Effect of Pressure on the Electrical Conductivities of Some Fused Nitrates, Nitrites, Chlorates, Perchlorates, Dichromates and Thiocyanates

By Brian Cleaver

Department of Chemistry, The University, Southampton SO9 5NH

The pressure dependence of the electrical conductivity (κ) has been measured over the range 1-1000 bar (1 bar = 10^5 N m^{-2}) at temperatures up to 420°C, for the following fused salts: LiClO$_3$, LiClO$_4$; NaNO$_2$, NaClO$_3$, Na$_2$Cr$_2$O$_7$; KClO$_3$, K$_2$Cr$_2$O$_7$, KSCN; AgNO$_3$. The volumes $\Delta V_\kappa = -RT(\partial \ln \kappa/\partial P)_T$ were calculated from these results. For a given cation, the value of ΔV_κ increases as the size of the anion increases and *vice versa*. ΔV_κ was approximately independent of temperature for some of the salts studied, but for others (notably LiClO$_3$ and KSCN) ΔV_κ increased steeply as the temperature was lowered. This behaviour is interpreted as being due to a rise in the glass transition temperature with pressure. An equation is proposed which allows the high-temperature limiting value of ΔV_κ to be estimated using experimental data obtained at lower temperatures.

Several studies have been made of the isothermal effect of pressure on the electrical conductivities of molten salts.[1-8] It is convenient to present the results of such studies in the form of " activation volumes ", defined empirically by the equations:

$$\Delta V_\kappa = -RT(\partial \ln \kappa/\partial P)_T \tag{1}$$

and

$$\Delta V_\Lambda = -RT(\partial \ln \Lambda/\partial P)_T. \tag{2}$$

κ and Λ are, respectively, the conductivity and the molar conductivity of the melt. ΔV_Λ is related to ΔV_κ by the equation

$$\Delta V_\Lambda = \Delta V_\kappa + \beta_T RT \tag{3}$$

where β_T is the isothermal compressibility of the molten salt.[9] The temperature dependence of the molar conductivity at constant pressure and at constant volume is described by Arrhenius equations:

$$\partial[\ln \Lambda/\partial(1/T)]_P = -(E_\Lambda)_P/R \tag{4}$$

and

$$\partial[\ln \kappa/\partial(1/T)]_V = -E_V/R. \tag{5}$$

The " activation energies " $(E_\Lambda)_P$ and E_V are related to ΔV_Λ by the equation

$$(E_\Lambda)_P = E_V + (\alpha T/\beta_T)\Delta V_\Lambda \tag{6}$$

in which α is the expansivity of the melt.

For the molten alkali nitrates [1, 3, 4] and halides,[2] ΔV_Λ was found to be approximately zero for all lithium salts and increased when the cation was changed in the sequence Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$. For the molten halides, a smaller increase in ΔV_Λ was observed when the anion was changed in the sequence Cl$^-$, Br$^-$, I$^-$. Ion size therefore appears to be an important factor determining the magnitude of ΔV_Λ.

Theoretical considerations [10, 11] indicate that another significant factor is the shape of the anion–cation pair potential function, especially in the short range, repulsive region.   The compressibility of the melt is also important.[2]   To study the effect of ion size in isolation, we have measured ΔV_κ and ΔV_Λ for a series of molten salts in which the other factors just mentioned are approximately constant.   The compounds chosen were the lithium, sodium and potassium salts of the anions NO_2^-, ClO_3^-, ClO_4^- and $Cr_2O_7^{2-}$ (KSCN and $AgNO_3$ were also included).   All these anions have oxygen atoms at their periphery, so the shape of the repulsive part of the anion–cation pair potential should be approximately the same for each anion with a given cation.

The salts investigated all have relatively low melting points ($< 400°C$) and the measurements were made over the range 0-1000 bar in the externally heated pressure vessel described previously.[1]   The very stable temperature and pressure conditions obtainable with this apparatus allow results of good precision to be obtained. Against this experimental advantage must be set the fact that the anions are not spherical.   This complication prevents a rigorous discussion of the results in terms of statistical mechanical theory, but some useful qualitative conclusions can be drawn.

