Schlieren Studies of the Critical Region

Howard B. Palmer

Additional information on J. Chem. Phys.

the retractable furnace. The absence of disproportionation can hardly be attributed to higher activation energies than for the combinations in view of the elevated temperatures but is more probably the result of low steric factors for such reactions.

ACKNOWLEDGMENT

The authors wish to thank Dr. L. C. Leitch, Mr. A. T. Morse, and Mr. R. Renaud of these laboratories for preparing the mercury dimethyl, allyl iodide, and benzyl iodide used in this work. The assistance of Dr. J. B. Farmer in the determination of the ionization potential of benzyl is gratefully acknowledged.

Note added in proof.—In view of the difference of

0.18 ev found between the ionization potentials of CH_4 and CD_4[25], it was of interest to compare the ionization potentials of CH_3 and CD_3 radicals. The CD_3 radicals were produced from the pyrolysis of $Hg(CD_3)_2$ and values of 9.96 and 9.95 were obtained for the ionization potential. It may be concluded that the ionization potentials of CH_3 and CD_3 are the same within 0.03 ev. The ionization potentials of CD_4 and CH_4 were redetermined under comparable conditions and $I_{CD_4}-I_{CH_4} = 0.12\pm0.03$ ev. This may be compared with the difference of 0.18 ± 0.03 ev found previously.[25] It is interesting to note that a similar difference has been found between I_{ND_3} and I_{NH_3}.[31] In this case $I_{ND_3}-I_{NH_3} = 0.22$ ev.

[31] H. Neuert, Z. Naturforsch 7A, 293 (1952).

Schlieren Studies of the Critical Region*†

Howard B. Palmer‡
University of Wisconsin, Naval Research Laboratory, Madison, Wisconsin
(Received September 21, 1953)

The critical regions of ethane, carbon dioxide, and xenon have been studied, using a Schlieren optical system. The material to be studied was confined in a thermostatted high pressure cell having optically flat windows, and placed in the test section of the optical system. At temperatures over a range of about two degrees, in the critical region, refractive index gradients within the cell were determined as a function of height along the cell. From these data were calculated the density distribution, the pressure distribution, and the shapes of the pressure-volume isotherms at the various temperatures. The technique permitted detailed study of the isotherms over a narrow range of pressures, too small to be observed by usual experimental methods. Extensive visual observations were made throughout the course of the experiments. Particular attention was devoted to the question of the equilibrium state in the critical region and the process of equilibrium attainment.

I. INTRODUCTION

IN recent years, numerous attempts have been made to obtain accurate experimental data concerning the properties of a pure substance in its critical region. The experiments have dealt principally with the density distribution within a cell containing a fluid in its critical region,[1,2] the detailed shapes of pressure-volume isotherms near the critical temperature,[3,4] the shape of the coexistence curve as the critical temperature is approached,[5,6] and the structure of a fluid in its critical

region.[7,8] Interpretation of the experimental results has rested chiefly upon the concepts of molecular clustering in gases and local order in liquids, and upon knowledge of the effect of gravity upon a compressible fluid. The magnitude of the effect of gravity in causing such phenomena as flat tops on coexistence curves has only recently begun to be appreciated, although the theoretical basis for such phenomena has been established for some time.[9,10] The theoretical treatment of condensation by Mayer,[11] with its controversial prediction[12,13] of a temperature region of anomalous behavior, near the critical temperature, has provided much of the impetus for many of the experimental investigations.

The present study was undertaken in hopes of elucidating further the problem of the equilibrium behavior of a fluid in its critical region, particularly as

[1] O. Maass, Chem. Revs. 23, 17 (1938).
[2] M. A. Weinberger and W. G. Schneider, Can. J. Chem. 30, 847 (1952).
[3] R. H. Wentorf, dissertation, University of Wisconsin (1951). Portions of this thesis have appeared as University of Wisconsin CM-724, May 12, 1952.
[4] Weinberger, Habgood, and Schneider, Can. J. Chem. 30, 815 (1952).
[5] M. A. Weinberger and W. G. Schneider, Can. J. Chem. 30, 422 (1952).
[6] S. G. Whiteway and S. G. Mason, Can. J. Chem. 31, 569 (1953).
[7] R. L. Wild, J. Chem. Phys. 18, 1627 (1950).
[8] H. A. Cataldi and H. G. Drickamer, J. Chem. Phys. 18, 650 (1950).
[9] M. Gouy, Compt. rend. 115, 720 (1892).
[10] R. Ruedy, Can. J. Research 16A, 89 (1938).
[11] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).
[12] B. H. Zimm, J. Chem. Phys. 19, 1019 (1951).
[13] J. E. Mayer, J. Chem. Phys. 19, 1024 (1951).

manifested in the density distribution within a cell under the influence of gravity. The use of a Schlieren technique permitted detection of density gradients, with high sensitivity, without perturbing the fluid.[14]

II. EXPERIMENTAL DETAILS

A. The Cell Assembly

The material to be studied was confined in a cell 3 in. high, which had been cut out of a block of steel 6 in. square by $1\frac{1}{4}$ in. thick. The block was recessed so that the thickness of the cell was only $\frac{3}{8}$ in. Its width was also $\frac{3}{8}$ in. The cell windows were of "Crystallex" plate glass, a very clear glass which permitted accurate visual observation of the cell contents. Use of plate glass was possible because the small sections used for windows were found to be flat to the order of a few wavelengths of light, at worst. Because of glass breakage, the final configuration of the cell had one window of $\frac{1}{2}$-in. glass and the other of $\frac{3}{4}$-in. glass. The windows were pulled against the cell block by means of $\frac{1}{2}$-in. steel plates, tightened down by bolts which threaded into the cell block. Lead gaskets were used between the windows and the cell block. For access to the cell, $\frac{1}{16}$-in. holes were drilled into the cell from the top and bottom of the cell block, and their openings at the block surface were machined to take standard $\frac{1}{4}$-in. Aminco "superpressure" fittings. The bottom outlet was used only for preliminary cleaning of the cell. The top outlet was provided with a valve which permitted the cell to be filled with the material being studied and which then could close off the outlet at the surface of the cell block. This was necessary in order to insure that the entire body of fluid under study would be subject to the thermostatting action of the large steel cell block.

