

THE SOLUBILITY OF SOLIDS IN GASES

PART 3.—THE SOLUBILITY OF SOLID XENON AND SOLID CARBON DIOXIDE

By A. H. EWALD*

Chemistry Division, National Research Council, Ottawa, Canada

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The solubility of solid xenon in compressed nitrogen, hydrogen and helium has been measured in order to test the theory describing this solubility in terms of van der Waals' interactions in the gas phase. Using only published values of the interaction parameters of the pure components the calculated solubility was found to be in good agreement with experimental results, except for the system with helium in which, it is suggested, a solid solution may be formed. The solubility of solid carbon dioxide was measured in hydrogen and helium. The solubility in hydrogen was found to be greater than the calculated values, indicating a carbon dioxide + hydrogen interaction in excess of ordinary van der Waals' forces.

In part 1 of this series¹ it was shown that the solubility of a solid in a compressed gas could be calculated in terms of van der Waals' interactions in the gas phase, and could be expressed in a power series in $1/V$ and the virial coefficients of the mixed gas phase. The theory of corresponding states was used to find the interaction parameters of the Lennard-Jones (12 : 6) potential and to calculate the virial

* Present Address : C.S.I.R.O. Division of Industrial Chemistry, High Pressure Laboratory, Sydney University, Australia.

coefficients. It was shown that the expression for $\ln(x_2/x_2^\circ)$ takes a particularly simple form if the total solubility is small. (x_2 is the actual mole fraction of the solid component 2 in the gas phase while x_2° is the mole fraction it would have if its concentration in the mixture were that of the pure saturated vapour of the solid.) The solubilities thus calculated were shown to be in qualitative agreement with experimental results.

The experimental solubility data which were then available were not very well suited to test the theory, as the components involved did not meet the assumptions of either the principle of corresponding states or the Lennard-Jones (12:6) potential very well. The present work was undertaken to obtain experimental data for systems to which the theory could be applied with greater confidence. Most suitable for this purpose are systems consisting of simple molecules for which the interaction parameters of the pure components are already known. Solid xenon provides an almost ideal component from this point of view and its solubility was therefore measured in compressed helium, hydrogen and nitrogen.

Recent measurements of the second virial coefficient of carbon dioxide² have suggested that, in contrast to the rare gases, carbon dioxide has a directional force field which may be described in terms of a molecular quadrupole.¹¹ In addition to the ordinary van der Waals interaction one would therefore expect a more specific interaction of carbon dioxide with such molecules as hydrogen, due to quadrupole-quadrupole interaction. At low temperatures the contribution of such forces may be appreciable and may lead to a solubility of solid carbon dioxide in compressed hydrogen greater than that calculated on the basis of pure van der Waals forces. To test this hypothesis the solubility of solid carbon dioxide was measured in compressed hydrogen at 190° K and, as a comparison, in compressed helium also at 190° K.

EXPERIMENTAL

APPARATUS.—Solubilities were measured by a static method in which the solid component 2 was allowed to come into equilibrium with the gaseous component 1 and a small sample was then taken from the gas phase and analyzed by low temperature fractionation.

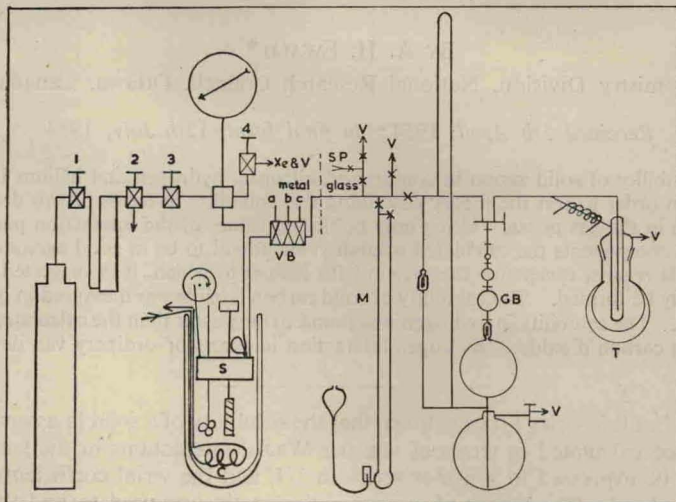


FIG. 1.—Diagram of apparatus.

The essential parts of the apparatus are shown diagrammatically in fig. 1, the remainder consisting of a conventional gas handling system. The saturator S consisted of a brass bomb of about 100 cm³ capacity. It was rocked slowly and the fluid in it was agitated