THE EFFECT OF ADDITIVES ON CRITICAL PHENOMENA IN CO_2

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The density distribution over the height of a vessel has been investigated in a gravitational field using floats with magnetic suspension. The substance studied was carbon dioxide containing small amounts of added noncondensible gases. It is shown that near the critical point the density distribution over the height of the vessel depends to a large extent on the amount of additive.

The study of critical phenomena is of special interest both for mixtures of materials having similar physical properties and for those which differ widely. Krichevskii [2] has carried out a thorough investigation of binary mixtures over a wide range of temperatures and pressures. Schneider and Atack [3] have observed the density change with height near the critical point, while Palmer [4] has carried out a similar investigation of the density distribution on the critical isotherm using the Toepler method, and also determined the density distribution over the height of the vessel. Other studies [5, 6] have recently been published on this question.

Among the large number of methods available for studying the density distribution in a liquid from the height of a piezometer, the hydrostatic suspension method is the simplest. Using this method the density can be determined fairly accurately, but a disadvantage is that some mixing occurs due to movement of the float in the vessel during the suspension process. Unlike Maass [1], we have determined the weight of the float in the experimental liquid with a magnetic balance (Fig. 1) rather than with a spring balance. This balance made it possible to study the density distribution close to the temperature at which the meniscus disappeared, according to the minimum solenoid current necessary to hold the float within the solenoid.

High-pressure glass tubing (3) containing carbon dioxide was placed along the axis of the solenoid (1). A hollow, sealed glass float (2), diameter 4.5 mm, wall thickness 0.1 mm, and specific gravity about 0.5, was able to move freely inside the tube. In the lower part of the float was a ring made from transformer iron; this interacted with the magnetic field of the solenoid. Current was supplied to the solenoid along flexible leads from a storage battery (4) and was measured with a precision ammeter (A), class 0.2, correct to 0.001 A. Sliding rheostat (5) was used to regulate the current. The solenoid could be moved along the tube by means of a rod (6). The magnetic balance was calibrated with liquid carbon dioxide at temperatures at which its density is well known.

The molybdenum glass tube (3) had an external diameter of 11 mm and internal diameter 7 mm, and was placed in thermostatted water bath (7). The ends of the tube were clamped in collars (8). Carbon dioxide was purified by sublimation under vacuum at low temperatures in storage vessels (9), and from there was fed into the system through a valve in the lower collar.

The metal frame of the thermostat bath was clamped between two plexiglas walls so that the float and the carbon dioxide meniscus could be seen inside the tube.

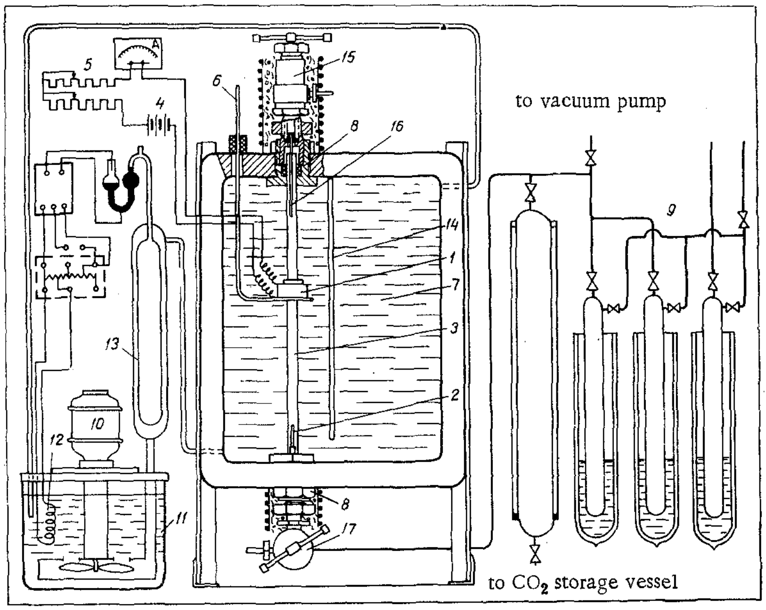

Fig. 1. Diagram of the apparatus.