Cylindrical brass vacuum housings attached to the cell block prevented the cell windows and the portions of the block in the vicinity of the cell from being subjected to fluctuations in the surrounding air temperature. The windows on the vacuum housings were of $\frac{1}{4}$-in. Crystallex. The cell assembly was supported on four wheels, made to fit the circular flanges on the ends of the vacuum housings. The wheels were mounted on a small frame of iron pipe, which was in turn mounted on a wooden base. The entire assembly stood within an air thermostat which had double windows of Crystallex. Strings, attached to the vacuum housings and running out of the thermostat, permitted inversion of the cell. A $\frac{5}{16}$-in. steel ball bearing inside of the cell assured vigorous stirring during inversion. This type of stirring had the asset of being entirely internal, with no possibility of energy exchange between the exterior and the cell contents during the stirring process. The cell assembly was insulated thoroughly with asbestos before being placed in the thermostat.

The volume of the cell was measured by a gas expan-

---

[14] After the work was begun, it was discovered that Ruedy (reference 10) suggested the use of a Schlieren method in critical studies.

sion method. It was found to be 7.53 cc, accurate to about $1\frac{1}{2}$ percent. For calculations, it was necessary to know the volume of the cell from the top of the ball bearing in the bottom to the highest point visible, namely the bottom edge of the portion of the lead gasket running across the top of the cell. This volume was calculated to be 6.66 cc, with a probable error of 3 to 4 percent.

The temperature along the height of the cell was measured by means of five copper-constantan thermocouples, located in wells which extended into the cell block to within $\frac{3}{16}$ in. of the cell wall. Readings were taken on a Rubicon Type B high-precision potentiometer, in conjunction with a Rubicon 3201 wall galvanometer having a sensitivity of 0.1 microvolt per mm at one meter. The sensitivity was increased by moving the galvanometer scale to a distance of about five meters. A detectable deflection at this distance corresponded to a temperature change of around 0.001°C. Each of the thermocouples was calibrated against a Leeds and Northrup platinum resistance thermometer which had in turn been calibrated at the National Bureau of Standards. The absolute accuracy of measurement with the thermocouples was approximately ±0.01°C, with an available precision of about ±0.001°C in the measurement of temperature differences.

The temperature of the air thermostat was controlled by a Western Electric thermistor, type D-169604, connected as one arm of a wheatstone bridge, the balance of which controlled a relay in the heating circuit. The heater consisted of 60 feet of No. 18 nichrome wire, distributed over the two sides of the thermostat furthest from the cell. Stirring of the air was provided by a combination of convection currents and the action of two small fans in the top of the thermostat. The temperature of the air was found to fluctuate as much as 0.2°C about its mean value. The thermostatting action of the insulated steel cell block evened out this variation to the extent that no fluctuations in the cell temperature could be detected as accompanying the periodic changes in air temperature. Thus, the fluctuations due to this cause were of the order of ±0.001°C or less. However, changes in room temperature, plus changes in the line voltage, placed a limit upon the regulation over long periods of time. With some manual attention to the regulation, the cell temperature could be preserved constant to about ±0.01°C over periods of several hours. The temperature remained constant to about ±0.05°C without any supervision, e.g., overnight.

B. Substances Studied

The substances studied were carbon dioxide, ethane, and xenon. The carbon dioxide was prepared from reagent grade sulfuric acid and sodium carbonate, the liberated gas being bubbled through several sulfuric acid traps and passed over a dry ice trap before being

collected. Analysis by absorption in 6 N KOH showed it to be about 99.997 percent pure, the 0.003 percent impurity probably being air. The ethane was "research grade" ethane, obtained from the Phillips Petroleum Company. Its purity was specified by them to be 100.00 percent. The xenon was the "reagent grade" product, purchased from the Air Reduction Sales Company. The average purity of the xenon in the several flasks in which it was shipped was about 99.9 percent, according to the report of mass spectrographic analysis which accompanied the shipment. The 0.1 percent impurity was composed primarily of krypton and nitrogen or carbon monoxide. No attempt was made to purify the gas further.

The materials were introduced into the cell by condensation. To facilitate this, use was made of the loading bomb designed by Wentorf.[3] The bomb could be weighed on an analytical balance, which yielded the sample weight to an accuracy of about 0.1 percent. The cell contents were also weighed at the end of each study. It was discovered that the cell had a very slow leak, giving rise to a loss of contents at the rate of about 0.01 percent per hour. Mean densities of loading were calculated for each day by using the average rate of leakage.

C. Optics

A Z-type Schlieren system[15] was used to study the refractive index gradients in the fluid. An excellent discussion of Schlieren systems may be found in the monograph by Schardin.[16] The light source was an Ediswan "Pointolite" tungsten arc lamp. It emitted essentially white light. The light was not filtered, since error from other causes far exceeded error from variation of refractive index with wavelength.

For a Z-type system

$$\Delta a = \epsilon f, \qquad (1)$$

where Δa is the deflection of the source image at the knife edge, ϵ is the angular deviation given the ray in passage through the test section, and f is the focal length of the mirror nearest the knife edge. For the sort of test section employed, *viz.*, one of rather small and virtually constant thickness, the relation

$$\epsilon = W d\mu/dz \qquad (2)$$

holds to a good approximation in most instances. W is the thickness of the cell and $d\mu/dz$ is the change of refractive index with height. The relation is not valid when $d\mu/dz$ is extremely large, e.g., at a meniscus. The Lorenz-Lorentz equation can be differentiated to

give

$$d\rho/dz = [6M\mu/([R](\mu^2+2)^2)]d\mu/dz, \qquad (3)$$

where $[R]$ is the molar refractivity, μ is the refractive index, M is the molecular weight, and ρ is the density. Substitution into (2) yields

$$d\rho/dz = \{6M\mu/([R](\mu^2+2)^2 Wf)\}\Delta a. \qquad (4)$$

Over the range of densities of interest in a study of the critical region, the expression in brackets is constant to within 3 percent.[17] In this work, it was treated as a constant, for the sake of simplicity in calculations.