EXPERIMENTAL

MATERIALS

$LiClO_3$ was prepared by mixing equivalent amounts of $Ba(ClO_3)_2$ and Li_2SO_4 (reagent grade) in aqueous solution at 80°C.   After standing, the $BaSO_4$ precipitate was filtered off and the solution of $LiClO_3$ was evaporated.   The last traces of water were removed by repeatedly melting and freezing the salt under continuous evacuation using a rotary oil pump.   The freezing point of the product was 126°C.   The melt was filtered through a glass frit (porosity 4) before use.

$LiClO_4$ (B.D.H., Reagent grade) was melted, filtered (porosity 4 Pyrex frit) and vacuum dried at 270°C before re-freezing.

$NaNO_2$ (B.D.H., AnalaR) was oven-dried at 120°C, fused and filtered.

$NaClO_3$ and $KClO_3$ (B.D.H. Reagent grade, purity > 98 %) were fused, filtered, frozen and stored at 120°C.

$Na_2Cr_2O_7$ and $K_2Cr_2O_7$ (B.D.H. Reagent grade) were used without purification.

KSCN (B.D.H. AnalaR) was dried at 120°C in air, melted and filtered (porosity 3 frit).

$AgNO_3$ (Johnson Matthey) was dried at 120°C, fused and filtered.

CONDUCTIVITY MEASUREMENTS

These were made in an externally heated pressure vessel, pressurised with argon. Capillary-type conductance cells were used and contamination of the melt between the electrodes by dissolved argon was prevented by providing a long diffusion path between this part of the cell and the free surfaces of the melt.   Full experimental details are given in a previous publication.[1]

For evaluation of the results, the thermal pressure coefficient $(\partial P/\partial T)_V$ and the isothermal compressibility $\beta_T [= -(1/V)(\partial V/\partial P)_T]$ of the melts are required.   The measurement of these quantities is described elsewhere.[9]

RESULTS

In fig. 1, selected isothermal plots of log κ against pressure are shown for the melts investigated.   In table 1, values of ΔV_κ, ΔV_Λ, $(\partial P/\partial T)_V$ and β_T are given for each melt and temperature.   Fig. 2-4 show plots of ΔV_κ against temperature for molten lithium, sodium and potassium salts, respectively; included in these diagrams are some previously published results for the molten nitrates.[1]
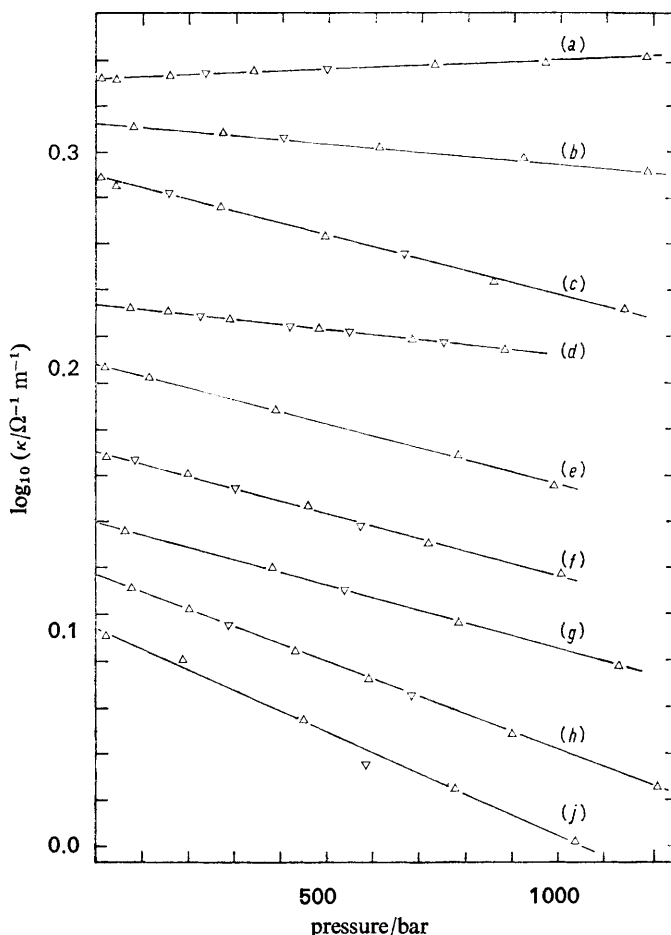
FIG. 1.—Selected isothermal plots of $\log_{10}$ (conductivity) against pressure for molten lithium, sodium and potassium salts. $\triangle$, rising pressure; ∇, falling pressure.   (a) $LiClO_4$, 550 K;   (b) $LiClO_3$, 516 K;   (c) $LiClO_3$, 417 K;   (d) $NaNO_2$, 606 K;   (e) $Na_2Cr_2O_2$, 638 K;   (f) $NaClO_3$, 556 K; (g) $KClO_3$, 653 K;   (h) KSCN, 508 K;   (h) $K_2Cr_2O_7$, 692 K.   To facilitate presentation, the lines have been displaced along the log κ axis by arbitrary amounts.

