MUTUAL LIMITED SOLUBILITY OF GASES IN THE WATER-BUTANE SYSTEM

Table 1

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Abstract

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The phenomenon of mutual limited solubility of gases, theoretically predicted by Van der Waals, Kamerlingh Onnes, and Keesom (^{1,2}), has until recently been experimentally confirmed in fourteen systems (^{3}) (Table 1).

Table 1

Systems in which mutual limited solubility of gases has been found at high pressures and temperatures

System	Temperature interval, °C	Maximum pressure, atm	System	Temperature interval, °C	Maximum pressure, atm
NH_3–N_2	90–175	16 000	He–CO_2	25–100	10 000
SO_2–N_2	35–40	9 000	He–C_2H_4	25–150	10 000
NH_3–CH_4	46–100	10 000	He–C_3H_8	100–150	7000
NH_3–Ar	70–140	10 000	He–C_6H_6	300	4000
NH_3–N_2–H_2	100–120	5 000	He–CH_3OH	245	3000
NH_3–N_2–CH_4	45–100	5 000	He–C_6H_{12}	245	2000
NH_3–He	125–175	10 000	He–SO_2	175–200	7000

Two types of phase equilibria between two gas phases were found. In systems belonging to the first type, the critical curve extending from the critical point of the less volatile component is directed (in pressure-temperature coordinates) toward higher temperatures. In systems of the second type, the critical curve is initially directed toward low temperatures, passes through a minimum (a double homogeneous point), and then proceeds toward higher temperatures.

The experimental results showed that systems containing helium as one of the components give the first type of demixing. The second type is observed in

Fig. 1. Apparatus for studying phase equilibria at high pressures and temperatures

Figure 1: Fig. 1. Apparatus for studying phase equilibria at high pressures and temperatures

systems containing dipolar substances (ammonia, sulfur dioxide). It was of interest to investigate the water—butane system, since water is a dipole.

It is known that, having data on the concentration dependence of the volatility of the components of a system in the homogeneous region, one can predict the onset of demixing in this system. If, on a plot in coordinates of the logarithm of volatility versus mole fraction, there is an inflection point with a horizontal tangent, then the coordinates of this point correspond to the critical composition and pressure of demixing of the mixture at the given temperature ([4]).

The authors found no data in the literature on the volumetric behavior of the water—butane system from which it would have been possible to establish the concentration dependence of the volatility of the components of this system. Nevertheless, it could be assumed with a certain degree of confidence that the water—butane system has a two-phase region at temperatures higher than the critical temperature of water. This assumption is based on the following considerations.

1. Water, as already indicated, is a strong dipole. Its dipole moment is $1.87 \cdot 10^{18}$ e.s.u., whereas the dipole moments of ammonia and sul-

sulfur dioxide—the components of the separating systems—are, respectively, equal to 1.44 and $1.61 \cdot 10^{18}$ esu.

2. Kreglewski ([5]) showed that the Hildebrand solubility parameter Δ may serve as a criterion of separation. The greater the difference between the values of Δ for the components of a mixture, the more probable phase separation becomes. According to the authors' calculations, $\Delta^2_{H_2O} = 1460$ atm, and $\Delta^2_{C_4H_{10}} = 204$ atm. For comparison, we note that $\Delta^2_{NH_3} = 685$ atm, and $\Delta^2_{N_2} = 126$ atm, and in the system ammonia—nitrogen, a gas—gas equilibrium with a critical curve of the second type is observed.

Fig. 1. Apparatus for studying phase equilibria at high pressures and temperatures

Taking into account all of the above, the authors studied the phase behavior of the water—butane system at temperatures up to 430° and pressures up to 6000 atm.

The need to carry out investigations at temperatures higher than the critical temperature of water (374°) ruled out the use of the previously described ([6])

Fig. 2. Liquid-gas and gas-gas equilibria in the water-butane system

Figure 2: Fig. 2. Liquid-gas and gas-gas equilibria in the water-butane system

method with a mercury piezometer, owing to the high solubility of mercury in compressed gas at such high temperatures. Therefore, for the present work an apparatus was constructed, the scheme of which is shown in Fig. 1. The apparatus consists of a thick-walled vessel 1, made of heat-resistant steel and equipped with an electromagnetic stirrer 2. The vessel is connected to a valve box 3, to which are attached a multiplier (not shown in the figure), a press valve 4 for disconnecting the multiplier during its return stroke, a manganin manometer 5, and valves 6 and 7 for taking samples for analysis from the top and bottom of the vessel.