The values of Δa were found, for the most part, by using a grid, i.e., a "multiple knife edge," as the Schlieren stop. A continuous distribution of refractive index gradients in the cell yielded a series of bands in the cell image on the camera back. Knowledge of the grid constant and the position of the undeviated source image at the knife edge, plus one or often two values of the deflection at particular points in the cell made it possible to read the values of $d\rho/dz$ at all points along the cell directly from a single photograph. The grid employed was made by photographing a series of black and white lines of equal widths and printing them on a lantern slide. The grid constant was 0.0332 in. The grid and knife edge mounting was raised and lowered by a screw having a scale which permitted the height of the mounting to be read to ±0.001 in. An obvious limit to the measurable refractive index gradients was presented by the size of the mirrors and the aperture of the camera. As an auxiliary means of deflection measurement, used when extremely steep gradients were present in the fluid, one of a series of thin prisms was sometimes placed in the light path in such a way that light deflected downward by the steep gradient would be redeflected upward by the prism and enter the camera.

Experimental data were recorded in the form of photographs of the fringe pattern in the cell image. The films were read by means of a Gaertner comparator. It permitted the location of a fringe in the cell to be determined to within ±0.01 cm.

D. Procedures and Calculations

Observations were made, for the most part, over a range of about a degree, commencing around 0.2°C below the. temperature of meniscus disappearance. Below this point, gradients in the liquid and vapor extended over too small a distance to be analyzable, while at temperatures from about 0.8° to 1.0°C above the meniscus disappearance point, gradients throughout the cell became too slight to study.

The criterion taken for equilibrium was the constancy of appearance of the Schlieren pattern on the camera back over several hours' time or the return of contents to their former appearance after thorough shaking.

[15] Designed and assembled by H. L. Olsen, H. Rubin, and A. Ingersoll, at the University of Wisconsin Naval Research Laboratory, in 1947. The parabolic mirrors in the system were first surface, aluminized mirrors, 12 in. in diameter, having a surface accuracy of $\frac{1}{10}$ wavelength of sodium light and a focal length of 100±1 inches. They were manufactured by the Perkin-Elmer Corporation.

[16] H. Schardin, "Toepler's Schlieren Method," U. S. Navy Department, David Taylor Model Basin, Washington, D. C., 1949.

[17] A. Michels and J. Hamers, Physica 4, 995 (1937), provide data on the constancy of the molar refractivity of carbon dioxide. In the present study, it was assumed that the molar refractivities of ethane and xenon have constancies similar to that of carbon dioxide.

At temperatures at or below about 0.2°C beneath the meniscus disappearance temperature, equilibrium was established in at most a few minutes. Above this temperature, it was established much more slowly upon cooling or shaking, but appeared to be continuously established, in the absence of stirring, upon slow and continuous rise in temperature. Therefore, heating rates not over 0.03°C per hour were generally employed. When the temperature reached the level at which gradients could no longer be observed, it was allowed to fall slowly to a temperature below the condensation point. The rate of fall was made extremely small as the condensation point was approached. It was observed that at temperatures higher than a point about 0.05°C above the temperature of reappearance of the meniscus, the rate of fall of temperature made no perceptible difference in the establishment of gradients.

Photographs of the gradients were usually taken at intervals of a few hundredths of a degree. The cell contents were also observed visually, and occasionally some direct photographs were taken of the cell, for example, to show opalescence or fogging. A number of miscellaneous experiments were performed to test the stability of the gradients and to check upon reappearance of gradients after vigorous stirring.

Visual observation was employed in determining the temperature of disappearance of the meniscus. The criterion used for the existence of a meniscus was the ability to distinguish reflection of light from a surface within the fluid. The light source for this was a 100-watt bulb, turned on briefly in order to prevent heating of the fluid by radiation. It was located outside the air thermostat. It was found that reflection was observed to the highest temperature when the angles of incidence and reflection were about 60 degrees. The lowest temperature at which a reflection could no longer
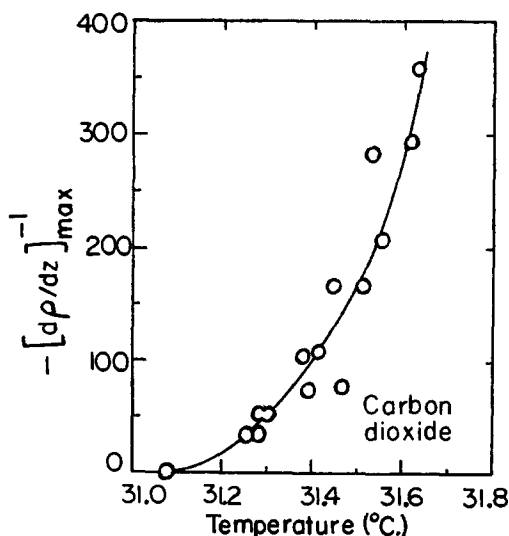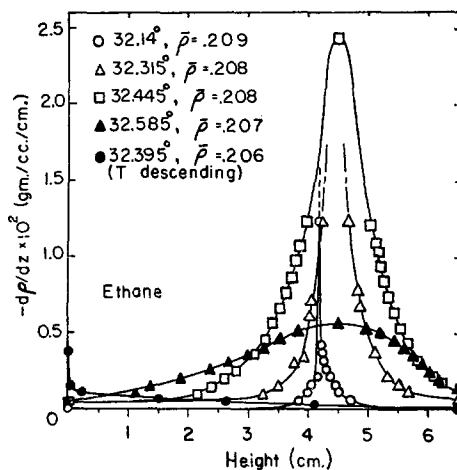

FIG. 2. Density gradients in ethane, at several temperatures in the critical region.

be distinguished was taken to be the temperature of meniscus disappearance.