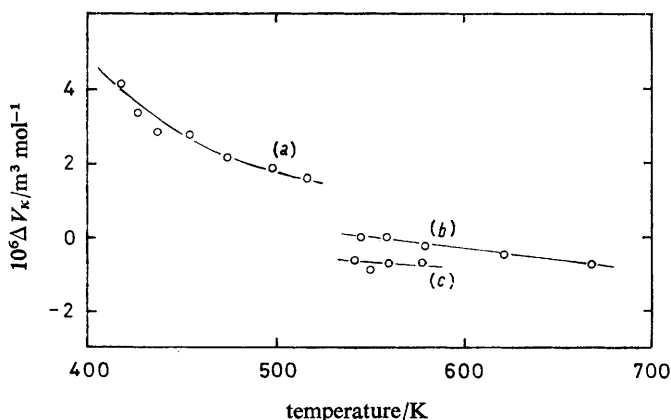FIG. 2.—Plots of ΔV_κ against temperature for molten lithium salts.   (a) $LiClO_3$;   (b) $LiNO_3$ [ref. (1)]; (c) $LiClO_4$.

TABLE 1.—VALUES OF ΔV_κ, ΔV_Λ, $(E_\Lambda)_P$ AND E_V FOR MOLTEN OXY-SALTS AND KSCN

salt	temp/K	$10^{-5}(\partial P/\partial T)_V$ /N m^{-2} K^{-1}	$10^4\alpha$ /K^{-1}	$10^{11}\beta$ /N^{-1} m^2	$10^6\Delta V_\kappa$ /m^3 mol^{-1}	$10^6\Delta V_\Lambda$ /m^3 mol^{-1}	$(E_\Lambda)_P$ /J mol^{-1}	E_V /J mol^{-1}	$E_V/(E_\Lambda)_P$
LiClO$_3$	417	—	4.1^b	—	4.2	—	25 780^b	—	—
	426				3.4		(404-446 K)		
	437				2.9				
	454				2.8				
	474				2.2				
	497				1.9				
	516				1.6				
LiClO$_4$	542	11.1^a	3.1^c	27.5^a	−0.6	0.6	—	—	—
	550	11.2	3.1	27.2	−0.85	0.4			
	560	13.3	3.1	23.0	−0.7	0.4			
	578	—	—	—	−0.7	—			
NaNO$_2$	575	23.0^a	4.1^d	18.0^a	2.7	3.6	12 330	7 670	0.62
	609				2.5				
	633				2.3				
	637				2.4				
	658				2.4				
NaClO$_3$	549	16.0^a	4.7^e	29.1^a	6.0	7.3	19 900^h	12 210	0.58
	556				5.5				
Na$_2$Cr$_2$O$_7$	638	18.1^a	—	—	6.3	—	—	—	—
KClO$_3$	651	15.4^a	—	—	6.5	—	—	—	—
	653	15.4	—	—	6.6	—	—	—	—
K$_2$Cr$_2$O$_7$	692	18.7^a	3.1^d	16.4^a	11.5	12.4	34 030^d	17 970	0.53
KSCN	467	20.0^a	5.1^f	25.3^a	8.5	9.5	25 420^d	16 500	0.65
	482	19.3	5.1	26.3	7.9	9.0			
	495	18.8	5.1	27.1	7.6	8.7	21 840^j	13 720	0.63
	508				7.3				
	522				7.0				
AgNO$_3$	528	—	2.6^d	11.6^g	2.9	3.3	12 110^d	8 180	0.67
	531				2.7				

