Physical Chemistry

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1965

SovietRxiv

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Abstract

Full Text

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Mutual Limited Solubility of Gases in the Water—Nitrogen System

(Presented by Academician Ya. K. Syrkin, 27 VIII 1964)

At the present time about 20 systems have been found in which limited mutual solubility of gases is observed ([1]). In approximately half of them the gas—gas equilibrium belongs to the second type ([2]). It is characterized by the fact that the critical curve, departing (in P—T coordinates) from the critical point of the less volatile component, is directed first toward lower temperatures, and then, having reached a minimum—the double homogeneous point—turns toward higher temperatures*.

Systems with the second type of gas—gas equilibrium are distinguished by a number of characteristic features. The double homogeneous point is located, as a rule, at pressures of the order of 1500-2000 atm (for example, in the systems ammonia—nitrogen, ammonia—methane, hydrogen sulfide—nitrogen, water—carbon dioxide, etc.). The difference between the temperature of the double homogeneous point and the critical temperature of the less volatile component is usually 80-100°. The critical phase of the gas—gas equilibrium contains approximately 0.5 mole fraction of both components, and the curves representing the dependence of the composition of the light and heavy phases on pressure are symmetrical with respect to the straight line drawn through the composition of the double homogeneous point.

Fig. 1. Gas—gas and liquid—gas equilibria in the water—nitrogen system

In studying the water—nitrogen system, we found that it too exhibits the phenomenon of limited mutual solubility of gases of the second type. However, in its properties this system differs markedly from all those studied previously. The present paper is devoted to presenting the results obtained by us.

The study of the water—nitrogen system was carried out in an apparatus described earlier ([4]). The experimental procedure was as follows. A calculated

Fig. 2. Critical curve in the water–nitrogen system

Figure 2: Fig. 2. Critical curve in the water–nitrogen system

amount of nitrogen, at the required pressure, was introduced into a high-pressure column purged with nitrogen. Then, by means of a hand press, such an amount of water was introduced into the column as to obtain a mixture of the specified bulk composition, and, after heating the apparatus, the required pressure. After the experimental temperature had been established, the mixture was stirred with an electromagnetic stirrer, the pressure was measured, and samples were taken for analysis from the top and bottom of the column. The analysis was performed in the same way as in ([4]); only the ice-and-salt bath was eliminated. Distilled water and nitrogen containing no more than 0.5% O_2 were used for the investigation. The experiments were carried out at temperatures of 330 and 365° and at pressures up to 4000 atm. The experimental data obtained are given in Fig. 1.

At 330°, from the point corresponding to the saturated-vapor pressure of pure water, two curves depart. The right-hand branch represents the solubility of water in compressed nitrogen, the left-hand branch the solubility of nitrogen in water. The curves encompass almost the entire composition range. On the curve of the solubility of nitrogen in water there is a maximum. Both of these features are characteristic of systems in which gas–gas equilibrium of the second type is observed.

Fig. 2. Critical curve in the water–nitrogen system

At 365° there are two regions of phase equilibria in the system. The liquid–gas equilibrium loop occupies a limited interval of compositions and pressures. Above it lies the gas–gas equilibrium curve. As is seen from the figure, the arrangement of these curves differs considerably from that established in previously investigated systems with this type of equilibrium.

In our case the difference between the temperature of the double homogeneous point and the critical temperature is only 10°. The pressure of the double homogeneous point is unusually low (~ 800 atm), and its composition is shifted toward the ordinate of pure water. The course of the critical curve in this system is shown in Fig. 2.

The great diversity of types of gas–gas equilibrium makes the need for a theoretical explanation of the experimental facts increasingly urgent. Attempts at a theoretical prediction of the phenomenon of limited mutual solubility of gases are known, as set forth in the works of A. Kreglewski ([5]) and M. I. Temkin ([6]).

* The course of the curve in some systems has been traced up to 15,000 atm and 175°, but the turn of the curve toward lower temperatures expected in accordance with the predictions of the theory at high pressures has not been found ([3]).

Kreglewski (5) applied the Hildebrand solubility parameter Δ and showed that the greater the difference between the values of $(\Delta)^2$ of the components of a mixture, the more probable is the fact of separation of the mixture. We calculated $(\Delta)^2$ for nitrogen and water. It turned out that the difference between them is greater than in all cases investigated up to the present.

Table 1

Values of $^1/_2(a_1+a_2)$ and a_{12} for the systems water–butane and water–nitrogen

System	$^1/_2(a_1+a_2)$, 10^6 atm · cm^3/mol	a_{12}, 10^6 atm · cm^6/mol
Water–nitrogen	2.9	0.376
Water–butane	9.47	0.512

M. I. Temkin (6), using the van der Waals equation of state for mixtures, considered the possibility of separation in the vicinity of the critical temperature of the less volatile component. He showed that separation is possible if:

for nonpolar substances $a_1 < 0.053\,a_2$;

for polar substances $^1/_2(a_1+a_2) - a_{12} > {}^8/_{27}a_2$,

where a_1, a_2, and a_{12} are the constants of the van der Waals equation for a binary mixture.

We calculated, by the method proposed in (6), the values of a_{12} and compared them with the half-sum of a_1 and a_2 for the systems water–butane and water–nitrogen. The data are given in Table 1.

As is seen from the table, a_{12} for both mixtures is considerably smaller than the half-sum of a_1 and a_2. Consequently, separation in these mixtures is possible. In both systems separation is in fact observed, but of different type. However, since M. I. Temkin’ s criterion is based on the approximate van der Waals equation of state, these calculations are approximate to a considerable degree.

A very interesting and fruitful attempt has been made to predict the behavior of a binary system on the basis of the properties of its components, using the statistical theory of conditional distributions (see (^8)). L. A. Rott considers the possibility of the existence of gas–gas equilibrium of the first type. Calculations show that such an equilibrium should exist in the water–butane system. This is confirmed by our work (^4). In the carbon dioxide–water system, gas–gas equilibrium of the first type is impossible. Experiment shows that in this system gas–gas equilibrium of the second type is observed (^7). Finally, calculation by this method shows that in the water–nitrogen system, gas–gas equilibrium of the first type likewise cannot exist, and this is confirmed by experiment.

Thus, the work we have carried out has made it possible to establish that in the water—nitrogen system there exists gas—gas equilibrium of the second type, and that the form of the critical curve differs from that observed in previously studied systems. It has also been shown that the criteria of M. I. Temkin and L. A. Rott make it possible to predict the occurrence of gas—gas equilibrium.

The authors express their gratitude to I. R. Krichevsky for his attention to the work and for his advice.

State Scientific Research
and Design Institute of the Nitrogen Industry and
Products of Organic Synthesis

Received
27 VIII 1964

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