

Solubilities of Helium, Argon, and Nitrogen in Molten Nitrates at Pressures up to 1 kbar

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The following solubilities have been measured over a temperature range of 100 deg. and at pressures up to 1 kbar: He in LiNO_3 and NaNO_3 ; Ar in LiNO_3 , NaNO_3 , RbNO_3 and AgNO_3 ; N_2 in LiNO_3 and NaNO_3 . Henry's law was obeyed approximately in all systems. For Ar in NaNO_3 , which was studied most extensively, a plot of solubility against pressure showed curvature above 500 bar. This could be accounted for by allowing for gas imperfection and for the finite partial molar volume of the dissolved gas (estimated to be 34 ± 8 ml/mol). The solubilities increased with rising temperature, with heats of solution in the range 13-20 kJ/mol. The standard entropies of solution were between -8 and $-24 \text{ J K}^{-1} \text{ mol}^{-1}$, referring to states of equal concentration in the gaseous and liquid phases. These entropies are more negative than those for solutions of the same gases in organic solvents or in molten halides, but less negative than for aqueous solutions. For a given melt at a given temperature, the solubilities decreased with increasing size of the solute molecule, while for a given gas in a series of melts the solubilities were in the inverse sequence of the surface tensions. These trends are correctly predicted by a model in which the free energy of solution is equated to the work of formation of cavities in the melt to accommodate the gas molecules.

Most of the previous work on the solubility of gases in molten salts has been carried out at pressures below 2 bar, often using mixed melts of technological importance.¹⁻⁸ In the absence of strong solute-solvent interactions, heats of solution are generally positive and standard entropies of solution are in the range 0 to $-6 \text{ J K}^{-1} \text{ mol}^{-1}$ (referring to equal concentrations of solute molecules in the gaseous and liquid phases).^{1, 5} The solubilities of inert gases in a given melt follow the inverse sequence of solute molecular size.¹ Negative heats of solution are observed when strong interactions occur between the solute molecules and the ions in the melt.^{3, 4, 7, 8} Only one group of workers has reported solubility measurements for gases in molten salts at high pressures,⁹⁻¹³ and the results conflict with the trends described above. Ar and N_2 were reported to have negative heats of solution in fused NaNO_3 , and to be about an order of magnitude more soluble than in fluoride melts. The solubility sequence at 369°C was $\text{He} > \text{N}_2 > \text{Ar}$, which is not the size sequence. In view of these differences, we thought it desirable to repeat this work by a different method. We have measured the solubilities of He, Ar, and N_2 in LiNO_3 and NaNO_3 , and of Ar in RbNO_3 and AgNO_3 , at pressures up to 1 kbar. This extension of the pressure range permits the determination of the partial molar volume of the dissolved gas, in addition to the heat and entropy of solution. Inert gases have been used as pressure-transmitting media in studies of the pressure dependence of transport processes in molten salts^{10, 12, 14-18} and the presence of dissolved gas has been a possible source of error.¹⁶⁻¹⁸ The solubilities reported here provide a basis for estimation of the effect which dissolved gas might have on transport phenomena at high pressures.

EXPERIMENTAL

The melt was saturated by stirring it in contact with gas at high pressure. A sample of the saturated melt was isolated, and subsequently analyzed.

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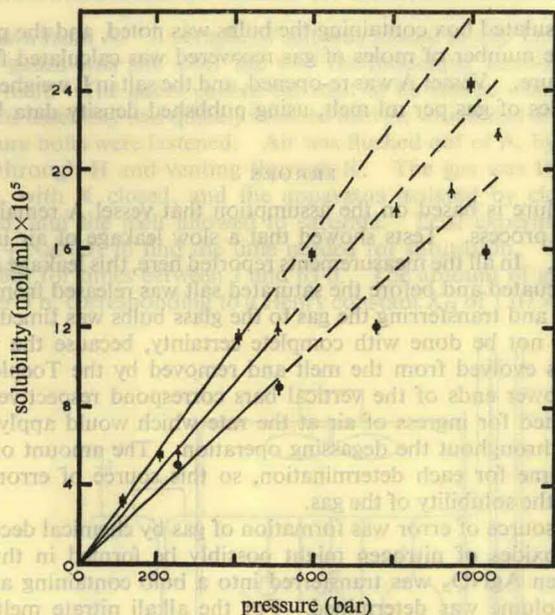


Fig. 4(a).—Solubility isotherms for the system He+NaNO₃. ■, 441°C; ▲, 391°C; ●, 332°C.

in the solution. The standard entropy of solution is derived from the heat of solution using the expression

$$\Delta S^\circ = (\Delta H/T) + R \ln (C_a/C_g),$$

where C_a and C_g are the concentrations of gas atoms in the solution and in the gas phase respectively.