The values of the density at various points in the cell were calculated by numerical integration of the function $d\rho/dz$ over the cell. For this purpose, all the density gradient data were plotted, and values at intervals of 0.25 cm in the height z were tabulated, so that integration could be performed over equal intervals. Integration could only be carried out over the entire cell at temperatures somewhat above the temperature of meniscus disappearance, since at lower temperatures, and in particular at temperatures below the meniscus disappearance point, values of $d\rho/dz$ could not be measured over the entire cell. In order to make an estimate, however crude, of the density distribution at temperatures only slightly above the meniscus disappearance temperature, values of the reciprocal of the maximum density gradient present in the fluid at higher temperatures were plotted as a function of temperature and extrapolated smoothly to a value of zero at the temperature of meniscus disappearance. Such a plot is shown for carbon dioxide in Fig. 1. Values of the maximum gradients in the region of immeasurability were then estimated from this graph. For these cases, using the estimated value of the maximum gradient, the integral of the density gradient was calculated over the immeasurable region in the cell, on the assumption that the gradient distribution had a Gaussian shape in the unknown region. This assumption was apparently quite good at temperatures 0.1°C or more above the meniscus disappearance temperature, as evidenced by a fit at a slightly higher temperature to a gradient distribution which was known in its entirety; but the assumption became very poor at temperatures only a few hundredths of a degree above the meniscus disappearance point. This fact was apparent from the calculation of negative densities in the upper part of the cell, in the case of xenon at a temperature 0.025°C above the meniscus disappearance point.

FIG. 1. Plot of the reciprocal of the maximum density gradient in carbon dioxide, at temperatures above the temperature of meniscus disappearance.

The known portions of the density gradient distributions—i.e., the entire curves, at the majority of temperatures—were integrated over each 0.25 cm interval in z, using the partial-range formula[18]

$$\int_{z_i}^{z_{i+1}} f dz = h/24[-f_{i-1}+13f_i+13f_{i+1}-f_{i+2}], \quad (5)$$

where h is the length of the interval, and the subscripts refer to the regularly-spaced values of the independent variable z. The integration performed in this manner gave the value of the change in density, $\Delta\rho$, from the value at the bottom of the cell, as a function of the height. This function was then integrated over the cell height, using Simpson's rule, to permit calculation of the density at the bottom of the cell from the relation

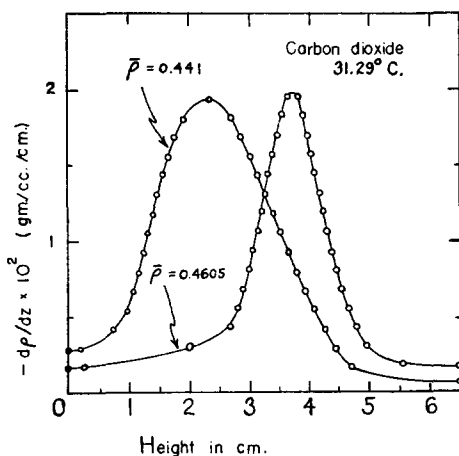$$\bar{\rho}H = \rho_0 H + \int_0^H \Delta\rho(z)dz, \quad (6)$$

FIG. 3. Density gradients in carbon dioxide, at two mean densities.

where ρ_0 is the density at the cell bottom and $\bar{\rho}$ is the mean density of loading of the cell. Absolute values of the density in the cell at regular intervals in z could then be found from the sum of ρ_0 and $\Delta\rho(z)$.

To find the pressure distribution in the cell, the change in pressure from the pressure at the bottom of the cell was calculated by integration of the equation

$$dp = -g\rho(z)dz, \quad (7)$$

over each of the 0.25-cm intervals in z. The same partial-range formula (5) was used in these integrations. Since no absolute value of the pressure at any point in the cell was known, it was not possible to calculate any absolute pressures. The shapes of pressure-volume isotherms could, however, be found by plotting the values of the molar volume, corresponding to the various density values, *versus* the change in pressure from the value at the cell bottom.

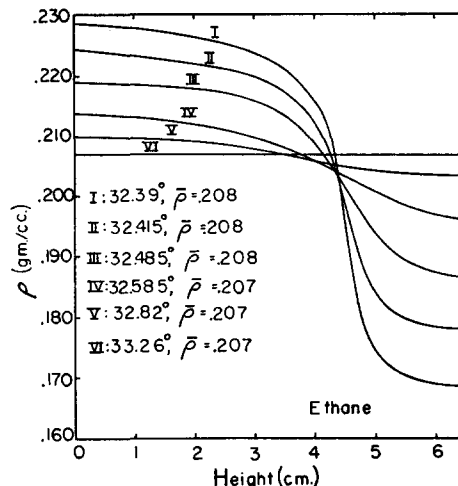[18] W. G. Bickley, Math. Gazette **23**, 352 (1939).

FIG. 4. Density distributions in ethane, at several temperatures.

III. RESULTS

The results for the three substances studied were qualitatively very similar. The distributions of density observed under conditions of rising temperature were all sigmoid in character, and a complete hysteresis was observed in all three cases; i.e., no sigmoid distributions were found under conditions of descending temperature. Because of the similar behavior, and for the sake of brevity, the pressure-volume isotherms found for all three substances are presented, but typical data for only one of the three are selected to show the other characteristics.

The observed meniscus disappearance temperatures were 31.08°C for carbon dioxide, 32.315°C for ethane, and 16.485°C for xenon, all with uncertainties of about ±0.02°C. The respective temperatures of reappearance of the meniscus observed were 31.09°C, 32.325°C, and 16.475°C, again with probable uncertainties of ±0.02°C. Thus, the temperatures of disappearance and reappearance coincided, within the experimental uncertainty, for all three substances, in the absence of stirring. The uncertainty was composed of a ±0.01°C uncertainty in temperature measurement, plus an observational uncertainty of approximately ±0.01°C.

