

$$C_d = (17.2 \times 10^{-7})P \pm 0.41 \times 10^{-4} \text{ mole of Ar} \\ (\text{cm}^3 \text{ of melt})^{-1} \quad (1)$$

where P is the saturating pressure in atm., and the error is the probable error calculated with respect to the best straight line. The Henry's law constant is the average slope

$$K = (17.2 \pm 1.7) \times 10^{-7} \text{ mole of Ar (cm}^3 \text{ of} \\ \text{melt})^{-1} \text{ atm.}^{-1} \quad (2)$$

where the error is the probable error of the slope. This value for K is in good agreement with the first crude results reported earlier by this laboratory.⁹ If this constant is converted to $K_c = C_d/C_g$ (where C_d and C_g denote concentrations of Ar in the liquid and gas phases, respectively), then (approximately)

$$K_c = 86 \times 10^{-3} \quad (3)$$

It is assumed that C_d is small enough to render the solution ideal, so that the activity of Ar therein may be equated to its concentration. Furthermore, ideal gas behavior is assumed for Ar at the high temperature, in spite of its pressure, so that its fugacity may be equated to pressure. The latter assumption involves errors of about 9.3% in the molar volume of Ar at the maximum employed pressure of 451 atm., and of about 2% at the lowest pressure of 70 atm., as deduced from Din's compilation.⁶

The simplified solubility model of Blander, *et al.*, equates the free energy of solution of the gas to the free energy of formation of holes the size of the gas molecules in a continuous fluid having the same surface tension as the solvent.³ Their derived relation for K_c is

$$K_c = \exp[-kA\gamma_{\text{mic}}/RT] \quad (4)$$

where A is the area of a hole created by a gas molecule, γ_{mic} is a microscopic "surface tension," R is the gas constant, T is the absolute temperature, and k is a conversion factor to obtain energy in calories. For spherical gas atoms, $kA = 18.08r^2$, where r is the atomic radius of the gas in Å. γ_{mic} is taken to be the same as that of the macroscopic fluid. For fused NaNO_3 at 369° , $\gamma = 109.7 \text{ dynes cm.}^{-1}$.¹⁰ The atomic radius of Ar is taken as $r = 1.92 \text{ Å}$.³ Equation 4 with these values gives a calculated K_c of 3.3×10^{-3} . Thus our experimental K_c agrees to an order of magnitude with the calculated value to about the same extent as did

some of the results of Blander, *et al.*,³ and Watson, *et al.*⁴

Two interesting extreme possibilities may exist for probable distribution of Ar atoms throughout the liquid NaNO_3 . One possibility is that the gaseous atoms take up holes of their own creation in the liquid. In this case, the volume of the solution would be expected to be greater than that of the pure solvent by an amount roughly equal to the total volume of the solute particles (about 3 cm^3 for the highest solubility observed in this work at 451 atm.). Unfortunately, measurements of such possible volume changes could not be made with the present apparatus. Another extreme possibility is that the solute atoms predominantly occupy existing free volume (as holes) in the liquid. In the hole theory of fused salts, the volume increase on melting is attributed almost entirely to holes.¹¹ Thus such free volume amounts to about $4.32 \text{ cm}^3 \text{ mole}^{-1}$ for fused NaNO_3 .¹² In this case, but little volume difference would be expected between the pure solvent and solution, especially in view of the relatively weak solvent-solute interactions. A third possibility, of course, is a combination of these two cases. If the availability of liquid free volume provides for enhanced solubility to some extent, then the solubility of Ar at an equivalent temperature in LiNO_3 should be greater than in NaNO_3 by virtue of a larger free volume for the former salt (about $6.84 \text{ cm}^3 \text{ mole}^{-1}$).¹² Similarly, the solubility should be less in KNO_3 (free volume of about $1.73 \text{ cm}^3 \text{ mole}^{-1}$), etc. Such studies are being undertaken in this laboratory in conjunction with conductance measurements on the solutions.⁹ It is hoped that the conductance measurements will help to elucidate the mechanism of solute distribution in such liquids.

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