Studies of Critical Phenomena in Carbon Dioxide contained in Vertical Tubes

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An accurate knowledge of the isotherms in the critical region is of great importance for problems of equations of state, for studies of liquid-gas phase interaction and many others. For the computation of the isotherms close to the critical point, the determination of the mass distribution of the substance in vertical tubes as a function of distance perpendicular to the original liquid-vapour interface might be useful. Previously, techniques such as the measurement of the position of small glass floats of known density or of a single spring-actuated float ¹, and the measurement of radiation intensity from radioisotope loaded samples ² have been used for the determination of mass distributions in vertical tubes.

It has appeared to me that a technique of greater simplicity and of potentially far greater resolving power could be developed by taking advantage of the relationship between density and refractivity. In this paper the apparatus developed for this work will be briefly described, and preliminary results for carbon dioxide presented.

The assembled equipment is shown in Fig. 1. It consists essentially of a cylindrical glass-jacketed thermostat containing the sample tube made of ordinary Pyrex tubing, and an optical system designed to focus an image of a pair of parallel vertical lines (illuminated by a sodium lamp) as seen through the sample tube and thermostat on a photographic plate. The thermostat and sample tube together may be regarded as a part of the optical system since they form a cylindrical lens. The telescope is focussed a few millimeters beyond the sample tube.

The photographic plate shows the image of two vertically running lines, the horizontal distances between which are determined by the extent of the refraction of the light which passes through the tube at whatever the height of the sample tube, and hence by the density of the substance in that region. One must, of course, establish the relationship between density and the distances between the lines, that is, calibrate the apparatus.

The line distance is found to increase nearly linearly with increased density. Therefore, each of the two lines on the photographic plate represents a mass

Fig. 1. Apparatus.

- 1) Steel frame (300 kg) mounted on 3 rubber blocks.
- 2) 3 thermostats (the one in front not fully mounted).
- 3) Screw for selecting the temperature of the thermostat. One turn of the screw changes the temperature about 50 millidegrees.
- 4) Reservoir of thermostat-water. Is used in the case of rough temperature selection.
- 5) Circulation pump, magnetically driven. The motor is inside the hollow foundation.
- 6) Electronic relays for switching off and on heating current on one of the thermostats.
- 7) Coil for additional heating of thermostat.
- 8) Lamp carrying vertical, illuminated lines (Na-light). The lamp is movable and can be placed in fixed position behind each thermostat.
- 9) Telescope can face any of the thermostats and can be raised and lowered for measuring at any level of the thermostats. (Screw and wheel not visible.)
- 10) Planed iron table which allows exact vertical placing of lamp and thermostats.

distribution curve of the carbon dioxide in the sample tube at the temperature of the thermostat. The same principle has been employed previously, but only by making direct visual observations and therefore without significant results³.

THE THERMOSTAT

The thermostat consists basically of a glass cylinder (390 mm long, 60 mm inner diameter) hermetically sealed at both ends and totally filled with de-aired water. A magnetically-driven pump wheel spinning like a top on the bottom of the thermostat forces the water up through the 5 mm intermediate space created by the wall of the thermostat and a second glass cylinder placed inside and coaxial with it. (About 50 recirculations per minute.)

The spinning of the pump wheel is maintained by a motor below the thermostat bottom, the motor being supported by a rubber ring and placed coaxially inside the hollow foundation of the thermostat. The top of the vertical shaft of the motor carries a permanent horseshoe magnet. The pump wheel inside the thermostat also consists basically of a permanent magnet formed as a cylindrical disc. Naturally, the magnetic

connection between the motor and the pump wheel does not transfer the vibrations of the motor to the thermostat construction. In fact, in spite of the relatively high speed of the motor and the pump wheel — 1 400 rpm — the thermostat is practically free from vibrations — this being of great importance for the measurements close to the critical point.

Heat is supplied by means of a low-voltage alternating current (about 4 watts) conducted by naked resistant wires directly immersed in the water. The heating current is controlled by a relay actuated by a mercury switch, which is constructed in the form of a U-tube with a tungsten wire contact inside one arm. The contact end of the tube is sealed off, and the space above the mercury is filled with hydrogen. The other arm is open and the whole U-tube immersed in the thermostat water, so that the thermostat construction operates as the bulb in a great water contact thermometer.

The intense (not visible) stirring of the water provides for homogeneous temperature in the thermostat. The mercury switch reacts almost immediately by changes in the average temperature of the water. The resistant wires, spun of fine nichrome filaments, allows for an almost immediate heat transfer to the water when the heating current is switched on. Thus the inertia factors of an off-on thermostat are greatly reduced and, in fact, the calculated "hunting" (energy $\times$ time/heat capacity) of this thermostat can be as low as less than 0.001° in periods of one second. In cases where the calculated "hunting" even exceeded the last-mentioned value, the actual "hunting" was not registered by the resistant thermometer employed.