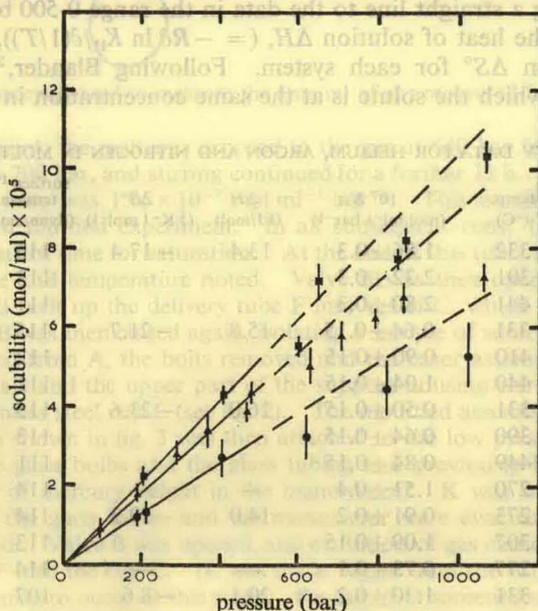


Fig. 4(b).—Solubility isotherms for the system Ar+NaNO₃. ■, 440°C; ▲, 410°C; ●, 331°C.

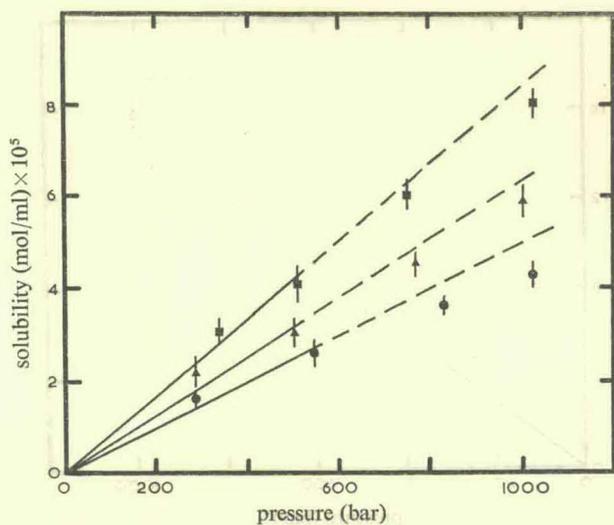


FIG. 4(c).—Solubility isotherms for the system $N_2 + NaNO_3$. ■, 449°C; ▲, 390°C; ●, 331°C.

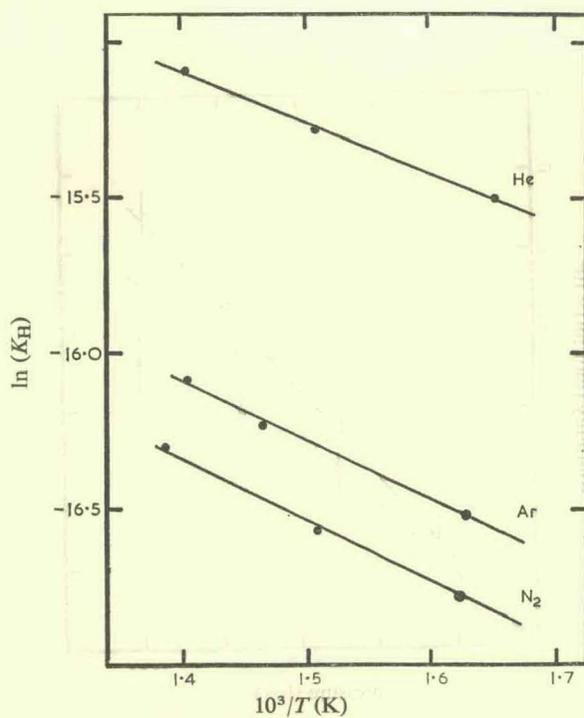


FIG. 4(d).—Plots of $\ln(K_H)$ against $1/T$ for He, Ar and N_2 in $NaNO_3$.

