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Abstract

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DIFFUSION OF IODINE IN COMPRESSED CARBON DIOXIDE NEAR ITS CRITICAL POINT

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Studies of molecular diffusion in binary liquid systems have shown that at the critical point of stratification the diffusion rate is equal to zero ($^{1-5}$). In thermodynamic terms, the critical point of any other type of equilibrium differs in no way from the critical point of liquid–liquid equilibrium. Consequently, the diffusion rate at the critical point of binary gas systems must also be zero.

Studies of molecular diffusion in gases under pressure are associated with great experimental difficulties. Investigations near the critical point are especially difficult and therefore have not previously been carried out by anyone. Taking advantage of the fact that iodine gives colored solutions in gases, the authors developed a method for determining the diffusion coefficient of iodine in compressed carbon dioxide. The experimental investigation was based on the method used by Fourt to determine diffusion coefficients in liquid colored solutions (^{6}), which consists in observing the rate of advance of a colored layer whose color intensity is equal to that of a standard solution.

The experimental procedure was as follows. At the bottom of a high-pressure ampoule (Fig. 1, *1*) with an internal diameter of approximately 3 mm, a tablet of pressed iodine (*2*) was placed. The free space above the tablet was filled with thin glass rods (*3*) to prevent the occurrence of convective currents (the free cross section between the rods was no more than 0.1 mm^2). The ampoule was closed with a fluoroplastic-4 stopper, the opening in which was sealed by the pin of a metal valve (*4*). The flanges of the stopper served as a gasket between the valve nipple and the end of the ampoule. Sealing was achieved by a union nut that tightened the flanges of the ampoule to the valve nipple. The ampoule assembled in this way was evacuated and secured in a stand (*5*). To reduce the elasticity of iodine vapors, the end of the working ampoule was kept in a bag with dry ice until the stand was placed in the thermostat. On the same stand, next to the working ampoule, a control ampoule (*6*) containing a solution of iodine in carbon dioxide was placed. The coloration over the entire height of the control ampoule had to be uniform. After the stand was placed in the thermostat at the specified temperature, carbon dioxide was introduced into the working ampoule through a heated capillary tube. The pressure was measured

Fig. 1. Apparatus for determining the diffusion rate of iodine in compressed carbon dioxide

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with a standard manometer.

Near the critical point of carbon dioxide, practically the same pressure is observed over a wide range of densities. In this case, dosing was carried out not by pressure but by density. For this purpose, the small cylinder from which carbon dioxide was supplied was thermostated at the specified temperature. Since the volume of the small cylinder was a thousand times greater than the volume of the ampoule, it could be assumed with sufficient approximation that the density of the carbon dioxide in the ampoule connected to the thermostated cylinder was equal to the density in the latter. The density in the small cylinder was known from its volume (the cylinder had been calibrated) and from the weight of carbon dioxide in it. The final check of the density of carbon dioxide in the ampoule was made after the experiment.

After carbon dioxide was introduced into the working ampoule, diffusion of iodine in the compressed carbon dioxide began. At the moment carbon dioxide was introduced, directly at the surface of the tablet there occurred a blurring of the front. Therefore, by moving slit (7), fixed immovably relative to the control ampoule, in the working ampoule they selected, at a certain height from the surface of the iodine tablet, a region having the same color intensity as in the control ampoule. The displacement of this region along the ampoule was determined with ruler (8). The rate of this displacement corresponded to the diffusion rate. At the end of the experiment the actual density of carbon dioxide in the ampoule was found; for this purpose the amount of carbon dioxide and the free volume of the ampoule were determined. The amount of carbon dioxide was determined from the difference between the weights of the ampoule with carbon dioxide and without it. To measure the free volume, the rods were removed from the ampoule, weighed (the specific gravity of the glass of the rods was known), and the empty ampoule was calibrated with mercury, taking into account the volumes of the stopper and the iodine tablet.

