# Regular Solutions of Gases in Liquids

## II. Concentrated solutions of hydrogen at high pressure

by M. G. Gonikberg

921

In many cases the emergence of high pressure technique into the domain of chemical and physico-chemical processes has facilitated operation with concentrated solutions of gases in liquids. Till now, however, we have not had at our disposal any theory of concentrated solutions of gases in liquids. This is due mainly to the lack of experimental data connected with investigations of the equilibrium concentrations in the liquid and vapour phases. Unfortunately, most investigations of gas/liquid equilibrium are confined to the determination of the solubility of the gas; the error involved in the analysis of the vapour phase makes a perfect interpretation of these data impossible.

The most extensive data we have at our disposal are concerned with solutions of hydrogen in a series of non-polar solvents at low temperatures. These include investigations on the equilibrium $H_2-N_2$[1,2,3], $H_2-CO$[1], $H_2-CH_4$[3,4,5], $H_2-C_2H_4$[6], and $H_2-C_2H_6$[7].

922

For working out the theory of concentrated solutions of gases in liquids at high pressure we shall try to interpret these data.

Another difficulty in the treatment of the results of the experimental investigations arises in the errors in the data on the compressibilities of most mixtures of the gases mentioned. This necessitates calculating the fugacity of the dissolved gases by the Lewis-Randall rule[8] which is only valid for low concentrations of the vapour in the solvent in the vapour phase. This fact reduces still further the amount of data suitable for calculation purposes.

We now consider the thermodynamic equations for solutions of gases in liquids.

For an infinitely dilute solution, Henry's Law is valid at low pressures:-

$$f_1 = K \cdot N_1 \tag{1}$$

where $N_1$ and $f_1$ denote the mole fraction and the fugacity of the dissolved gas and K the Henry coefficient.

The behaviour of the infinitely dilute solutions at high pressures is given very satisfactorily by Kritschewsky and Kasarnowsky's Equation:

$$\log \frac{f_1}{N_1} = \log K + \frac{\overline{v}_1(p-p_2^o)}{2.303 \, RT} \tag{2}$$

where $\overline{v}_1$ is the partial molar volume of the dissolved gas, p the total pressure, $p_2^o$ the vapour pressure of the solvent.

923

In previous work[10] we attempted to shew the applicability of Hildebrand's theory[11] of regular solutions (with certain assumptions) for solutions of gases in liquids at low pressures in the form of eqn. (3).

$$\log \frac{f_1}{N_1} = \log f_1^o + \frac{v_1}{4.58T} \left( \frac{N_2 v_2}{N_1 \, v_1 + N_2 \, v_2} \right)^2 \left( \frac{\sqrt{a_1}}{v_1} - \frac{\sqrt{a_2}}{v_1} \right)_p^2 \tag{3}$$

where $f_1^o$ denotes the fugacity of the pure gas at the vapour pressure of the liquid gas extrapolated to temperature T, $v_1$ and $v_2$ the molar volumes of the liquid gases at p = 1 atm[12], $(a_1)^{\frac{1}{2}}/v_1$ and $(a_2)^{\frac{1}{2}}/v_2$ the square root of the internal pressure of the components.

- 1 -