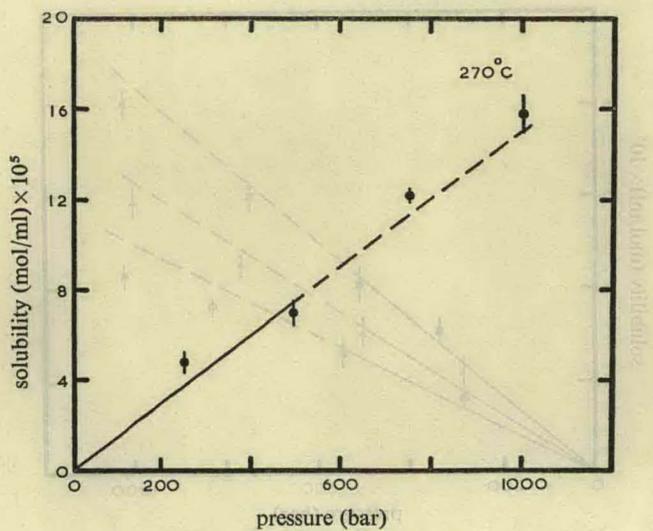


FIG. 5(a).—Solubility isotherm for the system He+LiNO₃.

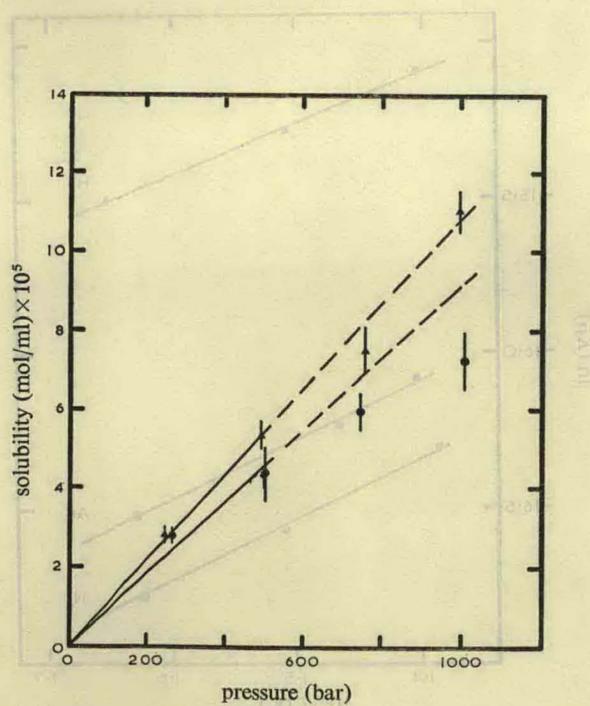


FIG. 5(b).—Solubility isotherms for the system Ar+LiNO₃. ▲, 307°C; ●, 273°C.

FIG. 5(c).—Solubility isotherm for the system N_2+LiNO_3 .

