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MAXIMUM SOLUBILITY OF A COMPONENT OF A GAS MIXTURE IN A LIQUID

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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MAXIMUM SOLUBILITY OF A COMPONENT OF A GAS MIXTURE IN A LIQUID

(Presented by Academician S. I. Volʹ fkovich, 12 VIII 1959)

It is known (1) that, when certain pure gases dissolve in liquids, a maximum of solubility is observed as a function of pressure.

A thermodynamic analysis of the phenomenon of a solubility maximum in a binary system, carried out by I. R. Krichevskii (1), gives the following condition for the maximum:

$$N_1''(\bar{v}_1' - \bar{v}_1'') + N_2''(\bar{v}_2' - \bar{v}_2'') = 0, \tag{1}$$

where N_1 and N_2 are the mole fractions, respectively, of component 1 (the solvent) and component 2 (the dissolved gas); $\bar{v}_1$ and $\bar{v}_2$ are the partial molar volumes of the components; the index $'$ (prime) refers to the liquid phase, and the index $''$ (double prime) to the gas phase.

If the content of solvent vapor in the gas phase may be neglected, then the condition for the maximum takes the simpler form

$$\bar{v}_2' = v_2'', \tag{2}$$

i.e., at the solubility maximum the partial molar volume of the gas in the dissolved state is equal to the molar volume of the pure gas at the same pressure and temperature ($v_2^{0''}$).

Fig. 1

The known cases of solubility maxima of pure gases in liquids pertain to high pressures, in the range from one thousand to several thousand atmospheres. When a mixture of gases dissolves in a liquid, the solubility maximum (for a component of the mixture) may be observed for certain gases at comparatively low pressures. Thus, by our calculation it was found that, upon dissolution in water at 40° of a propane-methane mixture containing a constant (but small)

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Fig. 2

Figure 2: Fig. 2

amount of propane, the content of propane dissolved in the water should increase up to a pressure of about 90 atm. With a further increase in the pressure of the mixture, the content of propane in the water in equilibrium with the mixture should decrease.

An analysis of the phenomenon of the solubility maximum of a component of a ternary mixture can be carried out on the basis of the differential equation of two-phase equilibrium. The ternary system considered consists of liquid component 1 (the solvent) and two gaseous components 2 and 3. We neglect the content of solvent vapor in the gas phase. Equating the differential of the chemical potential of component 3 in the gas phase $d\mu_3''$ ···

differential of this component in the liquid phase $d\mu_3'$ under conditions of equilibrium coexistence of the phases, constant temperature, and constant composition of the gas phase, we find

$$\left(\frac{\partial N_3'}{\partial P}\right)_{\text{coex.},\,T,\,N_2'',\,N_3''} = \frac{\overline{v}_3' - \overline{v}_3'' - \left(\partial\mu_3'/\partial N_2'\right)_{P,T,N_3'}\left(\partial N_2'/\partial P\right)_{\text{coex.},\,T,\,N_2'',\,N_3''}}{\left(\partial\mu_3'/\partial N_3'\right)_{P,T,N_2'}}. \tag{3}$$

The condition for a maximum of solubility is that the derivative $\left(\partial N_3'/\partial P\right)_{\text{coex.},T,N_2'',N_3''}$ be equal to zero, i.e., that the numerator of equation (3) be equal to zero.

For the system water (1)—methane (2)—propane (3), the quantities entering the numerator of equation (3) are known. The partial molar volumes of propane $\overline{v}_3''$ in its binary mixtures with methane were determined by Sage and Lacey (^{2}). The partial molar volume of propane dissolved in water was measured in (^{3}). From experimental investigations carried out by us jointly with M. M. Bondareva (^{4}) on the solubility of mixtures of methane and propane in water, it can be found that the quantity $\left(\partial\mu_3'/\partial N_2'\right)_{P,T,N_3'} \times \left(\partial N_2'/\partial P\right)_{\text{coex.},T,N_2'',N_3''}$ is small in comparison with $\overline{v}_3$. Neglecting this quantity, we obtain that the condition for a maximum of the solubility of propane present in a mixture with methane is the equality of the partial molar volume of propane in the gas phase to the partial molar volume of propane in the liquid phase.

Fig. 2

The partial molar volume of propane in the gas phase $\overline{v}_3''$ is shown in Fig. 1 as a function of pressure at a temperature of 37.8° and at $N_3' = 0.1$ (^{2}). On the same figure a straight line has been drawn corresponding to the value of the partial molar volume of propane dissolved in water at 29.1° and at atmospheric pressure (^{3}). Taking into account the comparatively low accuracy of the experimental determination of the partial molar volume of propane dissolved in water, it seems permissible to neglect a certain difference in the temperatures of determination of $\overline{v}'_3$ and $\overline{v}''_3$, as well as the dependence of the partial molar volume of propane dissolved in water on pressure.

In Fig. 1, at the two points P_1 and P_3, at which the curve $\overline{v}''_3$ intersects the straight line $\overline{v}'_3$, the derivative $(\partial N'_3/\partial P)_{\text{coex.},T,N''_2,N''_3}$ must be equal to zero, i.e., extrema of solubility as a function of pressure must be observed. The extremum at pressure $P_1 = 90_{\text{atm}}$ corresponds to a maximum of solubility, and the extremum at pressure P_3 to a minimum. The pressure P_2 corresponds to the inflection point of the solubility curve, the qualitative form of which is shown in Fig. 2.

The peculiarity of the solubility in liquids of propane from its gaseous mixtures with methane is determined by the fact that the partial volume of propane present in the gas phase in mixture with methane, at relatively low pressures, becomes smaller than the volume of liquid propane both in the pure state and in the state dissolved in liquids. In a certain range of pressures, compositions, and temperatures, the partial molar volumes of propane in its mixture with methane in the gas phase even have a negative value (2).

In a similar way, other hydrocarbons of the paraffin series—butane and heavier ones—behave in mixture with methane (2). For these components

in a mixture with methane when dissolving them both in water and in other liquids, a maximum of solubility should be observed at comparatively low pressures.

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Note: Figure translations are in progress. See original paper for figures.

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