

OCT 11 1966

EWAL AH53 0043

Reprinted from the *Faraday Society Discussion*, 1953, No. 10

THE SOLUBILITY OF SOLIDS IN GASES

by
C. G. OVERMAN and
J. H. DEVLIN

Department of Chemistry, University of California, San Diego, La Jolla, California 92037

Received March 10, 1954

Published May 1954

THE SOLUBILITY OF SOLIDS IN GASES

BY A. H. EWALD,* W. B. JEPSON AND J. S. ROWLINSON
Department of Chemistry, University of Manchester

Received 2nd February, 1953

The solubility of a solid in a compressed gas is usually greater than the concentration which corresponds to its normal vapour pressure. This excess solubility may be expressed in terms of a virial expansion in which the successive coefficients represent the clustering of single gas molecules, pairs of gas molecules, etc., around one molecule of solute. If the molecules are non-polar, the second virial coefficient of such a system can be calculated from the properties of the pure substances and the principle of corresponding states. The higher coefficients may be calculated from an approximate extension of this law. Theoretical solubilities, calculated in this way, are compared with recent measurements of solubilities in compressed air and ethylene.

1. INTRODUCTION.—In the system formed by a pure solid in equilibrium with a gas an exact expression may be derived for the change with pressure of the concentrations in the gas phase. The system is an interesting one, since this change depends primarily on the forces, in the gas phase, between molecules of the solid component and molecules of the gaseous component. It is a useful way of measuring directly the forces between unlike molecules. Other ways depend usually upon the measuring of small differences between the properties of a solution and those of its pure components. Only the rate of diffusion of one gas into another has so far been used extensively to measure these forces directly.

2. THEORY.—The Helmholtz free energy of one mole of a gas mixture may be written

$$\frac{F}{RT} = \sum_i x_i \left[\ln \left(\frac{x_i}{\phi_i V} \right) - 1 \right] + \sum_{l=2} \left(\frac{1}{l-1} \right) \frac{A_l}{V^{l-1}}, \quad (2.1)$$

* Present address: Department of Chemistry, National Research Council, Ottawa, Canada.