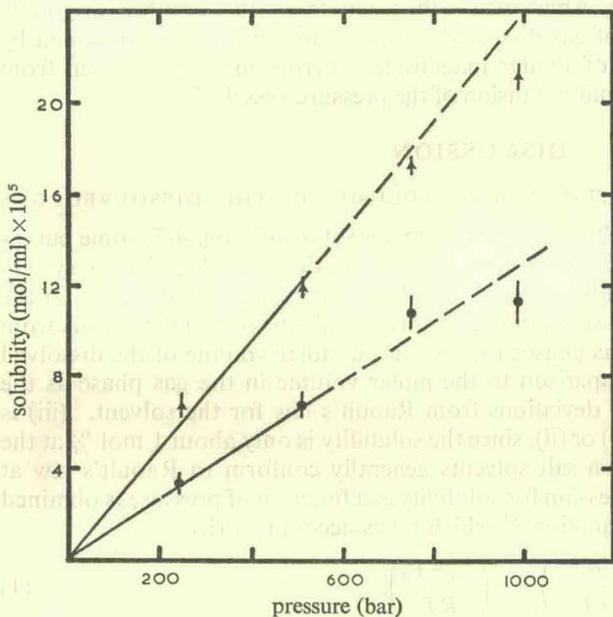
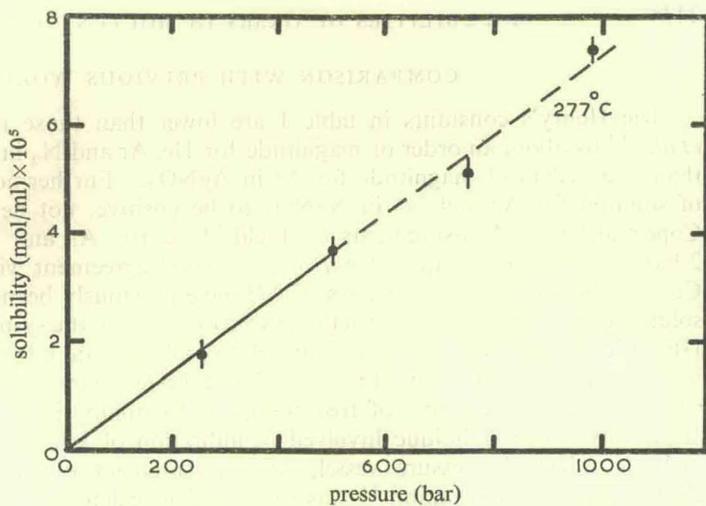
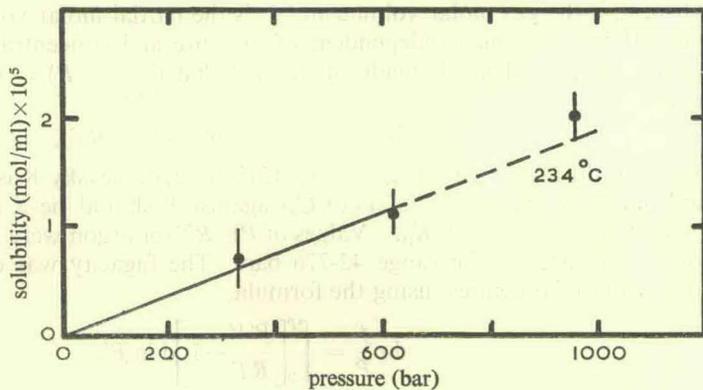


FIG. 6.—Solubility isotherms for the system $Ar+RbNO_3$.
▲, 440°C; ●, 331°C.

FIG. 7.—Solubility isotherm for the system $Ar+AgNO_3$.



COMPARISON WITH PREVIOUS WORK

The Henry's constants in table 1 are lower than those reported by Copeland *et al.*⁹⁻¹³ by about an order of magnitude for He, Ar and N₂ in NaNO₃, and by more than two orders of magnitude for Ar in AgNO₃. Furthermore, we find the heats of solution for Ar and N₂ in NaNO₃ to be positive, not negative as reported by Copeland.^{13, 14} Measurements by Field²⁰ on He, Ar and N₂ in NaNO₃ below 2 bar gave results for K_H and ΔH in fairly good agreement with ours. Apart from Copeland's work, negative values of ΔH have previously been found only when the solute gas interacts strongly with the solvent ions, e.g., in the systems HF + NaF/ZrF₄,³ HF + LiF/BeF₂,⁴ NH₃ + LiNO₃,⁷ and H₂O + alkali metal nitrates.⁸ Copeland attributes his negative ΔH values to ion-induced dipole interactions between solvent and solute,¹³ but the concepts of free energy and enthalpy have been confused in his arguments. The technique involved equilibration of known quantities of gas and melt in a heated pressure vessel, and measurement of the final pressure. The Beattie-Bridgeman equation²¹ was then used to calculate the number of moles of gas present in the gas phase, which was subtracted from the number originally admitted to give the amount of gas dissolved. The solubility was thus obtained by subtraction of two quantities of similar magnitude. Errors may have arisen from temperature gradients, or thermal expansion of the pressure vessel.²²

DISCUSSION

EVALUATION OF THE PARTIAL MOLAR VOLUME OF THE DISSOLVED GAS

For most of the plots of solubility against pressure shown in fig. 4-7, some curvature towards the pressure axis is discernible. This is particularly clear for the system Ar + NaNO₃ (fig. 4b), but tends to be obscured by the experimental scatter in the other cases. At least three causes of curvature may be identified: (i) deviations from the ideal gas equation in the gas phase; (ii) the partial molar volume of the dissolved gas becomes significant in comparison to the molar volume in the gas phase as the gas pressure is increased; (iii) deviations from Raoult's law for the solvent. (iii) is probably less important than (i) or (ii), since the solubility is only about 1 mol % at the highest pressures used. Molten salt solvents generally conform to Raoult's law at this concentration.²³ An expression for solubility as a function of pressure is obtained by integration of a standard equation²⁴ which takes account of (ii):

