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## Shape of the Coexistence Curve in the Perfluoromethylcyclohexane-Carbon Tetrachloride System. II. Measurements Accurate to 0.0001<sup>o</sup>

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The coexistence curve of the binary liquid system, perfluoromethylcyclohexane-carbon tetrachloride, has been redetermined, in order to test for the existence of a possible flat region at the top of the curve. A technique has been developed to control and measure the temperature of a sample with a precision for relative values of  $\pm 0.00005^\circ$ . Using this technique the density of the top phase of a sample whose composition was very near the critical composition was measured as a function of temperature, giving half of the coexistence curve. Simultaneous measurements of the meniscus position allowed calculation of the density of the bottom phase, giving the other half of the coexistence curve. It was necessary to allow for effects of gravity in producing a density gradient in the bottom phase. The measurements showed that the coexistence curve appears to follow a cubic relation to within  $0.0001^\circ$  of the critical temperature, and there is no evidence of a flat region in this system.

There is at present an overwhelming body of experimental evidence that coexistence curves for both binary liquid systems and liquid-vapor systems have the form

$$X_1 - X_2 = K(T_c - T)^{1/n}$$

in the immediate vicinity of the critical region, where  $X_1 - X_2$  is a measure of the difference between the two coexisting phases,  $T_c$  is the critical temperature,  $T$  is the temperature at which the phases are in equilibrium,  $K$  is a proportionality constant, and  $n$  is very close to 3. However, there is some doubt that this relationship holds all the way to the top of the curve.

A number of the investigations of the cyclohexane-aniline system,<sup>2</sup> made in this laboratory, indicate that in this case the coexistence, or solubility, curve has a flat region at the top, that is, there is a range of critical compositions over which the transition from one to two phases occurs at the same temperature (to within about  $0.001^\circ$ , and this occurs  $0.005^\circ$  below the temperature which would be the critical temperature if the relation  $X_1 - X_2 = K(T_c - T)^{1/3}$  held). This is attributed to vanishing of the interfacial tension at a point at which the two phases still have different compositions, due to cancellation of energy and entropy effects. However, attempts to find other systems in which this phenomenon occurs have been inconclusive or unsuccessful.

The system perfluoromethylcyclohexane-carbon tetrachloride ( $C_7F_{14}-CCl_4$ ) was first investigated by Zimm,<sup>3</sup> who found no evidence of a flat top. However, there was some question of the purity of the components used and his samples had been exposed to air. The matter of purity is very important, since it is thought that impurities may obscure a flat portion if one exists. This has been verified experimentally in the addition of water to the cyclohexane-aniline system.<sup>4</sup> Therefore the  $C_7F_{14}-CCl_4$  system was reinvestigated by Gopal and Rice<sup>5</sup> and it was thought that evidence of a flat top was found, though the amount of the truncation

was within experimental error and no definite conclusion could be reached. It was with the hope of clarifying the behavior of this system and adding to the rather meager store of high precision measurements on highly purified systems that the present work was undertaken. This work consists of two parts: (1) further work with temperature control and measurement to  $0.001^\circ$ , but with more rigorous purification of materials; and (2) work in which the temperature control was  $\pm 0.00005^\circ$ , and in which the density of coexisting phases of a single sample was measured.

### Experimental

**Purification of Materials.**—The perfluoromethylcyclohexane was a gift from Prof. Webster B. Kay of Ohio State University, to whom we express our appreciation. This sample had already been purified using the following treatment suggested by Dr. Eric Barthel of the Du Pont Jackson Laboratory, who furnished the original sample:

"Treat 2 volumes of the perfluorocarbon with 1 volume of di(*n*-butyl)amine by heating at reflux for 2 hr. At the end of this period of time, decant the amine layer and repeat with an additional volume of amine. Repeat the decantation and treatment still another time and follow this treatment by washing well with 10% sulfuric acid to remove traces of the amine. Drying of the perfluorocarbon layer over anhydrous potassium carbonate followed by distillation should give material of a relatively high degree of purity."

The ultraviolet spectrum of the fluorocarbon obtained from Prof. Kay showed some slight absorption between 2000 and 2600 Å, but after passing the material through a column of silica gel no absorption was detected.

About three-fourths of the perfluorocarbon was treated by a modification of the treatment suggested by Glew and Reeves.<sup>6</sup> It was refluxed for about 35 hr. with acid-saturated potassium permanganate solution, separated from the aqueous layer, and washed numerous times with water and with sodium hydroxide solution, the final washings being with water.

This material was then treated, as recommended by Grafstein,<sup>7</sup> sealing it into glass ampoules with powdered potassium hydroxide and heating at  $135^\circ$  for 48 hr. No discoloration was observable after only one treatment, so the perfluorocarbon was decanted from the ampoules, washed several times with water, and distilled.

The remaining fourth of the perfluorocarbon was treated with potassium hydroxide as described above without the potassium permanganate treatment and combined with the other perfluorocarbon.

Fisher's 99+ mole % pure carbon tetrachloride was distilled through a 3-ft. vacuum-jacketed column with glass helix packing. The temperature was observed with a thermometer graduated in  $0.1^\circ$  and found to be constant throughout the distillation. Twenty-four hours were required to collect about two-thirds of the starting material and the second one-third of about 150 ml. was taken for further purification. This fraction was saturated

(1) The work has been supported by the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency.