The entire apparatus, with the exception of the multiplier, the manganin manometer, and the press valve, is placed in an air thermostat. The temperature measured with three chromel-alumel thermocouples and controlled by means of LATRs and an EPV-11A potentiometer with an accuracy of up to ~ 2°. A manganese manometer with a coil isolated from the action of the medium by a sylphon served for pressure measurement. The sylphon was filled with pure dry kerosene. The manometer body was cooled with water to room temperature. The manometer was calibrated against a dead-weight manometer up to 5000 atm, and the resulting straight line (in atmosphere-ohm coordinates) was extrapolated toward higher pressures.

Fig. 2. Liquid-gas and gas-gas equilibria in the water-butane system

Distilled water and butane containing 9.1% isobutane and 0.39% impurities $(N_2, O_2, C_1, C_2, C_3$ and $C_5)$ were used for the study.

The experimental procedure was as follows. Into the evacuated vessel 1, of 30 ml capacity, a calculated amount of butane was introduced by a manual hydraulic press, and the apparatus was heated to a temperature exceeding its critical temperature (152.8°). Then, with a second press, such an amount of water was introduced that its content in the mixture reached ~ 30 mol %. The apparatus was then heated to the experimental temperature and an additional amount of water was introduced up to the required pressure. In this case the gross composition of the mixture was ~ 50% water. After the temperature had become established, the phases were stirred with an electromagnetic stirrer, and after equilibrium had been reached the lower phase was withdrawn for analysis through valve 6, and the upper phase through valve 7.

Analysis of the phases was carried out in the analytical part of the apparatus. For this purpose, the phase leaving vessel 1 was frozen with liquid nitrogen in an evacuated trap. The trap was connected through a Kovar-glass seal to one of the valves by means of a heated stainless-steel capillary. After the sample had

Fig. 3.

Figure 3: Fig. 3.

been released, the water remaining in the passages of the valve and capillary was pumped by a mercury pump into the trap. Then a bath of ice with salt was placed under the trap and, at a temperature of ∼ −10°, the butane was evaporated and pumped by the mercury pump into calibrated flasks, the amount of gas evolved being determined from the readings of a mercury manometer. The amount of water remaining in the ampoule was determined by weighing the warmed ampoule.

Fig. 3.

In the apparatus described, the phase compositions in the water-butane system were investigated at temperatures of 205, 250, 312, 350, 400 and 430°, at pressures from 200 to 6000 atm. The data obtained are presented in Fig. 2. In Fig. 3 is shown—

the critical curve in the investigated range of temperatures and pressures is shown.

As can be seen from the figure, at temperatures up to 350° in the water—butane system, liquid—gas phase equilibria are observed. It should be noted that the literature contains data on liquid—gas equilibrium in this system at temperatures from 40 to 150° and pressures up to 700 atm ([7], [8]). The compositions of the gas phase according to these data are indicated in the figure by points with crosses.

At temperatures of 400 and 430°, the phenomenon of limited mutual solubility of gases was discovered. It turned out that gas—gas equilibrium in this system belongs to the first type, which until now had been observed only in systems containing helium.

In order to eliminate any doubt, the authors investigated the system at 400° in the homogeneous region, taking samples of the phases for analysis from the top and bottom of vessel 1. The results of phase analysis showed that the compositions of the phases agree satisfactorily. These compositions at different charges are indicated by points in Fig. 2.

The discovery in the water—butane system of the phenomenon of limited mutual solubility of gases of the first type is of great interest and requires explanation. Recently a paper appeared in the literature ([9]) in which the authors discovered the phenomenon of limited mutual solubility of gases in the water—carbon dioxide system at temperatures up to 350° and pressures up to 3500 atm, and found that gas—gas equilibrium in this system belongs to the second type, with a temperature minimum. This is the first investigation of gas—gas equilibrium carried out abroad with a system not investigated by us.

The difference in the behavior of systems with water requires discussion, which the authors hope to undertake in the future.

After the investigation of the water—butane and water—carbon dioxide systems, the number of systems in which the phenomenon of limited mutual solubility of gases is observed has reached sixteen.

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