$$\left(\frac{\partial \ln C_d}{\partial P}\right)_T = \left(\frac{V_g - \bar{v}_d}{RT}\right), \quad (1)$$

where v_g is the gas molar volume and \bar{v}_d is the partial molar volume of the dissolved gas. If \bar{v}_d is assumed independent of pressure and concentration over the experimental range, and use is made of the fact that $\lim_{P \rightarrow 0} (C_d/P) = K_H$, integration of (1) gives

$$\ln C_d = \ln K_H + \ln f - (P\bar{v}_d/RT), \quad (2)$$

where f is the fugacity of the gas. Eqn (2) is the Kritchevsky-Kasarnovsky equation,²⁵ and indicates that a plot of $\ln(f/C_d)$ against P should be a straight line of slope \bar{v}_d/RT and intercept $-\ln K_H$. Values of $P\bar{v}_d/RT$ for argon were available²⁶ at 400°C, for 27 pressures in the range 42-776 bar. The fugacity was evaluated graphically for a series of pressures, using the formula,

$$\ln \frac{f}{P} = \int_0^P \left[\frac{P'V}{RT} - 1 \right] d \ln P'.$$

A plot of $\ln(f/P)$ against P had only slight curvature, and a short extrapolation allowed values of f to be obtained over the pressure range of the solubility measurements. The solubility data for Ar+NaNO₃ at 410°C were adjusted to 400°C, using the van't Hoff equation with $\Delta H = 15.8$ kJ/mol (see table 1). A plot of $\log(f/C_d)$ against P is shown in fig. 8. A straight line was fitted to the points by least squares, and \bar{v}_d and K_H were found from the slope and intercept. The values were: $\bar{v}_d = 34 \pm 8$ ml/mol and $K_H = (1.0 \pm 0.1) \times 10^{-7}$ mol ml⁻¹ bar⁻¹ at 410°C, where the intervals quoted correspond to 95% confidence limits. These values are not materially altered if the calculation is restricted to the pressure range 0-776 bar. Similar plots (not shown) were made for Ar+NaNO₃ at 440°C, Ar+NaNO₃ at 331°C and Ar+RbNO₃ at 440°C, and yielded values for \bar{v}_d of 26 ± 13 , 30 ± 13 and 34 ± 13 mol/mol, respectively. The corresponding K_H values were $(1.1 \pm 0.2) \times 10^{-7}$, $(0.65 \pm 0.1) \times 10^{-7}$ and $(2.9 \pm 0.5) \times 10^{-7}$ mol ml⁻¹ bar⁻¹. For N₂+NaNO₃ at 390°C, the same procedure gave $\bar{v}_d = 46 \pm 40$ ml/mol and $K_H = (0.8 \pm 0.5) \times 10^{-7}$ mol ml⁻¹ bar⁻¹. The PVT data used for N₂ were those of Bartlett.²⁷ The poorer precision of the results for Ar+RbNO₃ and N₂+NaNO₃ reflects the fact that fewer data points were available for these systems. The fact that straight lines are obtained

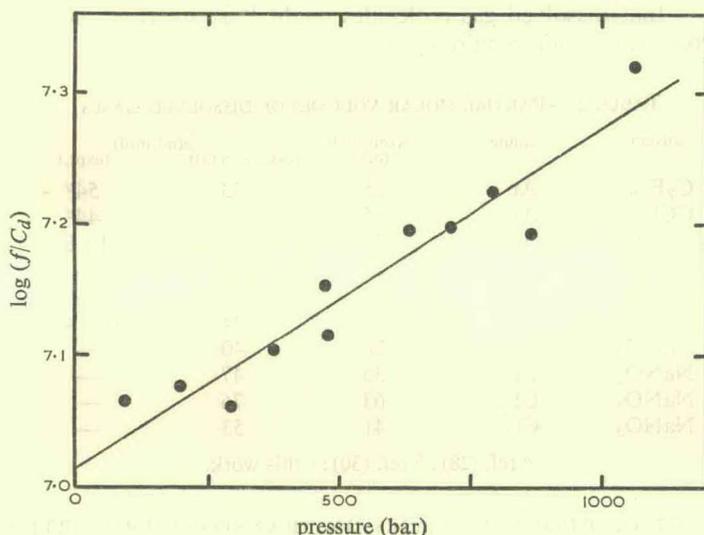


FIG. 8.—Plot of $\log(f/C_d)$ against pressure for the system Ar+NaNO₃ at 400°C.

when $\ln(f/C_d)$ is plotted against P is evidence that the solvent is not deviating from Raoult's law as the solute concentration increases. Such deviations would lead to curvature in these plots.