(2) R. W. Rowden and O. K. Rice, in "Changements de Phases," *Comptes rendus 2<sup>e</sup> réunion annuelle, Société de Chimie Physique, Paris, 1952*, p. 78; D. Atack and O. K. Rice, *Discussions Faraday Soc.*, **16**, 210 (1953); D. Atack and O. K. Rice, *J. Chem. Phys.*, **22**, 382 (1954); O. K. Rice, *ibid.*, **23**, 164 (1955).

(3) B. H. Zimm, *J. Phys. Colloid Chem.*, **54**, 1306 (1950).

(4) F. R. Meeks, R. Gopal, and O. K. Rice, *J. Phys. Chem.*, **63**, 992 (1959).

(5) R. Gopal and O. K. Rice, *J. Chem. Phys.*, **23**, 2428 (1955).

(6) D. N. Glew and I. W. Reeves, *J. Phys. Chem.*, **60**, 615 (1956).

(7) D. Grafstein, *Anal. Chem.*, **26**, 523 (1954).

with  $\text{Cl}_2$  gas and placed under a sunlamp for 5 hr. It was then washed numerous times with 8% sodium hydroxide solution followed by washing with water. It was finally distilled from a very simple distillation apparatus.

Five mixtures were prepared at various stages of the purification procedure with compositions very near the anticipated critical composition and their separation temperatures were determined. The preparation is described below, as is the measurement of separation temperatures. Table I shows the treatment, composition, and separation temperatures of these five samples.

TABLE I  
MEASUREMENTS TO TEST PURITY OF COMPONENTS

Sample	Treatment		Mole fraction of $\text{CCl}_4$	Separation temp., °C.
	$\text{CCl}_4$	$\text{C}_7\text{F}_{14}$		
1	Distillation	Silica gel	0.7137	28.626
2	Distillation	Silica gel $\text{KMnO}_4$	.7114	28.626
3	Distillation $\text{Cl}_2$	Silica gel $\text{KMnO}_4$	.7129	28.625
4	Distillation $\text{Cl}_2$	Silica gel $\text{KMnO}_4$	.7114	28.623
5	Distillation $\text{Cl}_2$	KOH	.7152	28.623
		Silica gel KOH		

It was observed that the meniscus appeared in the upper regions of the sample in all five of the mixtures and they all exhibited strong opalescence.

The separation temperature of a mixture is probably a sensitive indicator of the state of purity of the components. Certainly it should be so for impurities that are likely to affect the shape of the coexistence curve. Thus the very similar behavior of the five mixtures after such radical treatment of the components is taken as a strong indication of a high degree of purity.

The purity of the components was further examined by gas chromatography. The columns used were all of 2-m. length and the support for the liquid stationary phase was, with the exception of a Tide column, Chromosorb-P. The carrier gas was helium. A Tide column and a dimethylformamide column were used to examine  $\text{CCl}_4$ . For the fluorocarbon, columns of Kel-F grease, dimethylformamide, dioctyl phthalate, polyethylene glycol, and Apiezon-L grease were used. In no case was a peak other than the main peak observed. In some preliminary experiments with a sample of perfluoro-*n*-heptane, 1.5% Apiezon-L grease on Chromosorb-P separated out more components than any of the other columns, including, in addition to the ones mentioned above, a column of the ethyl ester of Kel-F acid which is recommended for the separation of fluorocarbons by Reed.<sup>8</sup> No separation was obtained on this column while the Apiezon-L showed five peaks.

All samples other than the five discussed above were prepared from the components after these had been subjected to the entire treatment discussed above.

**Preparation of Samples.**—Each component was weighed in a glass-stoppered vial on a Mettler semimicro balance. Care was taken, throughout the procedure, to keep the outside of the vials clean. Each vial was dipped into liquid nitrogen to freeze the liquid, the top was removed, and the vial was placed into a drying train that had been prepared on a high vacuum line. The tubes of the drying train into which the vials were placed had been immersed in Dry Ice-acetone mixtures leaving enough of the top out so that they could be sealed off. A check showed no appreciable loss of vapor through the ground glass joints in the time required for these operations.

The drying train consisted of a sample tube, two tubes containing ignited calcium oxide, an empty tube, and the two tubes for the vials. The sample tube was a 16-mm. break-seal closed at the bottom, with a glass-enclosed magnetic stirrer inside. The train was connected to the high vacuum manifold through a stopcock.

After the vials were sealed in the train, the sample was allowed to evaporate into liquid nitrogen and pumped from three to five times to remove air. A constriction between the train and the stopcock was sealed with a hand torch while the sample was frozen in liquid nitrogen. Then the sample was equilibrated with the calcium oxide in each calcium oxide tube for about 6 to 12 hr. Finally the sample was distilled to the empty tube then to the sample tube, and was frozen in liquid nitrogen and sealed off from the train.

(8) T. M. Reed, *Anal. Chem.*, **30**, 221 (1958).