^{a} Ref. (9); ^{b} ref. (12); ^{c} ref. (13); ^{d} ref. (14); ^{e} ref. (15); ^{f} ref. (16); ^{g} ref. (17); ^{h} ref. (8); ^{j} this work.
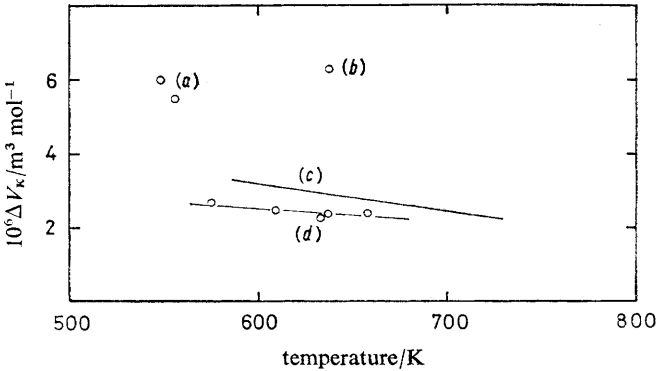

FIG. 3.—Plots of ΔV_κ against temperature for molten sodium salts. (a) NaClO$_3$; (b) Na$_2$Cr$_2$O$_7$; (c) NaNO$_3$ [ref. (1)]; (d) NaNO$_2$.
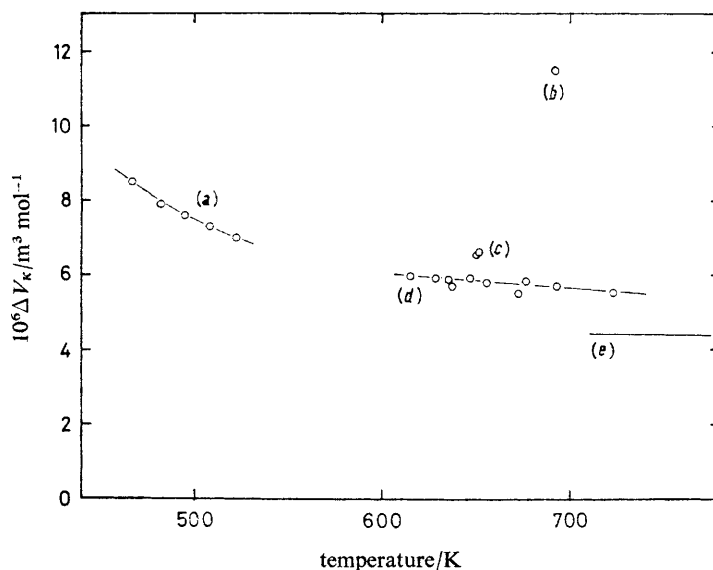
FIG. 4.—Plots of ΔV_κ against temperature for molten potassium salts. (*a*) KSCN; (*b*) $K_2Cr_2O_7$; (*c*) $KClO_3$; (*d*) KNO_3 [ref. (1)]; (*e*) KNO_2 [ref. (8)].
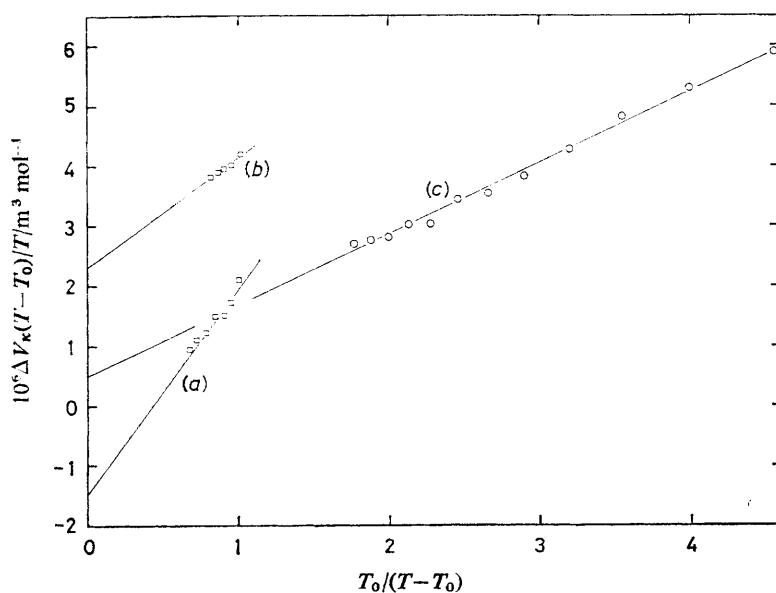

FIG. 5.—Plots of $\Delta V_\kappa (T-T_0)/T$ against $T_0/(T-T_0)$ for molten $LiClO_3$ (*a*), KSCN (*b*) and a $Ca(NO_3)_2 + KNO_3$ mixture containing 37.5 mol % $Ca(NO_3)_2$ (*c*). This curve is based on results taken from ref. (6).