In table 1, K_H was evaluated from the slope of the best straight line through the origin of an isothermal plot of C_d against P , over the range 0-500 bar. This corresponds to the approximation $\ln(f/P) - (P\bar{v}_d/RT) = 0$ (cf. eqn (2)). Since the K_H values in table 1 agree with those derived using eqn (2) within the combined limits of error, the use of the simpler procedure is justified in the general case.

Smith and Walkley²⁸ described a simple method for estimating the partial molar volume of a solute gas from a knowledge of the volume v_0 of the gas at 0 K and the thermal pressure coefficient of the solvent $(\partial P/\partial T)_v$. Their formula is

$$\bar{v}_d = v_0 \left[1 - \frac{R(\partial P/\partial T)_v^{-1}}{\bar{v}_d} \right]^{-3} \quad (3)$$

Eqn (3) was derived by treating the gas as a hard-sphere fluid, and calculating the volume for which the gas pressure was equal to the internal pressure of the solvent. This volume was equated to \bar{v}_d . Values of v_0 may be found either from the volumes of solidified gases, or from molecular diameters obtained from second virial coefficients or from gas viscosities. Calculated values of \bar{v}_d were in good agreement with experiment for simple solute molecules in a range of organic solvents. Eqn (3) has been used to calculate \bar{v}_d for argon, nitrogen, and some other gases in molten nitrates (see table 2). The results agree with those derived from our solubility data, within experimental error. No figures are tabulated for helium, as quantum effects make it difficult to assign a value to v_0 ; the liquid molar volume is 27.4 ml/mol at 1.2 K,²⁹ but the molar volume estimated from the molecular diameter is only 10 ml/mol.³⁰ For NaNO₃ as solvent, these values of v_0 give $\bar{v}_d = 39$ and 21 ml/mol respectively. Table 2 shows that for a given gas, \bar{v}_d is less in molten nitrates than in organic solvents. This reflects the higher internal pressure of the former group of liquids, for which $T(\partial P/\partial T)_v$ is in the range 10-12 kbar.³¹ Eqn (3) requires that, if $(\partial P/\partial T)_v$ is positive, \bar{v}_d must be greater than v_0 . This is confirmed by the experimental data for organic liquids, and by the more limited data for molten salts. The suggestion^{9, 32} that dissolved gas molecules might "fill up the holes" in the melt is not supported, as it would require $\bar{v}_d \sim 0$.

TABLE 2.—PARTIAL MOLAR VOLUMES OF DISSOLVED GASES

solvent	solute	v_0 (ml/mol) (a,b)	(calc., eqn (3))	\bar{v}_d (ml/mol) (expt.)
C ₇ F ₁₆	Ar	25	53	54 ^a
CCl ₄	Ar	25	44	44 ^a
NaNO ₃	Ar	25	37	34+8 ^c
AgNO ₃	Ar	25	36	—
CsNO ₃	Ar	25	41	—
NaNO ₃	N ₂	32	44	46±40 ^c
NaNO ₃	O ₂	28	40	—
NaNO ₃	CH ₄	35	47	—
NaNO ₃	CF ₄	63	76	—
NaNO ₃	Cl ₂	41	53	—

^a ref. (28); ^b ref. (30); ^c this work.

EFFECT OF DISSOLVED GASES ON TRANSPORT PROPERTIES

An applied pressure of 1 kbar changes the electrical conductivity of molten alkali nitrates by between 1% (LiNO₃) and 12% (CsNO₃).¹⁸ Considering argon or nitrogen as pressurizing gases, dissolution of gas to the equilibrium concentration at this pressure would cause a further change in conductivity by simple dilution. Assuming no change in ion mobility when the gas dissolves, the conductivity decrease is estimated to be not more than 1%, based on the solubilities and partial molar volumes in tables 1 and 2. It seems likely that the ion mobilities would increase, rather than decrease, when dilution occurs: this is observed when water is added to molten LiClO₃,³³ and when p-xylene is added to molten tetra-n-amyl ammonium thiocyanate.³⁴ The net decrease in conductivity when argon or nitrogen dissolve isothermally in a nitrate melt at 1 kbar is therefore unlikely to exceed 1%, which corresponds to a change of +0.6 ml/mol in the specific conductance activation volume ΔV_K . This is much less than the reported difference between the "gas-free" and "gas-saturated" values of ΔV_K for sodium nitrate,¹⁸ which may have other experimental causes. The "gas-free" value has been confirmed independently.³⁵