After the separation temperature of each sample, prepared as above, had been determined, it was introduced into another similar drying train. After the second treatment with  $\text{CaO}$  it was usually found that the separation temperature was raised, sometimes as much as  $0.05^\circ$ . However, after a third treatment the separation temperature was always found to be unchanged. All samples used in determining the coexistence curve were treated with  $\text{CaO}$  at least two times.

In an effort to find out what was producing the change with the second treatment with  $\text{CaO}$ , a sample was saturated with water, and  $\text{CO}_2$  was added to another. Water produced only a barely detectable effect, while  $\text{CO}_2$  lowered the separation temperature considerably.

The reproducibility of weighings was found to be  $\pm 0.0001$  g. giving a reproducibility of the mass of a component of  $\pm 0.0002$  g. This leads to an uncertainty in the mole fraction of a sample of about  $\pm 0.00005$ . The dead space above the sample in the sample tubes was about 8 cc. and since the vapor pressures of the two components are comparable, there should be no appreciable error in composition due to material in the vapor phase.

**Measurement of the Separation Temperature.**—The samples thus prepared were immersed in a bath whose temperature could be controlled to about  $\pm 0.0005^\circ$  by a toluene thermoregulator which actuated a thyatron relay, which in turn controlled a heater. The temperatures were measured to this accuracy by a platinum resistance thermometer-Mueller bridge assembly.

When measuring the separation temperature of a sample, it was stirred thoroughly at a temperature well above the separation temperature. Then the temperature of the bath was lowered, the sample was stirred again, and the temperature maintained for the desired length of time. One-half hour was found to be adequate. At the end of the equilibration period the sample was observed for the presence of a meniscus. For samples in the region of the critical composition it was necessary to raise the temperature a few thousandths of a degree to clear the opalescence enough to see the meniscus when it had formed. This process was repeated until the highest temperature at which a meniscus appeared was found and this value was taken as the separation temperature. Samples in the critical region were equilibrated at a temperature one-thousandth of a degree above the critical separation temperature for as long as 6 hr. and there was no indication of separation. Generally a number of samples were present in the bath and observed simultaneously.

## Results

The results are presented in Table II. It is to be observed that there are five samples with the transition

TABLE II  
MEASUREMENTS ACCURATE TO  $0.001^\circ$

Mass of $\text{CCl}_4$ , g.	Mass of $\text{C}_7\text{F}_{14}$ , g.	Mole fraction of $\text{CCl}_4$	Separation temp., °C.
2.3752	2.6754	0.6689	28.570
2.4320	2.6047	.6800	28.601
2.4647	2.5784	.6851	28.609
2.5645	2.4614	.7034	28.625
2.5653	2.4130	.7076	28.626
2.6114	2.4121	.7113	28.626
2.6560	2.4104	.7149	28.626
2.7023	2.4043	.7189	28.626
2.6919	2.3778	.7204	28.626
2.7844	2.4022	.7251	28.625
2.7162	2.2874	.7299	28.623
2.7823	2.2430	.7384	28.616
3.1130	2.4135	.7459	28.609
3.3235	2.4871	.7525	28.591

temperature  $28.626^\circ$ . Actually, however, all the points (except  $x = 0.7459$ , which shows a discrepancy which may indicate an error in its preparation) fall within the limit of error on two straight lines in the plot of  $(T_c - T)^{1/3}$  vs.  $x - x_c$  whose equations are

$$x - x_c = \pm 0.115(T_c - T)^{1/3} \quad (1)$$

Here  $x$  is the mole fraction of  $\text{CCl}_4$  and  $T$  is the tempera-

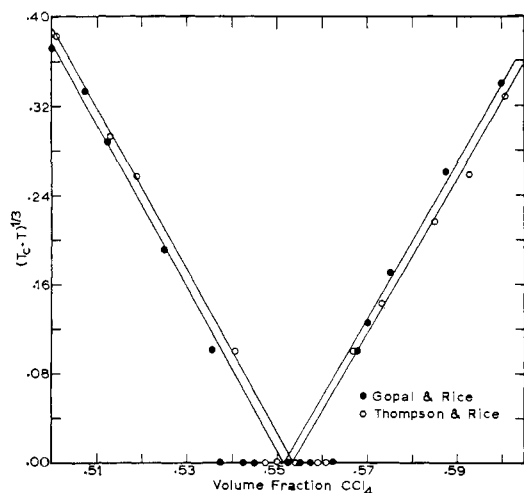


Fig. 1.—Coexistence curve of  $C_7F_{14}$ - $CCl_4$  system in comparison with measurement of Gopal and Rice.

ture ( $^{\circ}C$ ), and the critical values are taken as  $T_c = 28.626^{\circ}$  and  $x_c = 0.7145$ .

A comparison with the results of Gopal and Rice<sup>5</sup> is made in Fig. 1. The volume fractions of the present work were calculated from densities at  $25^{\circ}$ , while the volumes of the previous work were measured at  $20^{\circ}$ . This would tend to produce a discrepancy in the two sets of data, but there appears to be a systematic discrepancy in the correlation of the volume fractions that is somewhat larger than would be expected. It is interesting to note that, if one set of data is shifted about 0.003 along the abscissa toward the other, the agreement is quite good.