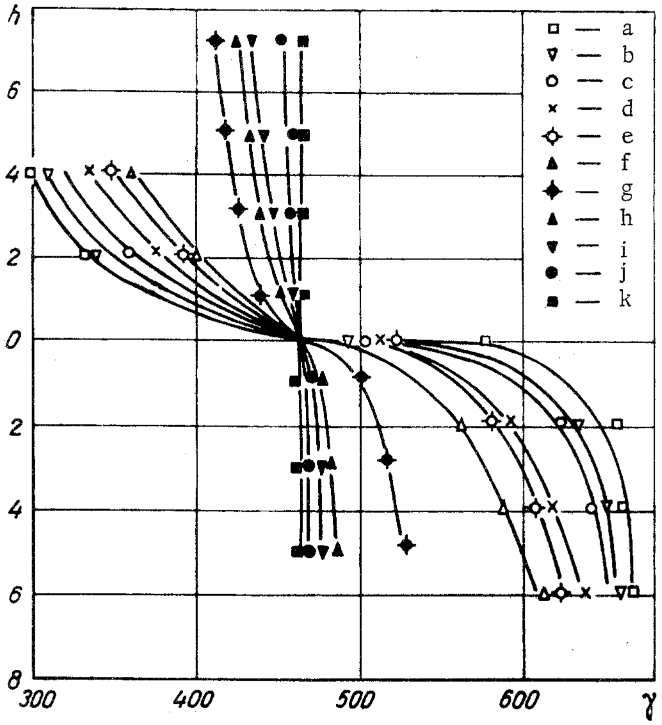

Fig. 2. Graph of the change of CO_2 density γ in kg/m^3 over the height of the experimental tube h in cm: a, b, c, d, e, f) at 30.11, 30.88, 31.58, 32.16, 32.84, and 33.30° C, respectively, with 3.46% of additive; g, h, i, j, k) at 31.57, 32.61, 33.01, 35.19, and 38.10° C and 0.12% additive.

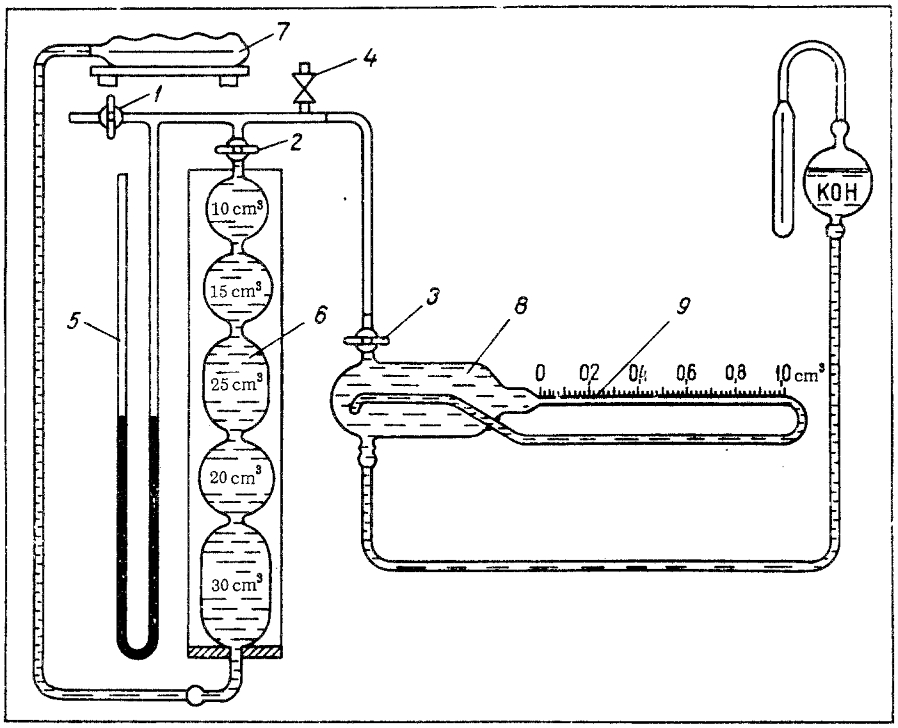

Fig. 3. Diagram of the gas analyzer.