Representative density gradient data for ethane are shown in Fig. 2, which contains plots of the gradient in
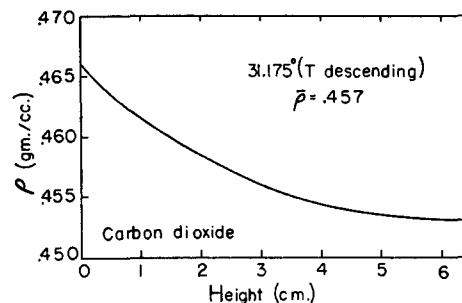

FIG. 5. A typical density distribution in carbon dioxide, under descending temperature conditions.
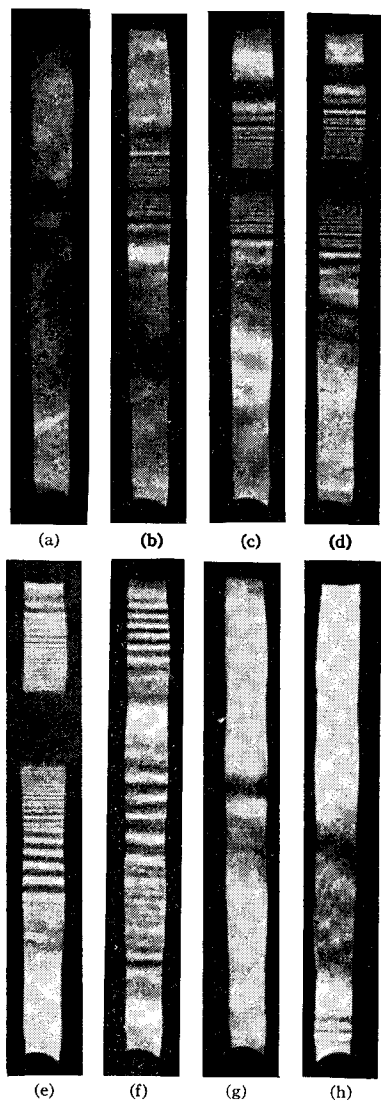
FIG. 6. Schlieren photographs of ethane in the critical region. (a) 31.57°C, (b) 32.21°C, (c) 32.29°C. An extremely flat and thin meniscus is still visible. (d) 32.32°C. No meniscus is distinguishable. (e) 32.445°C, (f) 32.585°C, (g) 33.235°C, (h) 32.41°C. T descending.

the fluid as a function of height, at several temperatures. The curve at 32.315°C shows the data at the observed temperature of meniscus disappearance. It will be noted that the data at 32.395°C (T descending) are the type one would expect if the gradient resulted from a simple sedimentation equilibrium of large molecular clusters in a medium of density somewhat smaller than that of a cluster. This sort of curve was typical of those observed under falling temperature conditions.

The approximate reproducibility of results is shown by Fig. 3, which is a plot of the gradient distribution in carbon dioxide at two different mean densities. The two curves also show the effect of changes in mean density upon the distribution. The peak gradient is the same in the two cases, within experimental error, as would be expected.

Several plots of the calculated density distributions in ethane at various temperatures, under conditions of slowly rising temperature, are shown in Fig. 4. The curves for the temperatures 32.39°C and 32.415°C were calculated with the aid of the assumption that the center portions of the gradient distributions had Gaussian shapes. Figure 5 shows the density distribution calculated for carbon dioxide at the temperature 31.175°C under conditions of slowly descending temperature.

It is felt that photographs of the cell as it underwent changes in temperature may be of interest. Therefore, in Fig. 6 are presented eight Schlieren photographs of ethane in the critical region. Each fringe across the cell represents an equal increment in the density gradient. From Fig. 6(c), it can be seen that at a temperature at which a meniscus was still visible, the gradient became large (indicated by the edges of the blacked-out region) at points well above and well below the meniscus. In xenon, this fact was emphasized by the use of prisms in estimating the values of the large gradients; e.g., it was found that at a temperature 0.045°C below the meniscus disappearance temperature in xenon the density gradient went to the extremely large value of 0.7 gm/cc/cm at points 0.5 mm above and below the meniscus. This may possibly indicate that in fact the density gradient at such a temperature proceeds continuously to a value of infinity at the meniscus, or to whatever maximum value is characteristic of the liquid-vapor transition region at this temperature, instead of undergoing a discontinuity. At lower temperatures a discontinuity was observed, within the limitations of the experimental measurements.

The fluid shown in Fig. 6(c) was in a condition of some interest visually, in that casual inspection of the cell revealed only a blur in the meniscus region; but closer examination showed that one could see by light reflection an extremely thin and flat meniscus within the blurred region.

Another phenomenon of visual interest in the critical region is opalescence. Two photographs of opalescence in carbon dioxide are shown in Fig. 7, for temperatures 0.01°C and 0.06°C above the meniscus disappearance
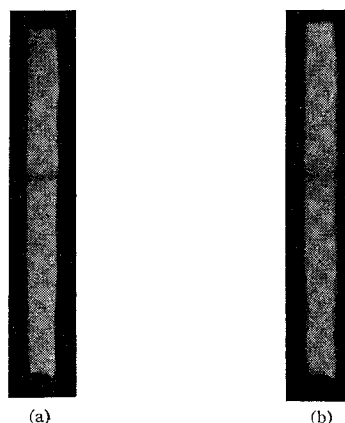

FIG. 7. Opalescence in carbon dioxide. (a) 31.09°C, (b) 31.14°C.

temperature. These were taken with a diffuse white light background. The temperature range in which opalescence was observed in all three substances was from perhaps 0.01°C below the meniscus disappearance temperature to 0.1°C or 0.15°C above that temperature. The range was approximately the same for both ascending and descending temperature conditions, but the opalescence was concentrated in a band in the former case and was distributed throughout the cell in the latter. Under rising temperature conditions, the band of opalescence became broader and less intense as the temperature rose. One unusual feature was noted in the study of xenon. At a temperature about 0.01°C above the condensation temperature, under conditions of descending temperature, the opalescence seemed to commence concentrating into a band about halfway up the cell. Unfortunately, the temperature fell to the condensation point before it could be found whether or not the concentration would become identical to that observed under rising temperature conditions. The opalescence was so pronounced at this temperature that no Schlieren pictures could be taken. Because of difficulties in temperature control, the experiment could not be repeated.

Isotherms calculated from the data for the three substances studied are shown in Figs. 8, 9, and 10. Several isotherms are included which were calculated using the assumption of a Gaussian shape in the center portions of gradient distributions. These are the isotherms at 31.14°C and 31.18°C for carbon dioxide, at 32.415°C for ethane, and at 16.69°C for xenon. The principal significance of the isotherms perhaps lies in their showing qualitatively the state behavior of the system over a range of pressures too small for measurement by ordinary experimental techniques. Their quantitative validity is not felt to be great. More will be said concerning this in discussing experimental errors.