Measurements were later made on the five samples that appeared to separate at the same temperature, with temperature control to  $\pm 0.0001^{\circ}$ , and they were found to separate rather randomly over a range of  $0.0007^{\circ}$ . The technique for control and measurement of temperature had not yet quite reached the state described in the section devoted to that topic but was essentially the same. The samples were equilibrated at each temperature for 1 hr. It is to be noted that, such is the sensitivity of  $(T_c - T)^{1/3}$  in the neighborhood of the critical point, a change in the observed transition temperature of  $0.0007^{\circ}$  would suffice to put any of the samples which separated at  $28.626^{\circ}$  on the curve.

#### Density Measurements—Experimental

**Measurements to  $0.0001^{\circ}$ .**—Temperature control to  $0.0001^{\circ}$  was accomplished by placing a second water bath inside the large bath controlled to  $0.001^{\circ}$ . This second bath was a 5-l., unsilvered dewar flask with a flat bottom, closed by a Styrofoam disk  $1\frac{3}{8}$  in. thick with a diameter slightly larger than the outside diameter of the flask. A flat circular strip of foam rubber attached to the bottom of the disk around the edge made a good seal with the dewar. Two glass tubes were passed through the disk. One acted as a guide for the stirrer shaft and the other had a rubber eye-dropper top placed over the lower end. The stirrer was a length of 4-mm. glass rod with a 5-cm. diameter Lucite disk attached at the end and was manually operated. All openings to the second bath were below the water level of the large bath. The only contact with the room was through the stirrer shaft. A 10-in. piece of 0.25-in. i.d. rubber tubing, extending through the disk, allowed easy equilibration of pressure during seating of the top and stirring, with very little exchange of water between the baths.

In operation, the temperature of the inside bath, with the top seated, was adjusted by adding small quantities of water at an

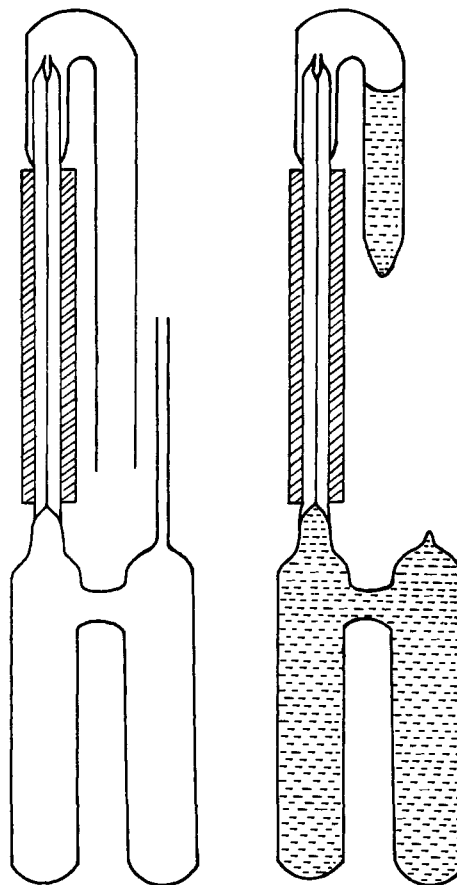


Fig. 2.—Thermometer for measurements accurate to  $0.0001^{\circ}$ : left-hand figure, glass structure of thermometer; right-hand figure, completed thermometer.

appropriate temperature (through a hypodermic needle inserted through the eye-dropper top) and stirring thoroughly. If the outside bath was set just right the temperature of the inside bath would remain within a range of  $0.0001^{\circ}$  indefinitely. When the temperature was maintained constant for long periods of time, the inside bath was usually stirred thoroughly at least once every 0.5 hr. The stirring motion was restricted so that no part of the stirrer that had contacted the air of the room re-entered the inside bath; otherwise a fall in temperature occurred. When strong light fell on the bath, the temperature rose, so light was excluded as much as possible.

The temperature of the inside bath was measured by a liquid-in-glass thermometer (diethyl phthalate in Pyrex) of special design, shown in Fig. 2. A 0.1-mm. i.d. capillary was used and the bulb had a capacity of about  $24 \text{ cm}^3$ . A piece of the scale of a Beckmann thermometer (cross-hatched in Fig. 2) was attached to the capillary with an epoxy cement. It turned out that the small scale divisions were equal to about  $0.0002^{\circ}$ . A galvanometer lamp beam was played on the meniscus, and it was viewed through a low power telescope making it very easy to read the thermometer to  $0.0001^{\circ}$  and the reading could be estimated to one more decimal place.

Considerable care was required in making the tip of the capillary and joining it to the reservoir. The tip was made by blowing a bubble in the capillary and pulling it out at the upper end to make the walls very thin; then, the tubing was scratched and broken at this point and left without fire polishing. The tubing to form the reservoir was placed over the tip and melted down to fuse with the outer part of the capillary wall by playing the flame of the torch only on the end of the tubing, avoiding the capillary as much as possible to reduce the chance of sealing the capillary. It was possible to make this joint tight without diminishing the capillary bore noticeably. This construction produces an undiminished capillary bore flowing smoothly into the bubble at the tip, which gives a safety chamber against losing the thermometer setting by overheating, and, more important, it provides an upper end to the capillary which does not tend to accumulate liquid.