Fig. 1. Apparatus for determining the diffusion rate of iodine in compressed carbon dioxide

To check the method, the diffusion rate of iodine in liquid carbon dioxide was measured. The value of the diffusion coefficient at 20° was obtained as $1.5 \cdot 10^{-5}$ $\text{cm}^2 \cdot \text{sec}^{-1}$, which corresponds to the usual values of the diffusion coefficient in liquids. The error of visual observation was ±1.5 mm. For the experiments, purified and dried carbon dioxide containing up to 0.1% inert gases was used.

The diffusion coefficient was calculated from the approximate equation (7)

$$D = \frac{l^2}{2t}, \tag{1}$$

where D is the diffusion coefficient, l is the displacement, and t is the time. Since the square of the displacement is directly proportional to time, on a plot in coordinates l^2—t, the experimental points for each experiment should lie on a straight line whose slope gives the value of the diffusion coefficient. As an illustration, Fig. 2 presents such a straight line, constructed from the experimental points of experiment No. 9 (Table 1). With the measurement error indicated above, the minimum values of the diffusion coefficient that could be determined were of the order of $1 \cdot 10^{-7}$ cm$^2 \cdot$ sec^{-1}. Equation (1) is strictly valid for infinitely dilute solut— parameters. Therefore, the values of the diffusion coefficients calculated from the experimental data are approximate. For the critical region, however, where deviations from ideality are considerable, equation (1) is not applicable at all. Near the critical point the authors visually observed no displacement of the color, despite the long duration of observation (Table 1). Consequently, without using calculation, the authors convinced themselves quite directly of the cessation of diffusion near the critical point of the system.

Table 1

Diffusion rate of iodine in compressed carbon dioxide

No. of experiment	Temp., °C	Pressure, atm	Density, g/cm^3	Duration of experiment, h	Diff. coeff., $D_{1,2} \cdot 10^5$, cm^2 sec^{-1}	No. of experiment	Temp., °C	Pressure, atm	Density, g/cm^3	Duration of experiment, h	Diff. coeff., $D_{1,2} \cdot 10^5$, cm^2 sec^{-1}
1	31.5	10.7	0.015	4.5	6.0	7	31.5	73.6	0.429	47.0	0.0
2	31.5	18.0	0.056	21.0	1.9	8	40.0	86.8	0.493	7.5	3.0
3	31.5	38.7	0.108	22.0	1.4	9	31.5	74.5	0.496	68.5	0.9
4	31.5	61.0	0.160	19.5	1.2	10	31.5	72.8	0.610	40.0	3.0
5	31.5	40.7	0.180	26.0	1.4	11	31.5	74.4	0.620	46.0	3.0
6	31.5	73.0	0.385	72.0	0.02	12	31.5	81.5	0.720	19.7	4.5

Diffusion of iodine in compressed carbon dioxide was investigated at 31.5° and at various densities of carbon dioxide, both greater and less than the critical density (Table 1, Fig. 3).

Fig. 2. Determination of the diffusion coefficient of iodine in carbon dioxide

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Fig. 3. Diffusion of iodine in compressed carbon dioxide

Figure 3: Fig. 3. Diffusion of iodine in compressed carbon dioxide

The literature contains no data on the critical parameters of the iodine–carbon dioxide system. However, it may be assumed that, because of the low solubility of iodine in carbon dioxide ([8]), the critical parameters of this system are close to the critical parameters of pure carbon dioxide (temperature 31.06°, pressure 72.9 atm., density 0.467 g/cm^3).

Fig. 3. Diffusion of iodine in compressed carbon dioxide

The experimental data obtained show that near the critical point, within the limits of error of our measurements, the diffusion of iodine practically ceases. The same was observed by us at 32° and 73 atm. ([9]). On moving away from the critical point, diffusion of iodine proceeds at rates normal for compressed gases.

Measurement of the diffusion rate at 40° and a density close to the critical one (experiment No. 8) showed that the influence of the critical point is already small here. The diffusion coefficient has a value almost usual for compressed gases.

Molecular diffusion is the result of the Brownian motion of individual particles. As shown in ([10]), at the critical point a Brownian particle must "tread" in place, i.e., the effect of cessation of Brownian motion should practically be observed and, consequently, the effect of cessation of molecular diffusion.

The data obtained by the authors on the diffusion of iodine in compressed carbon dioxide are an experimental confirmation of these views.

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