COMPARISON OF EXPERIMENTAL K_H AND ΔH VALUES WITH THOSE PREDICTED BY BLANDER'S THEORY

Blander² has used a theory originally proposed by Uhlig³⁶ to estimate the solubilities and heats of solution of inert gases in fluoride melts. The dissolution process is considered in three stages: (i) the gas is expanded from concentration C_g to concentration C_d . The free energy change is $\Delta G_1 = RT \ln (C_d/C_g)$. (ii) The gas molecules are contracted to points and mixed with the liquid. The free energy change is ΔG_2 . (iii) The gas molecules are expanded to their proper size. The work required to create the cavities in the melt to accommodate the molecules is $\Delta G_3 = 4\pi r^2 N\gamma$, where r is the radius of the gas molecule and γ is the surface tension of the melt, here considered as a continuum.

Since the gas is in equilibrium with the liquid, the sum of these free energy changes is zero. If no chemical interaction occurs between the gas molecules and the ions in the melt, ΔG_2 may be neglected and

$$RT \ln (C_d/C_g) = -4\pi r^2 N\gamma. \quad (4)$$

Eqn (4) may be used to calculate the solubility of the gas at different temperatures, using experimental values of the surface tension. The heat of solution can be calculated from the temperature dependence of the solubility. This has been done for the systems studied here, and the results are included in table 1. The radii used in the calculations were^{2, 11} (in units of 10^{-10} m): He, 1.22; Ar, 1.92; N₂, 2.00. This simple model predicts the solubilities to within an order of magnitude, and gives the heats of solution to within a factor of 2. The agreement is about as good as that obtained by Blander *et al.*,² and confirms the general validity of the model for inert gas solutions. The observed trends in our results are correctly predicted, i.e., (i) for a given gas and melt, the solubility increases with temperature. (ii) For a given melt and temperature, the solubilities of a series of gases follow the inverse sequence of the molecular diameters. (iii) For a given gas dissolving in a series of melts, the solubilities increase with decreasing surface tension. This is exemplified by the series Ar+AgNO₃, Ar+NaNO₃, Ar+LiNO₃, Ar+RbNO₃ (see table 1).

A feature of the results is that K_H (expt.)/ K_H (calc.) is about 0.1 for He+NaNO₃ and for He+LiNO₃. Blander² obtained a similarly low value for this ratio for He+NaF/ZrF₄. As he suggests, this may reflect thermal motion of the gas atom in its cavity, so that the cavity radius is larger than the radius of the gas atom deduced from gas phase studies.

The broad agreement between theory and experiment increases the confidence with which the theory may be used to estimate gas solubilities in systems which have not been studied experimentally. Conversely, if experimental results differ greatly from the predicted values (e.g., if the solubility is more than a decade higher than predicted, or if ΔH is negative), this may be taken as an indication that the free energy term ΔG_2 is not negligible.

STANDARD ENTROPIES OF SOLUTION

Entropies of solution have been calculated from the experimental results for those systems which have been studied over a temperature range, and are listed in table 1. ΔS° is negative, and takes values between -8 and -24 J K⁻¹ mol⁻¹. These are more negative than the corresponding entropy changes for inert gases dissolving in NaF/ZrF₄¹ ($\Delta S^\circ = 0$ to -6 J K⁻¹ mol⁻¹), for CO₂ in alkali halide melts⁵ ($\Delta S^\circ = -2.5$ to -5 J K⁻¹ mol⁻¹), or for inert gases in benzene ($\Delta S^\circ = -4$ to -7 J K⁻¹ mol⁻¹),

but less negative than for inert gases in water ³⁸ ($\Delta S^\circ = -54 \text{ J K}^{-1} \text{ mol}^{-1}$ for He, and $-82 \text{ J K}^{-1} \text{ mol}^{-1}$ for argon, at 25°C). The large, negative values for aqueous solutions are generally attributed to structuring of the water surrounding the gas molecule, to give an ice-like cage. For nitrate melts, the fact that ΔS° is more negative than it is for halide solvents may possibly be due to some restriction of the rotational movement of the nitrate ions near the gas molecules.

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