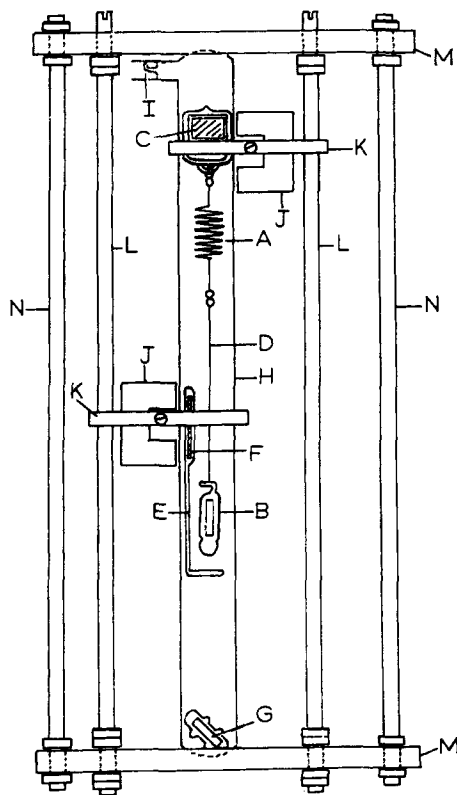


Fig. 3.—The density measuring apparatus: A, quartz helix; B, bob; C, magnet, enclosed in glass; D, 50-gauge platinum wire; E, support for bob when not in use, or when drawn out of liquid (necessary because bob was too heavy to be supported by helix) enclosing F; F, rod-shaped magnet; G, magnetic stirrer; H, Pyrex sample tube; I, break-seal; J, magnets; K, Lucite clamps and guides for magnets; L, threaded brass rods (by use of a screwdriver in the slots at the top these rods could be turned, thus adjusting positions of the magnets and hence of the equipment inside the sample tube; M, Lucite disks (the top one was largely cut away to allow good stirring of bath water and free access to the magnetic stirrer—support for thermometer was on bottom disk); N, brass support rods (not shown are three small diameter brass rods threaded through Lucite disks, M, used to level the support system).

The bulb was filled by injecting diethyl phthalate, *via* a hypodermic needle and syringe, through an open tube attached to the bulb. Then, with the bulb submerged in ice water and nitrogen blowing down the tube, it was sealed off with a hand torch, leaving a small bubble of nitrogen above the diethyl phthalate which was removed by tipping. The proper amount of liquid was added to the reservoir, with the thermometer inverted, and with the same precautions as before this chamber was also sealed giving a completed thermometer. The range of such a thermometer was about  $0.02^\circ$ . It could be set for a given temperature range much as one does a Beckmann thermometer.

The thermometer was found to be sensitive to pressure. It could be placed precisely in the bath to avoid significant changes in hydrostatic pressure, but changes in barometric pressure had to be taken into consideration. By carefully sealing the inside bath and connecting it to a water manometer, it was possible to measure the pressure sensitivity, which was found to be constant over a few centimeters of mercury for any given thermometer. For several thermometers prepared the value was found to vary from 2.5 to 6.0 mm. per ten-thousandth of a degree.

The thermometers used were compared to a platinum resistance thermometer over their entire range. This established their sensitivity and verified, within limits of accuracy, the linearity of the relation of meniscus position to temperature.

**Density Measurements.**—Since the measurements on small samples of different compositions to a higher sensitivity than  $0.001^\circ$  showed that the five samples which had appeared to separate at the same temperature were rather randomly scattered, it was decided to attempt measurements of densities on one large

sample as a function of temperature, thus avoiding the effects of small amounts of impurities. This of course assumes that the small amounts of impurities do not detectably affect the shape of the coexistence curve. If one can measure the compositions of the phases in equilibrium as a function of temperature in a sample whose composition is very near the critical, then one has determined the coexistence curve. Measurements of the density should effectively do this if the range is rather small, since the changes in density will be proportional to changes in composition.

A sample was prepared, using the same technique as in the preparation of the small samples, consisting of 18.186 g. of  $C_7F_{14}$  and 20.043 g. of  $CCl_4$ , giving 0.7149 mole fraction of  $CCl_4$ . The separation temperature of this sample was compared with that of a sample having the critical separation temperature and found to be  $0.002$  to  $0.003^\circ$  lower. A trace of  $CO_2$  may have remained in this sample, but we do not believe this would be sufficient to affect the results to be described.

The technique used for measuring the densities was the weighing of a glass bob submerged in the liquid by measuring the extension of a quartz helix (maximum load 80 mg., sensitivity 2.30 mg./mm.) from which the bob was suspended. Figure 3 is a schematic diagram of the density apparatus without the thermometer which, with the legend, is self-explanatory.