A rough temperature selection is obtained by adding or withdrawing water through a valve: withdrawing water causes, for example, the mercury contact to be broken and heat to be supplied to the system. The specific volume of the water will increase and the reduced mass of water will, due to the increased temperature, re-establish the balance of the mercury switch. An accurate temperature selection (0.001° intervals over about 1°) is obtained by screwing a plunger in or out of the thermostat, thus changing the volume. The easy regulation and the small size of the thermostat allow a convenient and rapid selection of desired temperatures. For precise work the thermostat has to be shielded by reflecting aluminium sheets.

The main difficulty which I met when designing this new type of thermostat was to secure a constant interior volume in the thermostat construction, a volume that was to be independent of exterior temperatures and air pressure changes, and to avoid leaks which tend to cause a constant rise or fall in temperature.

Through the top enclosure and almost all the way down the entire length of the thermostat a coaxial glass tubing (closed at the bottom and open at the top) form a "well", inside of which the test-tubes can be conveniently placed. The test-tubes are fully immersed in an oil with almost the same refractive index as the pyrex glass, thus reducing optical imperfections and securing good thermal conduction between the thermostat water and test tube. In the same oil and above the test tube, the thermometer is placed. Above the oil, but still inside the thermostat, a bobbin of wool yarn provides for adequate thermal insulation. FS Precision-Bore Tubing of Pyrex glass is used for the construction of the thermostat. The outside of these tubes is ground cylindrically and polished for optical perfection.

PREPARATION OF CARBON DIOXIDE

Carbon dioxide is prepared by dripping sulfuric acid into a solution of potassium-hydrocarbonate in an apparatus described by Reihler⁴. This author described the carbon dioxide to be airfree. The carbon dioxide is dried by passing through 4 U-tubes containing concentrated sulfuric acid and glass beads, while the last of the 4 tubes is cooled by solid carbon dioxide. At this temperature the drying power of the solid sulfuric acid distributed on the surface of the beads is calculated to be about as high as that of phosphorus pentoxide at ordinary temperature.

From the fourth drying tube the carbon dioxide is led through a valve into an all-fused glass tubing system, consisting of the sample tubes to be filled, a trap cooled with solid carbon dioxide and an open mercury manometer. Finally, a glass valve leads to a diffusion pump and a mechanical vacuum pump. The glass tubing system is repeatedly filled with carbon dioxide heated and evacuated below 10^{-4} mm Hg, and, filled with

carbon dioxide, allowed to rest for several days. Then it is evacuated and refilled before the carbon dioxide is finally precipitated by immersing the bottom of the sample tubes in liquid air. The sample tubes are then individually fused off and thereby sealed. The purity of the enclosed carbon dioxide was probably better than 99.999 %. I am indebted to Cand.real. Arne Almenningen, who has done the preparation work of the carbon dioxide.

When using heavy-walled capillary tubing as sample tube, the tubes are deliberately under-filled when fused off. By warming the tubes to a temperature close below the critical, inaccuracies in the filling proportions can be determined. When recooling the bottom of the sample tube in liquid air the carbon dioxide will again precipitate and vacuum be reestablished in the tube. If now the top of the tube is fused, the interspace of the tube will be reduced. By repeating the test and thus shortening the tube the interior volume, corresponding to the mass of the enclosed carbon dioxide and its critical density, can be attained with adequate exactness.

GENERAL DESCRIPTION OF THE MASS DISTRIBUTION PHENOMENA

The mass distribution in tubes filled with CO_2 and heated to temperatures near the critical was studied in 3 series, the first as early as in the autumn of 1951. The purity of the CO_2 enclosed in the tubes has been successively improved and only the tube of the last series was prepared with the accuracy described above. In the first two series the tubes were about 20 cm long and with an inner diameter of 6 mm. In the last series the tube used for the mass distribution measurements was 5 cm long and of 1.8 mm inner diameter.

Qualitatively, the mass distribution found in the tubes in all 3 series was such as is to be expected when determined by isotherms of classical type and if the pressure increase downward in the tube is computed as being due to the weight of the substance itself.