Water was supplied to the thermostat bath by a centrifugal circulating pump (10). The temperature required was achieved by heating the circulating water in reservoir (11) with heater (12), and held constant using toluene regulator (13) and a magnetic relay. Temperatures were measured with a mercury thermometer placed in socket (14). Temperature fluctuations during experiments of 6–8 hours duration did not exceed ±0.02°. Commercial carbon dioxide was used, and the amount of additive determined by precision gas analyses. The amounts of additives not absorbed by alkali varied from 0.12 to 3.46%.

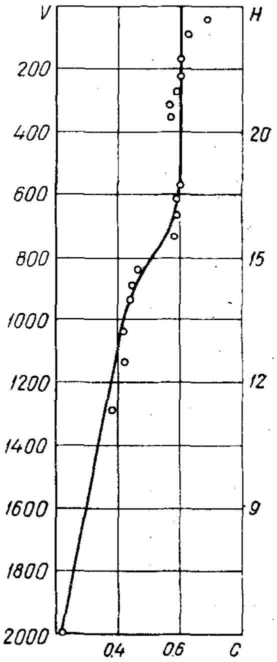

Fig. 4. Graph of the change in the percentage of additive C in CO_2 with height along the vessel (initial additive concentration 0.37%; H is the approximate point along the tube to which the sample refers, in cm; V is the amount of CO_2 extracted, in cm^3).

In order to investigate the nature of the additive concentration distribution over the height of the vessel, analyses were made of gas samples taken from the upper and lower parts of the tube at various temperatures above and below the temperature at which the meniscus disappeared. For this purpose a valve (15) was fitted on upper collar (8), with a thin tube (16) at its lower end entering the upper part of tube (3) 15 mm below the collar. Samples from the lower part of the tube were taken out through valve (17).

The experiment was carried out as follows: the experimental tube and the entire connecting system including the storage vessels (9) were evacuated before filling with carbon dioxide. During continuous operation of the vacuum pump a certain amount of carbon dioxide was frozen in one of the intermediate vessels by immersing one third of it in a Dewar vessel containing liquid nitrogen, and passing through it a gentle stream of carbon dioxide from the cylinder. After enough carbon dioxide had been frozen in the lower part of one of the storage vessels, the main cylinder was isolated, the apparatus shut off, and the carbon dioxide in the storage vessel was allowed to warm up and to pass into the experimental tube, which was cooled with tap water. The difference between the tap water temperature and room temperature, i.e., the temperature of the carbon dioxide storage vessel, was large enough for the carbon dioxide to distil over into the experimental tube. For these experiments the tube was filled with liquid carbon dioxide such that at the temperature of disappearance of the meniscus the specific volume of the carbon dioxide was close to the critical volume.

The carbon dioxide density was measured at a fixed level in the tube as follows: the solenoid was moved down to the lower position, the current switched on and maintained at a level sufficient to hold the float in position, following which the solenoid together with the float was raised to a prescribed level by means of rod (6). The current in the solenoid was then slowly decreased using the rheostat, the point at which the float began to drop (break away from the solenoid) was noted, and the current at that point determined. The dependence of current on density is linear and therefore the density can be calculated from the experimental data according to the formula

$$\gamma = \gamma_{cr} - K(i - i_{cr}).$$

The constant K was determined from an experiment at room temperature according to the relationship

$$K = (\gamma_v - \gamma_l)/(i_l - i_v),$$

where i is the current measured in the experiment; i_{cr} is the current corresponding to the critical density; i_l and i_v are the currents at which the float breaks away in the liquid and in the vapor, respectively; γ_{cr} is the critical density; γ_l and γ_v are the densities of liquid and vapor at room temperature. To allow for the effect of additives, two series of experiments were carried out with carbon dioxide containing different amounts of nonabsorptive gases (air).