The densities of the liquid were calculated from the equation

$$D = D_{\text{bob}} - (l - l_0)k/V_{\text{bob}} \quad (2)$$

where  $D_{\text{bob}}$  = density of the bob = 1.6507 (determined by weighing in air and water),  $l$  = length of helix with bob immersed in liquid,  $l_0$  = length of helix in air corrected for weight of platinum wire = 24.53 mm.,  $k$  = helix constant = 2.30 mg./mm.,  $V_{\text{bob}}$  = volume of bob = 1.7095  $cm^3$ , and  $D$  = density of liquid.

A run or a set of consecutive measurements of density vs. temperature was started with the large bath clean and regulating a little above the critical temperature and with the sample and thermometer out of the bath. The thermometer, at this point, either had the correct amount of liquid in the bulb or too much. Warm air was blown on the upper regions of the sample tube from a hair dryer for about 1 hr. and toward the end of this time a piece of Dry Ice was held to the tube to condense all the sample to the bottom. The treatment with warm air helped to condense the sample to the bottom and by warming the helix and its support prevented condensation of the liquid on them at a later time. The sample and thermometer were then placed in the inside bath. The sample was thoroughly mixed over a period of several hours or more at a temperature at least  $0.02^\circ$  above the critical temperature. Then the bob was placed in the desired position in the liquid and its support withdrawn well below it. The temperature was lowered to about  $0.004^\circ$  above the critical temperature and the top of the inside bath was sealed. At some time before the temperature was further lowered the length of the helix was measured. The temperature of the inside bath was lowered to a desired value and maintained for 2 hr. at the end of which the helix length was again measured. If no change had taken place, then the temperature was lowered and the process repeated. If a change had taken place, then the temperature was maintained and helix length measured at 2-hr. intervals until no change occurred after 2 hr. Of course, for the remainder of the run the equilibration process was repeated at each temperature.

A run required about 6 days. The first few points were taken without interruption and required about 36 hr. After this the outside bath temperature was raised a few thousandths of a degree at night while the equipment was unattended. This of course resulted in a similar increase of the temperature of the inside bath.

In making the density measurements the bob was submerged in the liquid but the helix was in the vapor of the sample. They were connected by the 50-gauge wire which passed through the surface of the liquid and therefore experienced a downward force due to the surface tension of the liquid. Taking the surface tension as 30 dynes/cm. and since the diameter of the wire was 0.001 in., the maximum force would be that equivalent to about  $2 \times 10^{-4}$  g. It seems very unlikely then that variations in this force would affect the results in the fourth decimal place. The effect of variations of the density of the vapor on the extension is completely negligible, as is the buoyant effect of the liquid displaced by the wire. A calculation of the effect on the total volume of the helix for a change from vacuum to the estimated density of the vapor if it were all  $C_7F_{14}$  gave the result  $4 \times 10^{-6}$  g.

The uncertainty in a single measurement with the cathetometer was 0.02 mm. This produced an uncertainty in a measurement of the helix length of 0.04 mm, and an uncertainty in the effective weight of the bob of  $0.04 \times 2.30 \text{ mg.} = 0.092 \text{ mg.}$  Dividing this by the volume of the bob gives an uncertainty in density of  $5 \times 10^{-5} \text{ g./cm.}^3$ . This figure can be taken as the sensitivity of the density measurements,<sup>a</sup> and as the experimental error when one is interested in only relative values as is the case in this work. The experimental error in the density values themselves is somewhat larger, being probably about  $\pm 0.0002 \text{ g./cm.}^3$ .

### Results of Density Measurements

Three runs were made, and the results are given in Table III. Run 1 was made with a thermometer with sensitivity 0.519 division per  $0.001^\circ$ , and the temperature control was  $\pm 0.0001^\circ$ . In runs 2 and 3, the sensitivity was 0.511 division per  $0.001^\circ$ , and the temperature control was  $0.00005^\circ$ .  $S$  is the scale reading of the liquid-in-glass thermometer used and  $S_c$  is the critical scale reading. In each case  $S_c$  was selected to give the best straight line for a plot of  $(S_c - S)^{1/3}$  against helix length. The smallest scale divisions correspond to a change in reading of 0.1.

TABLE III  
DENSITIES<sup>a</sup> OF THE LIQUID OR OF THE TOP PHASE AS A FUNCTION OF THERMOMETER READING  $S$

Run 1		Run 2		Run 3	
$S$	Helix length	$S$	Helix length	$S$	Helix length
12.8	36.92	10.50	36.91	10.40	37.55
12.7	37.60	10.40	37.23	10.30	37.85
12.6	37.72	10.30	37.70	10.08	38.29
12.5	37.86	10.23	38.01	9.56	38.88
12.4	38.19	10.03	38.35	9.05	39.24
12.1	38.60	9.55	38.90	8.56	39.53
11.6	39.00	9.08	39.19	7.50	39.94
11.1	39.32	8.58	39.48	$S_c = 10.45$	
10.2	39.73	7.58	39.89		
9.3	40.08	$S_c = 10.43$			
8.1	40.41				
6.5	40.80				
$S_c = 12.73$					

<sup>a</sup> Expressed as helix length in mm.

From these measurements the density was calculated using eq. 2, and  $S_c - S$  was converted to  $T_c - T$  from the known sensitivity of the thermometer. In Fig. 4 results of all the runs are plotted. Only the values at densities less than the critical density were directly measured, since the density bob was always in the upper part of the tube.