At temperatures below the critical the carbon dioxide is separated into vapour (upper part) and liquid (lower). On approaching the critical temperature pronounced density gradients are built up in the two formerly homogeneous phases, the vapour being denser near the surface than higher up, and the liquid less dense near the surface than lower down. At a certain temperature the brilliant reflecting surface is replaced by a region with a sharp density gradient between the still fairly homogeneous fillings in the extremities of the tube. The density difference between both ends of the tube is then 10—15 % depending on the length of the tube investigated. When the temperature is further increased the densities at the extremities approach each other. More marked, however, is the increase in height of the region with density gradient. In the case of proper filling proportions the density gradient will soon reach both ends of the tube, and the fairly homogeneous filling, formerly present in the extremities of the tube, will have disappeared.

At temperatures just below the critical, the surface in tubes containing too much carbon dioxide will, with increasing temperatures, move upwards, in the opposite case downwards. Above the critical temperature the region with density gradient which has replaced the surface continues the movement of the surface and will, on further heating, in the case of improper filling, soon "move out of" one of the ends of the tube. If the two phases were homogeneous at all temperatures up to the critical point, then the surface would always "move out of" one of the ends of the tube already before the critical tem-

perature had been reached. As stated above, this movement of the surface will always exist but, due to the fact that the density difference between the fillings in the extremities of the tube is greater than the density difference at the surface, the surface will not reach one of the ends of the tube before a region with density gradient has been established. This happens when the filling proportion does not deviate more than about $\pm 10\%$ from that corresponding to the critical density. These limits must depend on the height of the tube employed.

In my experiments the method of raising or lowering the temperature in steps was employed, thus allowing the tubes to remain for a considerable time at the selected temperatures before the photographs were made.

In practice the mass transportation which takes place when changing the temperature is slow. When selecting the time in which the tube was kept at the chosen temperature, regard was paid to the changes in mass distribution to be expected. In some cases, the time during which the tube was kept at constant temperature was as long as 8 days. Working carefully enough it must be expected that the distribution actually measured will not be far from an equilibrium distribution.

The new material seems to indicate very strongly that the mass distribution in the tubes in equilibrium is determined by the isotherm of the substance at the temperature selected. If this is so, the mass distribution curves will show parts of the isotherms, and the determination of the mass distribution in the vertical tube will make possible a determination of the isotherms substantially closer to the critical point than any previously known method.

If a simultaneous determination of the pressure inside the tube had been carried out, the position of the isotherm in the pv -diagram would have been known. However, in the region in question which is very close to the critical point, the $\frac{d p}{d t}$ of substances at critical density can be regarded as constant.

At the critical point $\frac{d p}{d t}$ is known for a series of substances.

The relation between line distances and actual densities

For the calibration of the apparatus the sample tube was heated to the temperatures 29.01° , 29.98° and 30.76° (2.03° , 1.06° and 0.28° below the critical). The horizontal distances between the vertical lines on the photographic plate which recorded the densities of the liquid and vapour phases were at these temperatures 1.745, 1.382; 1.698, 1.414; 1.639 and 1.460 (mm).

Fig. 2 shows the top of the coexistence curve. The densities of the liquid and vapour phase at the temperatures mentioned according to the curve are as follows: 0.623, 0.308; 0.593, 0.338; 0.545 and 0.380 (g/cm^3). Using these density data and the corresponding line distances the calibration curve was constructed. It is a slightly curved line which is almost straight at the densities found in the tube near and above the critical point.

For future work a more satisfactory way of calibration will be used.

Fig. 2. Top of Coexistence Curve.

C is the critical point. The ordinate is in the scale of $\Delta T^{0.357}$.

AC and *BC* are the vapour and liquid parts of the coexistence curve, *CD* is the rectilinear diameter.

Down to $\Delta T = 1^\circ$ *CD* is a straight line. Below it has slightly positive curvature. The lines *AC* and *BC* should have corresponding curvature. For simplification, however, the curves are drawn as straight lines and the points below $\Delta T = 1^\circ$ herefore slightly corrected. The 6 $\odot$ marked points correspond to the values of MBM, the 6 $\times$ marked points to those used for calibration of the measurements and the $\bullet$ marked points correspond to the determined densities of vapour and liquid at the surface at the temperatures 1.4, 9.6, 18, 90, 158 millidegrees below the critical.

The Top of the Coexistence Curve

A. Michels, B. Blaisse, and C. Michels⁵ (in the following abbreviated to MBM) have found that the coexistence curve for carbon dioxide at temperatures up to about 1° below the critical can be represented by the equation $d_l - d_v = C \cdot \Delta T^{0.357}$ where d_l and d_v are the densities of liquid and vapour and ΔT the distance from the critical temperature. Furthermore, the Matthias rule of rectilinear diameter was found to be correct up to the temperature mentioned. Above this temperature the coexistence curve was found to be less regular. If, however, the coexistence curve is supposed to be regular all the way up to the critical point, it will, when drawn with the temperature scale $\Delta T^{0.357}$ as ordinate, be represented by two symmetrical straight lines

Fig. 3. Mass Distributions Close To the Critical Point.