The minimum slope of each isotherm was read graphically and plotted *versus* temperature in the hope of determining the validity of a linear extrapolation to
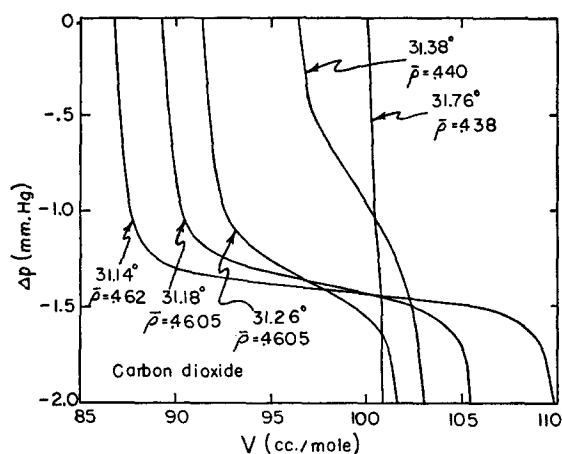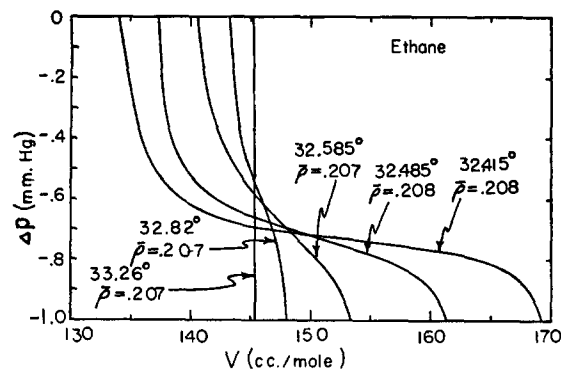

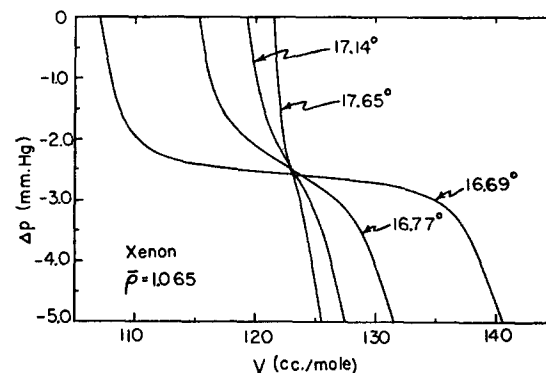FIG. 9. Isotherms for ethane, at several temperatures.

FIG. 10. Isotherms for xenon, at several temperatures.

zero of a plot of this quantity, used by some workers[3,19] as a method of estimating the critical temperature. Such a plot is shown for xenon in Fig. 11. The point at 16.56°C is an upper limit to the minimum slope, estimated by using prisms; it was not possible at this temperature actually to measure the largest gradient. The point at 16.625°C was also found by using the prisms; at this temperature it was possible to determine the value of the largest gradient in the cell, which permitted a good estimate to be made of the minimum value of $(\partial p/\partial V)_T$ from the relation

$$(\partial p/\partial V)_T = g\rho^3/[M(d\rho/dz)], \tag{8}$$

where g is the gravitational constant, M is the molecular weight, and ρ is the density. If one assumes the minimum slope of the isotherm at the temperature of meniscus disappearance to be zero, then it appears from the figure that the plot of the minimum slopes has a pronounced curvature, instead of being linear.

The importance of pressure corrections in PVT measurements in the critical region suggested that a plot of the calculated change in pressure, from the value at the bottom of the cell, as a function of height, would be significant. This quantity is plotted for ethane at a temperature of 32.37°C, 0.055°C above the observed meniscus disappearance temperature, in Fig. 12. This is a temperature for which the assumption of a Gaussian

FIG. 8. Isotherms for carbon dioxide, at several temperatures.

[19] Michels, Blaisse, and Michels, Proc. Roy. Soc. (London) A160, 358 (1937).
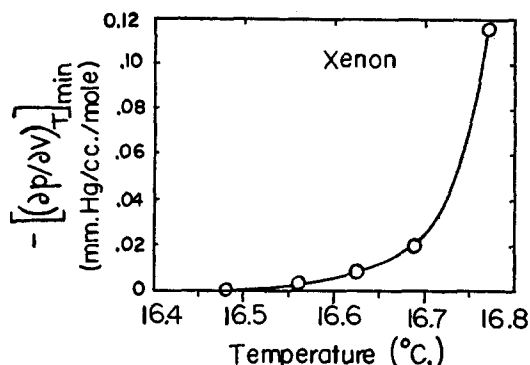
FIG. 11. The minimum slopes of the isotherms for xenon, at temperatures above the meniscus disappearance temperature.

gradient distribution was made, and it is virtually certain that the deviation of the change in pressure from linearity is quite exaggerated, as a consequence. This case was deliberately chosen, to show that within the present accuracy of pressure measurements in the critical region, a linear correction is generally adequate. The maximum difference between a linear curve and the calculated curve for xenon, at a temperature of 16.56°C (also an exaggerated case), was found to be 1.2 mm of mercury, just about the limit of present experimental accuracy in pressure measurements in the critical region. Of course, the maximum difference between the true curve and a straight line is a function of the height of the cell, so that for longer cells the maximum difference might exceed the experimental error. This would also be the case at lower temperatures.

The stability of the sigmoid gradients observed under rising temperature conditions was tested by raising ethane to a temperature of 32.42°C and retaining it there, within about ±0.05°C, for a period of about 40 hours. At the end of that time, the gradient configuration was approximately the same as that observed at 32.50°C, under conditions of slow and steady rise in temperature. That is, the final gradient was probably that which was characteristic of the highest temperature to which the cell was carried by temperature fluctuation.