The data of runs 2 and 3 were obtained in two separate series of measurements between which the sample was thoroughly mixed. They clearly agree within experimental error and in addition to showing the reproducibility of the correlation between density and temperature, they indicate the reproducibility of the thermometer when it has been maintained within a temperature range such that the meniscus does not go below the bottom of the capillary and no liquid flows out of the tip. The reproducibility of the density measuring apparatus itself was demonstrated by the very close agreement of many density measurements of the homogeneous sample slightly above the critical temperature.

A series of density measurements was made above the critical temperature with temperature control to  $\pm 0.001^\circ$  and the results are shown in Table IV. A plot of the data gives a straight line with a slope of

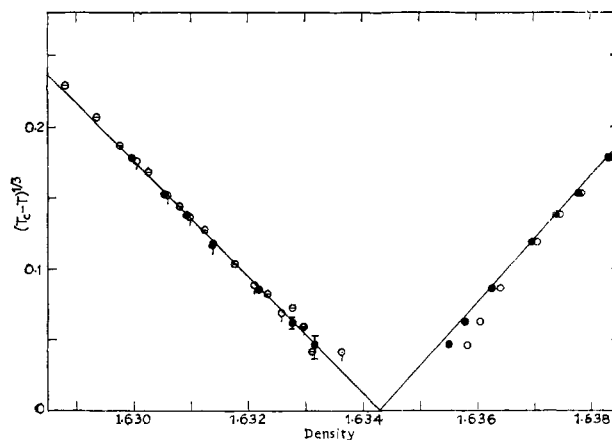


Fig. 4.—Coexistence curve for  $C_7F_{14}$ - $CCl_4$  system, measurements, accurate to about  $0.0001^\circ$ . Left-hand side, top phase:  $\circ$ , run 1;  $\odot$ , run 2;  $\bullet$ , run 3. Right-hand side, bottom phase:  $\circ$ , uncorrected points;  $\bullet$ , corrected points. The vertical lines attached to two of the points show the error which would be produced by  $0.00005^\circ$  error in the temperature.

1.9 mm./deg. From this value it is clear that no correction to the density measurements made below the critical temperature need be made, since the temperature range of the measurements (less than  $0.02^\circ$ )

TABLE IV		
Helix length, mm.	Temp., $^\circ C$ .	Density, g. cm. <sup>-3</sup>
39.29	29.868	1.6308
38.16	29.259	1.6324
38.06	29.206	1.6325
37.71	29.008	1.6330
37.51	28.909	1.6332
37.29	28.810	1.6335
37.08	28.707	1.6338
36.99	28.658	1.6339

would produce a thermal contraction of the liquid that would cause a helix length change of about 0.04 mm., roughly the experimental error of a single measurement.

### Discussion and Conclusions

If the experimental error is taken into consideration, it is clear that the data of Table III are well represented by the straight line in Fig. 4. This indicates that the coexistence curve is cubic and that it cannot be truncated more than  $0.0001^\circ$ .

However, some doubt arose about the meaning of the results when an attempt was made to calculate the density of the bottom phase of the sample from the measured density of the top phase and the measured position of the meniscus. These results are given in Table V and in Fig. 4. The density of the bottom phase was calculated from the equation

$$D_b = (D_s - D_t)L/l_b + D_t \quad (3)$$

where  $D_b$  = the density of the bottom phase,  $D_s$  = the over-all density of the sample,  $D_t$  = the density of the top phase,  $L$  = the length of the sample,  $l_b$  = the length of the bottom phase.

The meniscus position measurements were made during run 3. It was found that it was possible to see the meniscus in spite of heavy opalescence if sufficient settling time was allowed. The lengths in the equation above are corrected to what they would be if the sample were in the shape of a solid cylinder. This

TABLE V  
MENISCUS HEIGHTS AND DENSITIES OF THE BOTTOM PHASE

$S$	$(S_c - S)^{1/2}$ cor. <sup>a</sup>	$l_b$ , cm.	$D_b$ , g. cm. <sup>-3</sup>	$D_b$ , <sup>b</sup> g. cm. <sup>-3</sup>	$D_b$ cor., g. cm. <sup>-3</sup>
10.40	0.369	4.14	1.63318	1.63582	1.63550
10.30	.501	4.92	1.63278	1.63603	1.63579
10.08	.688	5.56	1.63219	1.63640	1.63624
9.56	.942	5.91	1.63139	1.63705	1.63695
9.05	1.103	6.03	1.63091	1.63746	1.63738
8.56	1.223	6.08	1.63052	1.63782	1.63776
7.50	1.424	6.13	1.62997	1.63834	1.63829

<sup>a</sup> The following values were used in eq. 4 to correct  $S_c - S$ :  $dT_c/dp = 0.0388^\circ \text{ atm.}^{-1}$  (ref. 9),  $c = 9.87 \times 10^{-7} \text{ atm. cm.}^2 \text{ dyne}^{-1}$ ,  $D_0 = 1.63 \text{ g. cm.}^{-3}$ ,  $g = 980 \text{ cm. sec.}^{-2}$ . <sup>b</sup> The following values were used in eq. 3 to calculate  $D_b$ :  $D_a = 1.63405 \text{ g. cm.}^{-3}$  (from measurements made just above the critical temperature),  $L = 12.58 \text{ cm.}$

involved correction for the volume occupied by objects in the sample and squaring off the ends of the sample.

