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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 J K^{-1} 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 J K^{-1} 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 $He > N_2 > Ar$, 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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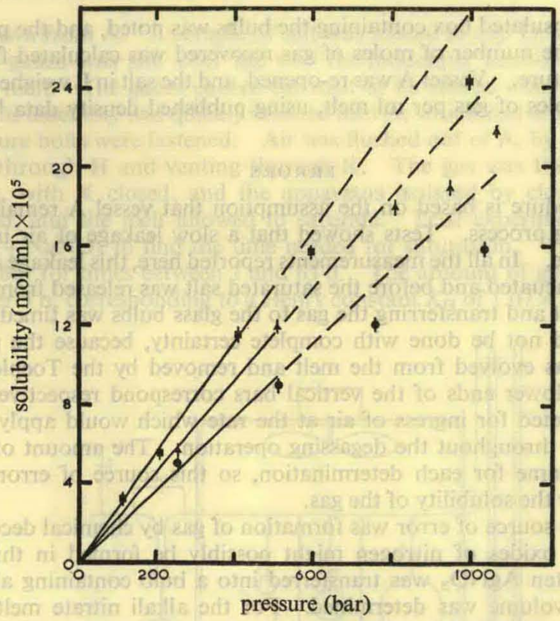

FIG. 4(*a*).—Solubility isotherms for the system He+$NaNO_3$. ■, 441°C; ▲, 391°C; ●, 332°C.

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

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

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

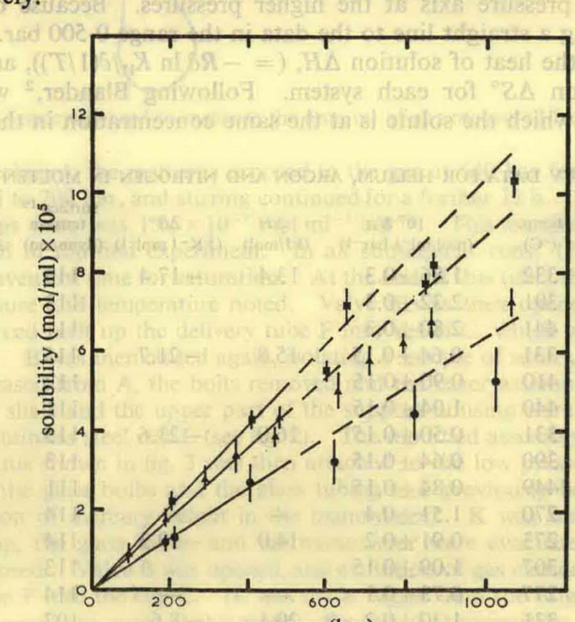

FIG. 4(*b*).—Solubility isotherms for the system Ar+$NaNO_3$. ■, 440°C; ▲, 410°C; ●, 331°C.