DISCUSSION

COMPARISON WITH PREVIOUS WORK

Since the completion of this study, Schamm and Tödheide have published [8] the results of conductivity measurements to 6 kbar on molten $NaNO_2$, $NaClO_3$ and KNO_2. For $NaNO_2$ they report $\Delta V_\kappa = 2.4$ cm^3 mol^{-1}, in excellent agreement with our results. For $NaClO_3$, in the temperature range 543-643 K, their mean value of ΔV_κ was 4.9 cm^3 mol^{-1}. This is lower than our mean result (5.7$_5$ cm^3 mol^{-1}, at 549-556 K), but the difference may be due in part to the fact that their upper limit of temperature was 90 K higher than ours (a small, negative temperature dependence is generally found for ΔV_κ). For KNO_2, which we did not study, ΔV_κ is reported as 4.4 cm^{3}mol^{-1} in the range 713-813 K. This is consistent with trends in our results, being smaller than the ΔV_κ values for KNO_3 or $KClO_3$.

VARIATION OF ΔV_κ AND ΔV_Λ WITH ION SIZE

In the previous work on alkali halides, it was noted that ΔV_κ and ΔV_Λ increase when either the cation or the anion is replaced by another of greater size. Table 1 and fig. 2-4 show that similar trends occur in the present results. For the oxyanions we take the size sequence to be

$$NO_2^- < NO_3^- < ClO_3^- < ClO_4^- < Cr_2O_7^{2-}.$$
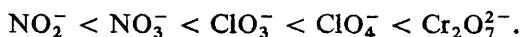
However, detailed examination of the ΔV_κ values in table 1 reveals some irregularities : ΔV_κ for $K_2Cr_2O_7$ is nearly twice that for $Na_2Cr_2O_7$, yet the ΔV_κ for $KClO_3$ and $NaClO_3$ differ by < 20 %. Also, ΔV_κ for $LiClO_3$ is positive (unlike that for $LiClO_4$ or $LiNO_3$) and increases steeply as the temperature is lowered. KSCN shows similar behaviour; as the temperature is lowered, ΔV_κ rises at an increasing rate. These two compounds are exceptions to our previous finding, based on the results for alkali metal nitrates and halides, that ΔV_κ shows only a slight temperature dependence $(\partial \Delta V_\kappa/\partial T \approx -0.005$ cm^3 mol^{-1} K^{-1}).

VARIATION OF THE GLASS TRANSITION TEMPERATURE WITH PRESSURE

A clue to the reason for these anomalies is provided by the fact that $LiClO_3$ and KSCN have much lower melting points than other lithium and potassium salts studied; consequently, ΔV_κ could be measured to much lower temperatures. In previous studies of the temperature-dependence of conductivity, viscosity and diffusion in molten salts, it has been found that the low-temperature behaviour is not correctly predicted by extrapolation from the high-temperature region. At high temperatures, the Arrhenius equation

$$\kappa = A \exp -(E_\kappa/RT) \tag{7}$$

is applicable, but a modified equation

$$\kappa = A \exp [-E_\kappa/R(T-T_0)] \tag{8}$$

is required to fit the data over the whole temperature range. Eqn (8) is the Vogel–Tammann–Fulcher equation and reverts to eqn (7) when $T \gg T_0$. Differentiation of eqn (8) indicates that the temperature coefficient of κ becomes greater as T is lowered towards T_0. T_0 is the temperature at which the configurational entropy of the melt would become zero, and all movement of ions would cease, if the melt remained in thermal equilibrium during cooling. In fact, non-equilibrium structures are

" frozen in " when the relaxation time for configurational changes becomes long in comparison with the duration of the experiment. For this reason the glass transition temperature T_g is usually higher than T_0, by some 10-40 K. T_g is found by a d.t.a. technique; it is the temperature at which the heat capacity undergoes an abrupt change when the glass is heated at a rate of order 10 K min^{-1}.

