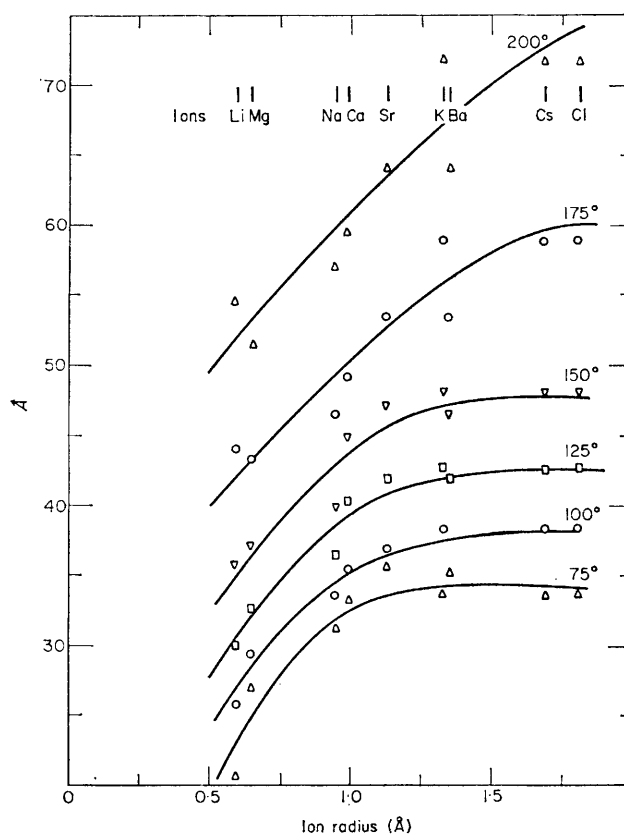


FIGURE 6 Trends in the coefficient A' with ionic radii, r_o , at various temperatures

lower electrostriction-volume loss, probably through the formation of an open structured water shell about themselves in the same manner as the lithium ion does over the whole temperature range.

TABLE 4

Values of the coefficient A' , which relates the electrostriction volume V^e to the charge z and \bar{r} for various ions ($V^e = A'z^{3/2}/\bar{r}$)

Temp.	25°	50°	75°	100°	125°	150°	175°	200°
Mg ²⁺	24.2	25.4	26.9	29.3	32.6	37.0	43.3	51.5
Ca ²⁺	31.0	31.8	33.2	35.4	40.3	44.9	49.2	59.5
Sr ²⁺	35.4	34.8	35.6	36.9	41.9	47.1	53.5	64.1
Ba ²⁺	35.1	34.6	35.2	36.1	42.0	46.5	53.5	64.0
Li ⁺	19.0	19.8	20.4	25.7	29.9	35.7	44.0	54.5
Na ⁺	32.8	31.0	31.2	33.6	36.4	39.8	46.5	57.0
K ⁺	} 34.3	34.0	33.5	38.5	42.6	48.2	58.5	71.7
Cl ⁻								
Cs ⁺	} 34.6	34.4	33.9	38.4	42.9	48.3	59.4	71.7
Cl ⁻								

Magnesium (ionic radius $r_0 = 0.65$ Å) produces values of the electrostriction coefficient, A' , at all temperatures which are very similar to those for the lithium ion ($r_0 = 0.60$ Å). The calcium ion ($r_0 = 0.99$ Å) behaves in a manner parallel to that for the sodium ion ($r_0 = 0.95$ Å). The trends in values of A' with ionic radii, r_0 , are shown

for uni- and bi-valent ions in Figure 6; at each temperature a constant A' value is approached with increasing ion size. At temperatures up to about 75°, A' is constant for r_0 values above about 1.1 Å, but with rising temperature a constant A' value is approached at increasingly greater r_0 . By 200° the correlation between A' and r_0 is still good but individual variations from the mean line for various ions are more marked. Figure 6 [with Table 4 and equation (4)] can be used to estimate the electrostriction-volume loss contribution to the partial molal volume of spherical ions for temperatures up to 200°. An accuracy of ± 2 c.c./mole in estimating V^e is probable for temperatures up to 150°, and ± 4 c.c./mole at 175–200°. The addition of the calculated⁴ intrinsic volume of the ion gives an estimate of the ionic partial molal volume.

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