The temperature of the thermostat was raised in steps to the temperatures of 1.5 millidegrees below and 1.5, 6.5 and 12 millidegrees above the critical. The curves show the mass distribution in the middle section of the tube. The line marked 1 mm corresponds to 1 mm height difference in the tube. The horizontal part of the curve -1.5 corresponds to the density difference at the surface.

meeting at the critical point. Down to 1° below the critical temperature the inclination of the rectilinear diameter is of no practical importance. In Fig. 2 the coexistence curve is drawn in the way just described. The 6 centered circles correspond to the values of MBM for the temperatures 2.99° , 1.11° and 0.63° below the critical with a minor correction for the lower two. The 6 points marked by crosses correspond to those used for the calibration as described above. The filled circles thus correspond to my measurements of the coexistence curve up to 1.4 millidegrees below the critical temperature.

Mass distribution close to the critical point

In the second series carried out in the autumn of 1952 the tube was heated in steps of 3 millidegrees per hour past the critical temperature. Some of the mass distribution curves obtained are shown in Fig. 3. In the third series the tube was cooled from a temperature some millidegrees above the critical, past the critical temperature in steps of about 1 millidegree per 20 minutes. In Fig. 4 the mass distribution curves for the temperatures $+1.2$ and -1.4 millidegrees are shown. A mass distribution curve made at a temperature between these two is not shown on the figure, but runs, as is to be expected, in between the curves $+1.2$ and -1.4 .

The agreement between the curves $+1.5$ and -1.5 in Fig. 3, and $+1.2$ and -1.4 in Fig. 4, is as good as can be expected. In the second series (Fig. 3)

Fig. 4. Mass Distributions Close to the Critical Point.

The temperature of the thermostat was lowered in steps to 1.2 millidegrees above and 1.4 and 9.8 millidegrees below the critical. Ordinate and abscissa as in Fig. 3.

The straight line (*a-a*) represents a calculated tangent of the mass distribution curve +1.2 at the inflexion point.

the inner diameter of the tube was 6 mm. For optical reasons this diameter is too large for really good measurements of a very sharp density gradient. Moreover, as the calibration of the apparatus was not carefully done, the density scale of Fig. 3 is uncertain by about $\pm 10\%$.

The line *a-a* in Fig. 4 is the calculated tangent of the isotherm + 1.2 millidegrees of carbon dioxide at the inflexion point. The calculation is based on the data given by MBM in their Fig. 9 and the average pressure increase downward in the tube of 0.000046 atm. per mm. In addition, the tangents for the isotherm + 7 millidegrees and + 90 millidegrees have been calculated and found to be in adequate agreement with the mass distribution curves + 7 and + 90 in Figs. 5 and 6.

Fig. 4 also shows the liquid and vapour curves at — 9.8. The inhomogeneity of the two phases can be seen.

The critical temperature

In the second series (Fig. 3) the critical temperature was determined as the temperature at which the surface was no longer seen as a horizontally, brilliantly reflecting disc. In the third series (Fig. 4) the density gradient was visible at the temperature + 1.2 millidegrees. Moreover, the photograph shows clearly

the smooth transition between the densities in the upper and lower part of the tube. In the next step it was not possible to determine visually whether a very large density gradient or a real surface existed. Nor did the photograph allow this determination. The temperature of this step was chosen as the critical in this series. At the temperature -1.4 millidegrees, however, the brilliantly reflecting disc of the surface was clearly visible and, moreover, the photograph showed definitely the density step at the surface.

The critical temperature was found to be 31.04° , the same as found by MBM.

Mass distributions at equilibrium

Already in the first series the mass distributions were determined in the tube at a temperature ($+25$ millidegrees) which was reached by cooling as well as by heating. The mass distributions were found to be similar, but definitely different from the distributions which were found at higher and lower temperatures. Corresponding experiments which, however, showed poorer agreement between the final mass distributions at $+20$, are reported in the next paragraph.

Identical mass distributions by heating and by cooling have never been obtained, most probably because insufficient time has been allowed for equilibration at the temperatures selected.

More precise experiments will be carried out when the accuracy of the system is improved. Any serious hysteresis effect, however, would have been detected in the great number of mass distribution measurements which have been carried out.

Mass transportation phenomena

When the mass distribution in the tube, at temperatures below the critical, is in equilibrium, the surface will appear at certain heights in the tube, dependent upon the temperature and the ratio between the interior volume of the tube and the mass of the enclosed substance.

