

The Poynting term $V_2^s(P - p_2^0)/RT$ expresses the general effect of pressure on the vapour pressure of a solid and in comparing the solvent action of different gases it is therefore desirable to subtract this from $\ln(x_2/x_2^0)$. It was shown in part 1 that $\ln(x_2/x_2^0)$ in first approximation was a linear function of density and in fig. 4 and 5 we have therefore plotted the solubility function $\ln(x_2/x_2^0) - V_2^s(P - p_2^0)/RT$ against the density of the solvent gas. The curves were calculated by eqn. (5) while the points were calculated from the measured solubilities.

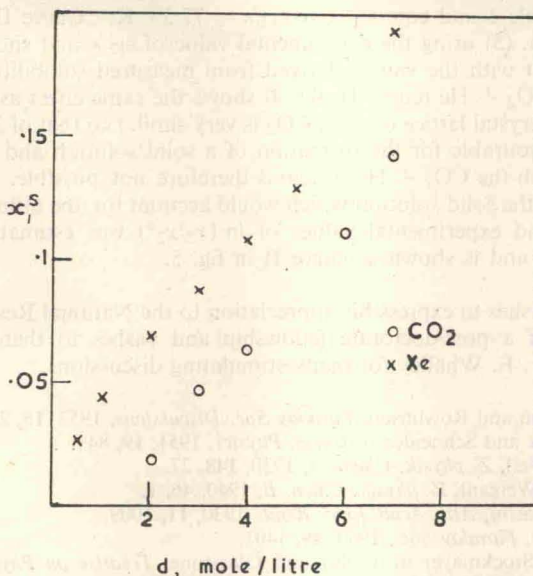


FIG. 5.—Estimated concentration of He in solid phase.
I, \circ Xe + He, 155° K. II, \times CO₂ + He, 190° K.

For the systems Xe + N₂ and Xe + H₂ the solubilities seem to be fairly well represented by eqn. (5) using the interaction parameters calculated by eqn. (6) and (7). The differences between the calculated and experimental values are just outside the experimental error and may be due partly to the uncertainty in the interaction parameters of the pure component. For hydrogen particularly there is some doubt as to how far quantum effects should be considered in the interactions in the mixed gas phase. The parameters shown in table 1 and used in the calculations are classical.

For the system Xe + He the calculated values are very much higher than the experimental values and it seems likely that some effect other than gas phase interaction enters in this system; here again, quantum effects are likely to introduce complications and may particularly affect the validity of eqn. (6) and (7). However, the very large difference in size between xenon and helium atoms and the lattice parameters of solid Xe suggest the possibility of He entering the interstitial spaces of Xe crystals without greatly distorting the crystal lattice and therefore readily forming a solid solution.

It is possible to allow for the formation of a solid solution in the calculation of $\ln(x_2/x_2^0)$ by introducing a factor $RT \ln a_2^s$ on the right-hand side of (5),⁹ where a_2^s is the activity of component 2 in the solid phase. Making the plausible assumption that $a_2^s = x_2^s$, the mole fraction of 2 in the solid phase, it is possible to calculate this concentration from the difference between the experimental and calculated values of $\ln(x_2/x_2^0) - V_2^s(P - p_2^0)/RT$. The result of such a calculation for the system Xe + He is shown as curve 1 in fig. 5.

The calculated and experimental values of the solubility functions of the systems $\text{CO}_2 + \text{H}_2$ and $\text{CO}_2 + \text{He}$ are shown in fig. 4. The curve I was calculated for the $\text{CO}_2 + \text{H}_2$ system using the parameters given in table 1 and by eqn. (6) and (7). As expected the curve lies considerably below the experimental values indicating a gas phase interaction greater than the van der Waals interaction considered in the calculations. Since these measurements were made values of the $\text{CO}_2 + \text{H}_2$ interaction parameters derived from volume changes on mixing have been reported.¹⁰ The value thus found was $\epsilon_{12}/\kappa = 89.39^\circ \text{K}$ whereas the parameters of table 1 and eqn. (6) give $\epsilon_{12}/\kappa = 77.39^\circ \text{K}$. Curve II in fig. 4 was calculated by eqn. (5) using the experimental value of ϵ_{12}/κ and shows very satisfactory agreement with the values derived from measured solubilities.

The system $\text{CO}_2 + \text{He}$ (curve II, fig. 4) shows the same effect as the $\text{Xe} + \text{He}$ system. As the crystal lattice of solid CO_2 is very similar to that of Xe , conditions may again be favourable for the formation of a solid solution and a comparison of this system with the $\text{CO}_2 + \text{H}_2$ system is therefore not possible. The concentration of He in the solid solution which would account for the difference between the calculated and experimental values of $\ln(x_2/x_2^\circ)$ was estimated as for the $\text{Xe} + \text{He}$ system and is shown as curve II in fig. 5.

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