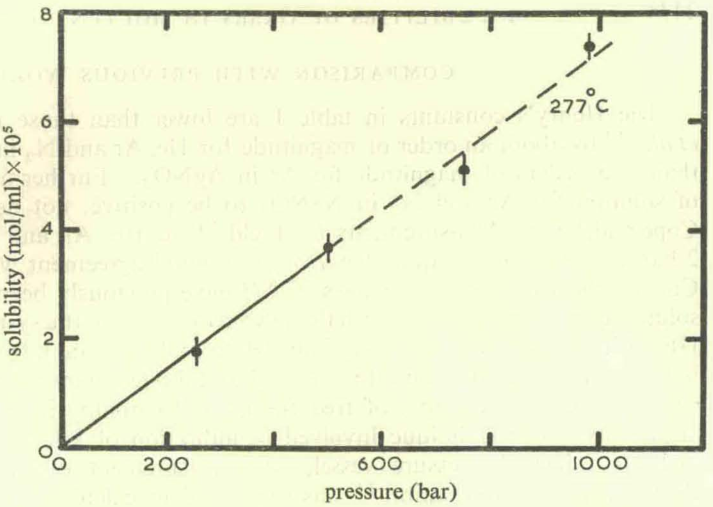

FIG. 5(*c*).—Solubility isotherm for the system N_2+LiNO_3.

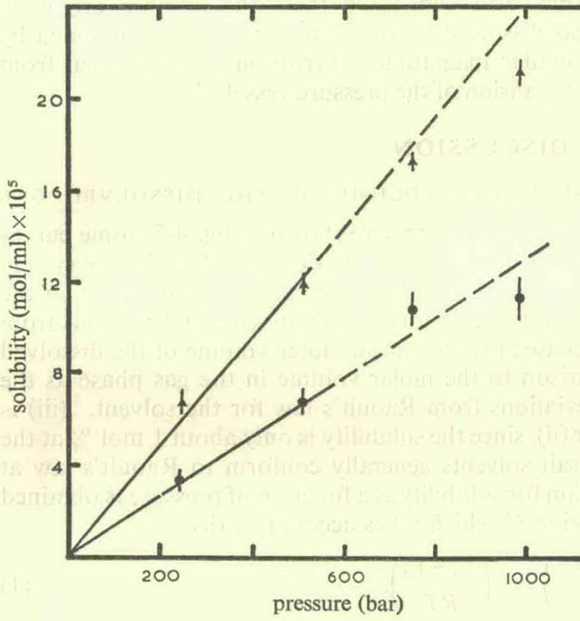

FIG. 6.—Solubility isotherms for the system $Ar+RbNO_3$. ▲, 440°C; ●, 331°C.

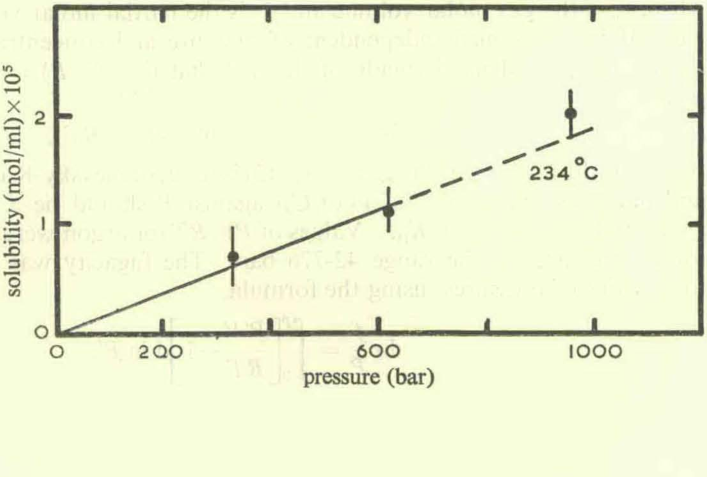

FIG. 7.—Solubility isotherm for the system $Ar+AgNO_3$.

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 N_2 in $NaNO_3$, and by more than two orders of magnitude for Ar in $AgNO_3$. Furthermore, we find the heats of solution for Ar and N_2 in $NaNO_3$ to be positive, not negative as reported by Copeland.[13, 14] Measurements by Field [20] on He, Ar and N_2 in $NaNO_3$ 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 $HF + NaF/ZrF_4$,[3] $HF + LiF/BeF_2$,[4] $NH_3 + LiNO_3$ [7] and H_2O + 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 equation [21] 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 $Ar + NaNO_3$ (fig. 4*b*), 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 equation [24] which takes account of (ii):

$$\left(\frac{\partial \ln C_d}{\partial P}\right)_T = \left(\frac{V_g - V_d}{RT}\right), \tag{1}$$

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 $\lim\limits_{P\to 0} (C_d/P) = K_H$, integration of (1) gives

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

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 PV/RT for argon were available [26] 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,

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