Eqn (7) and (8) apply at atmospheric pressure. A pressure-dependent term can be introduced into eqn (7) by writing

$$\kappa = A \exp{-\frac{(E_\kappa + P\Delta V)}{RT}}. \tag{9}$$

If this equation is obeyed and A, E_κ are independent of pressure and temperature, ΔV may be identified with the empirically-defined ΔV_κ of eqn (1). When eqn (8) is similarly generalised, account must be taken of the fact that the glass transition temperature T_0 rises with increasing pressure. Assuming a linear pressure-dependence for T_0, we have

$$\kappa = A \exp{-\frac{(E_\kappa + P\Delta V)}{R[T - T_0(1 + bP)]}} \tag{10}$$

where E_κ, A, ΔV, T_0 and b are constants for a given substance. This equation should describe the variation of conductivity with temperature and pressure in the whole liquid range down to the glass transition. We wish to use the equation to predict how ΔV_κ should change as the temperature is lowered. Since the isotherms of $\ln \kappa$ against P are linear (fig. 1), we may regard ΔV_κ as the low pressure limiting value of the differential defined in eqn (1).

Taking logarithms of eqn (10) and differentiating with respect to pressure at constant temperature,

$$-RT(\partial \ln \kappa / \partial P)_T \equiv \Delta V_\kappa = \frac{T\Delta V}{T - T_0(1 + bP)} + \frac{(E_\kappa + P\Delta V)bT_0T}{[T - T_0(1 + bP)]^2}.$$

In the limit of low pressure, $E_\kappa \gg P\Delta V$ and $1 \gg bP$, so

$$\Delta V_\kappa = \Delta V\left(\frac{T}{T - T_0}\right) + \frac{bE_\kappa T_0 T}{(T - T_0)^2}. \tag{11}$$

The high-temperature limiting form of this equation (when $T \gg T_0$) is

$$\Delta V_\kappa = \Delta V.$$

As T is lowered towards T_0, eqn (11) predicts that ΔV_κ would increase steeply, becoming infinite when $T = T_0$. Even if $\Delta V \leqslant 0$, the second term in eqn (11) would ensure that ΔV_κ took positive values as T_0 was approached. Qualitatively, the equation correctly describes the results shown in fig. 2-4.

The parameter T_0 can readily be found by fitting eqn (8) to the conductivity results at atmospheric pressure. If $\ln \kappa$ is plotted against $1/(T - T_0)$ for a range of trial values of T_0, the plot is a straight line when T_0 has the correct value and is a curve otherwise. By calculating the standard deviation for a linear regression of $\ln \kappa$ on $1/(T - T_0)$ and selecting the value of T_0 for which this standard deviation is a minimum, the best value for T_0 can be computed. This was done for LiClO$_3$ and for KSCN. A and E_κ are also obtained in this procedure. To find ΔV, eqn (11) was rearranged to give

$$\Delta V_\kappa \frac{T - T_0}{T} = \Delta V + \frac{bE_\kappa T_0}{T - T_0}.$$

$\Delta V_\kappa (T - T_0)/T$ was plotted against $T_0/(T - T_0)$. A straight line was obtained in each case (fig. 5) and ΔV and bE_κ (and hence b) were found from the intercept and slope. The values are given in table 2, for $LiClO_3$ and KSCN.

TABLE 2.—VALUES OF T_0, E_κ, ΔV AND b FOR MOLTEN SALTS [SEE EQN (10)]

salt	T_0/K	E_κ/J mol^{-1}	$\Delta V/10^{-6}$m^3 mol^{-1}	$b/10^{-10}$m^2 N^{-1}
$LiClO_3$	209	6390	-1.5	5.5
KSCN	236	6160	2.3	3.1
$Ca(NO_3)_2$ (37.5%)+ $KNO_3(62.5\ \%)$[6]	320	4540	0.5	1.6

Angell et al.[6] incorporated a pressure-dependent T_0 in their analysis of the variation with temperature and pressure of the conductivity of molten $Ca(NO_3)_2 + KNO_3$ mixtures. However, in their treatment, ΔV is assumed zero. This neglect of ΔV did not prevent them from obtaining an adequate fit to the experimental results but these were all obtained in a temperature range between $1.2T_0$ and $1.56T_0$; if they had extended their work to higher temperatures, the need for the extra term might have become apparent. The fit is also helped by the fact that ΔV is fortuitously close to zero for this system, because of the small size of the calcium ion; for the mixture containing 37.5 mol % $Ca(NO_3)_2$, a plot of $\Delta V_\kappa (T - T_0)/T$ against $T_0/(T - T_0)$ is a good straight line (see fig. 5) from which we obtain $\Delta V = 0.5$ cm^3 mol^{-1} and $b = 1.63 \times 10^{-10}$ m^2 N^{-1}.