Stirring of a fluid containing a sigmoid gradient was observed to destroy the gradient and fill the cell with turbulent regions of inhomogeneity. If opalescence was originally present, it became immediately distributed throughout the cell. The inhomogeneity tended to decrease upon continued stirring, but the Schlieren camera still clearly showed it to be present. In carbon dioxide the cell was retained at constant temperature (within ±0.05°C) for a period of 24 hours after stirring, at a mean temperature 0.1°C above the meniscus disappearance temperature, without any sign being observed of the return of a sigmoid density distribution.

The gradients observed under descending temperature conditions showed no tendency to become sigmoid. More than 48 hours were devoted to the cooling process in the study of carbon dioxide, 52 hours in the case of ethane, and 24 hours in xenon. The data for Fig. 5

were taken after the cell had been retained at constant temperature (within ±0.05°C) for some 24 hours.

IV. ERRORS AND UNCERTAINTIES

The uncertainty in measuring deflections at the Schlieren knife edge was estimated to be about 0.005 in. This figure was confirmed by a check of the system using a plano-convex lens of 20-meter focal length, ground to very exact optical specifications by the Naval Gun Factory Optical Shop. The assumptions implicit in the derivation and use of Eq. (4) introduced errors of about 2 percent in the measured density gradients, for moderately large gradients. For extremely large gradients, the error approached 6 percent. Uncertainties in the cell width and in the focal length of the Schlieren mirror contributed a relative error of perhaps 3 percent in the measured density gradients. In reading the photographs, there may occasionally have been a counting error of a fringe. Possibility of such an error was minimized by the requirement that the total number of fringes counted had to agree with the value of the maximum deflection visible, as determined by adjusting the knife edge or by allowing the source image to fall upon a piece of ruled paper held at the knife edge. If a fringe counting error occurred, the error in a gradient of average value was about 10 percent.

A possibly reasonable estimate of the total relative error in the measured density gradients, exclusive of counting errors, might be about 12 percent for a small gradient value and a smaller error of 8 or 9 percent for a gradient of large magnitude. Error in the function $\Delta\rho(z)$ was of the same order, aside from errors introduced in the numerical integration process. The consequent error in the calculated value of the density at the cell bottom, ρ_0, was around 2 or 3 percent for cases in which there was a large difference in density between the bottom and top of the cell, and much less for cases in which the distribution of densities extended over a small range. The uncertainty in the measured values of the mean densities of loading increased the error in the
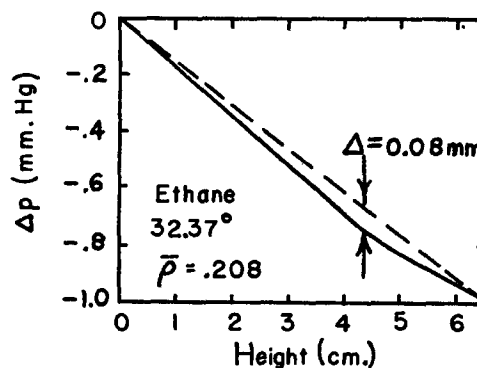

FIG. 12. The change in pressure, from the value at the bottom of the cell, as a function of height, for ethane at a temperature somewhat above the meniscus disappearance temperature. Solid line: calculated from the experimental data. The maximum deviation from simple linearity is 0.08 mm Hg.

calculated density values by about 1.5 percent. For the extreme density distributions, then, the density at the cell bottom may have been in error by 4 percent, and that at the top by 7 or 8 percent. For narrow distributions, all calculated density values should have been accurate within 2 or 3 percent. The relative error in the calculated values of the change in pressure from the value at the bottom of the cell was of the order of magnitude of the error in the density values.

V. DISCUSSION

The average temperature of meniscus disappearance-reappearance found for carbon dioxide, 31.085±0.02°C, may be compared with the values 31.045°C, 31.04°C, and 31.04°C, found, respectively, by Wentorf,[3] Michels, Blaisse, and Michels,[19] and Meyers and Van Dusen.[20] The higher temperature observed in the present work may well be a consequence of the use of reflected light as a criteron for the existence of a meniscus. The average temperature for ethane, 32.32±0.02°C, may be compared with the value of 32.27°C listed in the tables of the American Petroleum Institute,[21] and with the values 32.23°C and 32.167°C reported by Whiteway and Mason.[6] The difference between the latter two values and that found in the present work seems too large to be accounted for by differences in the technique of observing the meniscus. The temperature observed in the case of xenon, 16.48±0.02°C, is 0.11°C below the value 16.59°C reported by Weinberger and Schneider[2] and by Whiteway and Mason[6] for very pure xenon. A crude calculation of the expected effect of 0.06 percent krypton and 0.04 percent nitrogen upon the observed meniscus disappearance temperature of xenon, assuming a linear dependence relation and taking 16.59°C as the correct value, yields a predicted temperature of 16.48°C. The agreement is partly accidental.

The results of the present study seem to indicate that equilibrium in the critical region can be continuously achieved under conditions of very slowly rising temperature. Stirring destroys equilibrium, which is not reattained in any reasonable length of time, except possibly at temperatures very slightly above the meniscus disappearance temperature. Similarly, the approach to equilibrium under descending temperature conditions appears to be imperceptibly slow, except perhaps at temperatures within a few hundredths of a degree of the meniscus reappearance temperature. These observations are consistent with the concept that a fluid in the critical region possesses a degree of order intermediate between that of a gas and that of a liquid, and that within the fluid there is a near equality of the energies of motion and of attraction.

The quantitative agreement between the density distributions and isotherms found in this study and the results of Wentorf[3] for carbon dioxide, and of Weinberger and Schneider[2] for xenon, is not very good. The high quality of these studies cited for comparison suggests that the results reported here probably should be regarded as being largely of qualitative and heuristic interest. This casts some doubt upon the results shown in Fig. 11; however, in their defence it may be added that a tangential approach to the value zero at the critical temperature of the minimum value of the slopes of isotherms above this temperature seems far more reasonable than the sort of discontinuous break necessitated by a straight-line approach; furthermore, the results of Wentorf[3] for sulfur hexafluoride fit the tangential condition much better than they do a straight-line approach.