Results are shown in Fig. 2 for two additive concentrations: 0.12% and 3.46%. The carbon dioxide density is plotted on the abscissa and the height of the measurement point calculated from the level at which the meniscus disappeared, is plotted on the ordinate. It can be seen from Fig. 2 that for 0.12% of additive there is a considerable dependence of CO_2 density on height at all temperatures above the meniscus disappearance temperature, the dependence being greater the nearer the experimental temperature is to the meniscus disappearance temperature. At 4.7° above the meniscus disappearance temperature there is still an observable variation of CO_2 density with height. At about 6.6° above the meniscus disappearance temperature the density along the tube is almost constant. For an increased amount of additive the density-height dependence is many times greater for the same temperature excess. It is obvious from this that the density gradient along the vessel greatly depends on the CO_2 purity.

Further experiments with CO_2 were carried out with widely differing floats; in each case the nature of the density distribution along the vessel remained the same. The curves under consideration refer to experiments carried out with different floats. The series of experiments using different concentrations of admixtures are superimposed in Fig. 2, so that they can be conveniently compared. It is interesting to note that all the curves, which relate to different experimental temperatures, intersect at almost the same point, corresponding to the meniscus disappearance point. The density at this point corresponds to the critical density. From the large effect of additives on the density distribution, it can be assumed that the presence of additives is the important factor determining the anomalous density distribution at temperatures above the meniscus disappearance temperature.

Since taking a sample of gas for analysis causes some change in the state of the material inside the tube, it is obvious that the volume of gas taken out must be as small as possible. Taking into account the fact that the amount of additive is extremely small, a precise method of gas analysis had to be devised once the absorption apparatus and sample buret had been perfected.

The gas analyzer used in this work is shown in Fig. 3. Before taking a sample the gas analyzer is evacuated through stopcock (1), while stopcocks (2) and (3) and valve (4) are closed. The analyzer is filled from the experimental tube through valve (4), and the slow rise in pressure in the analyzer is followed on mercury manometer (5), made up from a barometer tube of internal diameter 2 mm. When the level of the mercury in the left limb of the manometer is higher than in the right limb, stopcock (2) is opened and CO_2 starts to enter buret (6). Before finally filling the buret it is desirable to flush the system with the gas being investigated, evacuate the system once more, and then, repeating the procedure described above, refill it with the gas. Excess gas from the buret is let out through valve (1) and the volume of gas in the buret is finally read off, placing the rubber bag (7) on the same level as the liquid in the buret. When stopcocks (2) and (3) are opened and bag (7) is raised to the highest position, gas is transferred from buret (6) into the absorption buret (8), which is filled with a 50% solution of potassium hydroxide. The extremely small volume of nonabsorbable gas which remains is measured with microburet (9).

The total volume of the microburet is 1 cm^3, and one division is equivalent to 0.01 cm^3. Thus, with a sample volume of 25 cm^3 the gas can be analyzed with an accuracy of 0.02%, measuring the volume of nonabsorbable gas correct to 0.5 division. To achieve this degree of accuracy it is necessary for the liquid in buret (6) to be saturated with CO_2 of approximately the same composition as the CO_2 being investigated, and therefore the buret is flushed several times with the same carbon dioxide being analyzed from the storage vessel. Rubber bag (7) protects the water in buret (6) from contact with air.

Measurements of the concentrations of additives not absorbable by KOH, in gas samples taken from the upper and lower parts of the apparatus, verified the assumption mentioned above. In fact, the impurity concentration in the upper part of the apparatus proved to be 3–5 times larger than the concentration of these impurities in the lower part. Apparently the procedure for mixing the contents of the experimental tube does not lead to the formation of a homogeneous mixture. To establish the height-concentration distribution, experiments were carried out by gradually extracting gas only from the upper part of the tube and taking a large number of samples for analysis. The results of these measurements are shown in Fig. 4. The additive concentration is plotted on the abscissa and the amount of gas extracted is plotted downwards along the ordinate. Since the relative amount of gas extracted can be considered as an "equivalent height," representing the product of height by density, the curve in Fig. 4 can be considered as the concentration distribution along the vessel. It can easily be seen that the nature of the concentration distribution is very similar to that of the density distribution at the corresponding average additive concentrations. It is considered that the experimental results verify the viewpoint expressed above and show that hear the meniscus disappearance point, at temperatures above the critical temperature, the concentration distribution along the vessel and a corresponding density distribution are observed simultaneously.

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