On rapid heating, however, the surface will start an unexpected movement upwards in the tube. The reason for this may be that the thermal expansion of the liquid is faster than the mass transfer from liquid to vapour. In the case of heating rapidly past the critical temperature the surface will degenerate at a position too high in the tube.

Fig. 6 demonstrates that a similar phenomenon takes place when the tube is rapidly heated from $+7$ up to $+20$ millidegrees above the critical. Curve $+7$ shows the mass distribution in a tube which had remained at this temperature over night. Curve *a* shows the mass distribution 10 minutes after the temperature was raised up to $+20$. The density gradient has moved upwards in the tube. Curve $+20$ shows the mass distribution in the tube after having been kept for 3 hours at this temperature.

On the other hand, by rapid cooling of the tube past the critical temperature, the reappearance of the surface will take place in a lower position in the tube than expected. By cooling the tube to a temperature above the critical

Fig. 5. Mass Transportation.

Ordinate and abscissa as in Fig. 3. The temperature of the thermostat was raised from 7 millidegrees above the critical (curve +7) to 20 millidegrees above the critical. Curve *a* shows the mass distribution when tube had remained 10 minutes at this temperature, curve +20 shows the mass distribution after 3 hours.

a similar phenomenon seems to take place. In Fig. 6, curve + 90 shows the mass distribution in the tube after the tube had stayed at + 90 millidegrees over night. By lowering the temperature the density of the lower part of the tube increases almost immediately and a density gradient is built up which moves very slowly upwards in the tube — cf. curves *a* and *b*. Curve + 20 shows the mass distribution after 48 hours at 20 millidegrees above the critical.

Fog

Fog formation, commonly found by cooling the tubes past the critical region, may be connected with the mass transportation phenomena. In the tubes of the two first series heavy fog was formed by cooling and gave the impression of being a subcooling phenomenon. Fog was generally not produced by heating. However, when the tube was slowly heated past the critical temperature (second series Fig. 3), a light fog was observed in the region of a sharp density gradient.

In the tubes prepared for the last series, and with the care described above, no fog formation at all was produced by either heating or slow cooling. On cooling rapidly past the critical temperature, however, a 5 mm high white belt introduced the reappearance of the surface.

Fig. 6. Mass Transportation.

Ordinate and abscissa as in Fig. 3. The temperature of the thermostat was lowered from 90 millidegrees above the critical (curve +90) to 20 millidegrees above the critical. Curve a shows the mass distribution immediately after the thermometer had reached the new temperature, curve b the mass distribution 3 hours later. Curve +20 shows the mass distribution when the tube had remained for 48 hours at 20 millidegrees above the critical.

SUMMARY

The initial purpose of this work was to study the supposed deviation from classical behaviour of a substance (carbon dioxide) enclosed in a vertical tube of adequate filling and heated within the critical region. However, no anomalies could be observed. The mass distributions were as expected if determined by isotherms of the classical type. Furthermore, the coexistence curve has a rounded top. The measurements of mass distribution in vertical tubes can very likely provide a method for the determination of the isotherm in the very neighbourhood of the critical point.

Although the equipment has not yet reached the desired perfection for precise quantitative determinations, it appears most likely that the isotherms have been determined and further that the top of the coexistence curve conforms to the "cubic rule".

The carbon dioxide, which was prepared with the greatest caution, did not show the commonly observed fog-formation when heated or cooled in the critical region.

Measurements in the close neighbourhood of the critical point require a very good thermostat. A new thermostat with the temperature control based

on the thermal expansion of the thermostat water itself has been designed and built. For the measurements of the mass distributions in the vertical tubes the refractivity of the enclosed carbon dioxide could be measured at any desired level. For this purpose a cylindrical lens method was developed.

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REFERENCES

1. Maass, O., and co-workers *e. g.* Tapp, J. S., Steacie, E. W. R., and Maass, O. *Can. J. Research* 9 (1933) 217.
 2. Weinberger, M. A., and Sneider, W. G. *Can. J. Chem.* 30 (1952) 847.
 3. Young, F. B. *Phil. Mag.* [6] 20 (1910) 793.
 4. Reihlen, H. *Ber.* 72 (1939) 112.
 5. Michels, A., Blaisse, B., and Michels, C. *Proc. Roy. Soc.* 160 A (1937) 358.
- For a general survey concerning the critical phenomena and the supposed anomalies reference can be made to Partington, J. R. *An Advanced Treatise on Physical Chemistry I*, Longmans, Green and Co., London, 1949, p. 630.

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