From their analysis [6] based on the assumption that $\Delta V = 0$, Angell et al. reported that dT_0/dP was 8 ± 2 K kbar^{-1} for this mixture. This figure was later revised to 7 ± 2 K kbar^{-1} after more careful analysis.[18] Our treatment of the same data, based on eqn (10), gives dT_0/dP as 5.2 K kbar^{-1} (obtained from the above value of the constant b). In a recent publication,[19] Williams and Angell report the direct experimental measurement of dT_g/dP for some $Ca(NO_3)_2 + KNO_3$ mixtures. dT_g/dP did not vary significantly with composition and for the mixture containing 40 mol % $Ca(NO_3)_2$ they find $dT_g/dP = 5.8 \pm 0.2$ Kkbar^{-1}. Assuming that $dT_0/dP = dT_g/dP$ for these systems, this figure compares well with that obtained from our analysis. However, it agrees scarcely less well with Angell's dT_0/dP, having regard to the uncertainty they assign to their value. From this evidence, it is not possible to decide clearly whether the $P\Delta V$ term in eqn (10) is required or not. A more conclusive outcome might result if dT_g/dP could be measured for a melt for which a value of ΔV larger than 0.5 cm^3 mol^{-1} is expected. If our earlier discussion is correct, this implies a melt with a large, univalent cation such as K$^+$, Rb$^+$, Cs$^+$ or a polyatomic organic cation. Unfortunately, the propensity to form glasses is most pronounced in ionic systems containing a mixture of cations, one of which is small or highly charged, and for these melts ΔV is likely to be small. The range of melts available for the proposed experiment is therefore very restricted. Possibly the polysulphides of sodium or potassium would be suitable; some of these readily form glasses when pure and these glasses are stable enough for T_g to be measured by the d.t.a. technique referrred to above.[20]

The above discussion can be summarised by the statements: (i) At " high temperatures " $(T \geqslant 2T_0)$ $\Delta V_\kappa \approx \Delta V$ and ΔV is systematically related to the sizes of

the ions within a group of compounds of similar nature (*e.g.*, alkali metal halides, or alkali metal oxy-salts). (ii) At " low temperatures " $(T_0 < T < 2T_0)$ ΔV_κ is greater than ΔV and the differences between these quantities increases as the temperature falls.

If it is possible to measure κ and ΔV_κ over a range of temperatures, then the rate of variation of ΔV_κ with temperature can be used to indicate whether the experimental temperature range is in the " high " or " low " regime. However, some of the salts included in this study are thermally stable over only a narrow temperature range just above the melting point and this criterion cannot be used. For these compounds, we may use the fact that ΔV_κ appears anomalously high as an indication that the measurements fall in the " low temperature " range. From the data in table 1, we can place $NaClO_3$ and $K_2Cr_2O_7$ in this category.

" ACTIVATION ENERGY " AT CONSTANT VOLUME

Using eqn (6), the " activation energy " E_V has been calculated from $(E_\Lambda)_P$ for each compound for which the necessary values of α and β_T are available. The ratio $E_V/(E_\Lambda)_P$ has been calculated and is given in table 1. For the nitrates [3] and halides [4] this ratio is close to unity for lithium salts, is in the range 0.56-0.66 for sodium salts and is ≈ 0.5 for salts of larger cations. The new results for $NaNO_2$, $NaClO_3$ and $K_2Cr_2O_7$ conform to this pattern of behaviour. $E_V/(E_\Lambda)_P$ for $AgNO_3$ also comes within the range normally expected for sodium salts, which is not surprising in view of the closely similar ionic radii of Na^+ and Ag^+. For KSCN, $E_V/(E_\Lambda)_P$ is 0.63 at 495 K and 0.65 at 467 K. Both these values are higher than those for potassium nitrate or the potassium halides, which may indicate that factors other than ion size are involved in determining $E_V/(E_\Lambda)_P$ as the temperature is lowered towards T_0.

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