It seems to the author that at present there is no experimental evidence to support the making of a distinction between the "meniscus disappearance" temperature and the "critical" temperature of a substance, so long as experiments on the critical region are performed in a gravitational field. An initial reason for saying this is that the meniscus disappearance temperature of carbon dioxide, observed in the present work, corresponds within the experimental uncertainty to the highest temperature for which Wentorf[3] observed a flat portion in the isotherm. Use of reflected light in observing the meniscus probably accounts for the ability to see a meniscus in this work at a temperature for which Wentorf was unable to see one. Thus it appears that, for carbon dioxide at least, the meniscus disappearance temperature and the critical temperature coincide, in a gravitational field.

The theory of Mayer,[11] which has provided the theoretical basis for making a distinction between the two temperatures, says nothing as to whether or not gravity may create a meniscus which otherwise would not exist, in a fluid having a region in which $(\partial p/\partial V)_T$ is zero. In Mayer's anomalous region, the predicted condition of the fluid is that its isotherms have flat portions, but no condensation into a bulk liquid phase can occur (thus creating a meniscus). However, it is seen from Eq. (8) that when $(\partial p/\partial V)_T$ is zero, dp/dz is infinite. This is the condition for the existence of a meniscus, and implies that even if the anomalous region exists, gravity will create a meniscus in the fluid in this region. The implication should be qualified, however, by pointing out that the actual ability to see the meniscus in this region (or in the critical region in general) is complicated by the thickening of the liquid-vapor transition region as the critical temperature is approached.[22,23,24]

If Mayer's prediction is correct, but gravity causes a coincidence of the meniscus disappearance temperature and the critical temperature, it should still be possible to detect a lower characteristic temperature (Mayer's

[20] C. H. Meyers and M. S. Van Dusen, J. Research Natl. Bur. Standards 10, 381 (1933).
[21] A.P.I. Research Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons," Natl. Bur. Standards. Washington, D. C.

[22] G. Bakker, Z. physik. Chem. 171 (Ser. A), 49 (1934).
[23] T. L. Hill, J. Chem. Phys. 20, 141 (1952).
[24] P. S. Epstein, Proc. Natl. Acad. Sci. U. S. 16, 627 (1930).

T_m) at which the meniscus would disappear in the absence of gravity. The results of the present study lead to the tentative conclusion that there may be such a temperature, lying a few hundredths of a degree below the critical temperature. In a gravitational field, this temperature could be determined by finding the temperature at which $(\partial p/\partial V)_T$ commences proceeding continuously, instead of discontinuously, to the value zero as the isotherms enter the liquid-vapor equilibrium region. In the present work, the possible evidence for such a temperature was the increase of density gradients to a very large value at points well away from the meniscus, commencing at temperatures the order of 0.05°C below the temperature of meniscus disappearance.

An interesting implication of the above conclusions is that investigators looking for Mayer's anomalous region at temperatures above the temperature of meniscus disappearance have probably been looking for it in the wrong temperature region, and should instead have been looking for it below the meniscus disappearance temperature. The possibility of making critical studies in the absence of gravity at some time in the future, which could clear up the entire question of an anomalous region, is an intriguing prospect.

VI. CONCLUSIONS

The Schlieren optical technique has proven to be a very useful tool in studying the critical region. Its most striking potentialities appear to be its use in studies of the attainment of equilibrium and in determining the isotherms, at temperatures above the critical temperature, as they behave over pressure intervals too small to be studied by ordinary experimental methods. The improvements which should be incorporated into any future work of this sort are extremely refined temperature control, plus a means of measuring the very steep density gradients which occur just above the critical temperature. A detailed study of the reflection of light by liquid-vapor interfaces should also be made, in order to provide a sound basis for decisions regarding the existence of a meniscus.

Magnetic Susceptibilities of K₃MoCl₆ and RuCl₃†

Charles Epstein* and Norman Elliott
Chemistry Department, Brookhaven National Laboratory, Upton, New York
(Received November 18, 1953)

Magnetic susceptibilities of K₃MoCl₆ and RuCl₃ were measured in the temperature range 76°–297°K. Curie's law is obeyed by both salts. The magnetic moments 3.83β and 2.07β are calculated for the ions Mo³⁺ and Ru³⁺, respectively.

THE palladium and platinum transition elements are structurally similar to the iron group. They contain an unfilled $4d$ and $5d$ shell of electrons, respectively. With wider multiplets than the iron series, it might be expected that the magnetic properties of compounds of the palladium and platinum groups would conform more closely to theory than those of the iron group. This is not the case, however, and the existing data are too scanty to permit an understanding of these elements at present. More low temperature measurements and, if possible, investigations of magnetically dilute salts are needed.

Extrapolation of published data for the magnetic susceptibilities of K₃MoCl₆[1–3] and of RuCl₃[4–6] suggest

that these salts obey Curie's law. The data are insufficient for this conclusion to be drawn with certainty though, and we have prepared the compounds and extended the measurements down to liquid nitrogen temperatures.

K₃MoCl₆ was prepared by the electrolytic reduction of a solution of MoO₃ (starting material Eimer and

TABLE I. Magnetic susceptibility of K₃MoCl₆.

Temp.°K	77°	195°	295°
$\chi_{atom} \times 10^6$	6175	9300	23 100

Table II. Magnetic susceptibility of RuCl₃.

Temp.°K	64°	76°	161°	191°	296°
$\chi_{atom} \times 10^6$	8400	7240	3330	2790	1810

* Present address: Harvard University, Cambridge, Massachusetts.

¹ P. Ray and H. Bhar, J. Indian Chem. Soc. 5, 497 (1928).
² B. Th. Tjabbes, Proc. Acad. Sci. Amsterdam 35, 693 (1932).
³ W. Klemm and H. Steinberg, Z. anorg. u. allgem. Chem. 227, 193 (1936).

⁴ D. M. Bose and H. G. Bhar, Z. Physik 48, 716 (1928).
⁵ A. N. Guthrie and L. T. Bourland, Phys. Rev. 37, 303 (1931).
⁶ B. Cabrera and H. Fahlenbrach, Ann. Physik 21, 832 (1934).