The lengths were measured relative to the top of the Lucite disk holding the sample tube at the bottom. The bottom of the sample tube was round and its volume was estimated as that of a segment of a sphere. Then the length equivalent of this volume for a cylinder with cross-sectional area equal to that of the rest of the sample tube was calculated to be 3.8 mm. The reference point was 2.2 mm. below the point where the tube began to curve to form the bottom. Therefore, one needs to add to the measured lengths  $3.8 - 2.2 = 1.6 \text{ mm.}$  However, the magnetic stirrer occupied a volume at the bottom of the sample, and the length equivalent for this volume should be subtracted. This value was found to be 1.6 mm. by measuring the position of the top meniscus with the stirrer in the sample and with it removed. Therefore, the measured lengths for the bottom phase need no correction. The length of the sample with the bob and its support removed was measured. The position of the liquid-vapor meniscus was found to be the same several hundredths of a degree below the critical temperature as it was above the critical temperature showing that  $L$  can be considered constant.

The reproducibility of the meniscus position measurements was checked by remeasuring the meniscus position and helix length at a point where both are changing relatively fast and exact agreement was obtained with the previously measured values.

It is clear from the plot in Fig. 4 of these calculated densities against  $(T_c - T)^{1/2}$  that they do not follow a relation similar to the measured densities of the top phase. If the calculated densities were accepted as correctly representing the coexistence curve, they would indicate a truncated top of about  $0.0002^\circ$ .

The disagreement arises, we believe, from a failure to take into account the effect of gravity. The effect of pressure on the critical temperature of this system has been measured,<sup>9</sup> and if the pressure of the sample on itself is considered, the critical temperature of the sample varies over a range of about  $0.0007^\circ$  from top to bottom. If  $T_{c,0}$  is the critical temperature at the top surface of the liquid, then the critical temperature  $T_c$  at a distance  $l$  below this surface will be given by

$$T_c = T_{c,0} + (dT_c/dp)cD_0gl \quad (4)$$

where  $p$  is the pressure, the increase of pressure at a

distance  $l$  from the top being  $cD_0gl$  where  $c$  is a conversion factor,  $D_0$  is the (roughly constant) density of the liquid, and  $g$  is the acceleration due to gravity. In practice it was assumed that  $S_c$  given for run 3 in Table III was correct for the first point below the critical temperature, and all the other points were corrected using eq. 4. The values of  $(S_c - S)^{1/2}$  given in Table V have been thus corrected. The correction was then plotted against the uncorrected value of  $(S_c - S)^{1/2}$  and from this graph corrections were read off for runs 1 and 2. The values of  $(T_c - T)^{1/2}$  for all the points in Fig. 4 have been corrected. Actually this correction made little difference in the appearance of the graph and no progress was made in this way in explaining the behavior of the calculated densities of the lower phase. This behavior has to do, we believe, with density gradients in the bottom phase, arising from the fact that each level in the sample has a different critical temperature. One might think of a coexistence curve for each level differing from the others only by a displacement along the temperature axis. Since the critical temperature increases with pressure the curve is displaced upward as one goes down the tube, and separation will take place first in the lower regions of the sample whatever its composition. If a region in the bottom of the sample is below its separation temperature, then separation will take place at every point according to the local coexistence curve. Lighter material formed at a given point will travel up, being replaced by the material just above it, and will have no reason to separate further. The material traveling down to replace the lighter material will now separate slightly and gradually a density gradient will be built up in the bottom of the sample. We expect that the equilibrium condition in the bottom phase will be readily attained and will be such that the composition at each point is determined by the local coexistence curve and the temperature of the sample.

Since the light material traveling toward the top is very finely divided, it is not difficult to imagine that it becomes rather well mixed with the material in the upper regions of the sample. Another condition that will produce mixing in the top phase is the tendency to form an inverted density gradient above the meniscus. This will exist when the temperature of the sample is such that a region of the sample above the meniscus is below its separation temperature. Then separation just above the meniscus will produce lighter material than will be produced at any higher point and this light material will be replaced by heavier material which will separate. This process should continue until all the material above the meniscus has found its way to the meniscus and separated, always producing a light component of the composition determined by the temperature of the sample and the coexistence curve at the meniscus. This light material would have no reason to separate further and we expect the top phase eventually to reach the composition of the light material separating just at the meniscus. The assumption of effective mixing in the upper regions of the sample leads to an equilibrium condition with a density gradient in the bottom phase such that the composition just below the meniscus is in equilibrium with the homogeneous top phase as pre-

(9) J. H. Hildebrand, B. J. Alder, J. W. Beams, and H. M. Dixon, *J. Phys. Chem.*, **68**, 577 (1954).

scribed by the temperature of the sample and the coexistence curve at the meniscus.

According to this view, to obtain the behavior of the sample that would persist in the absence of a gravitational field, it is only necessary to correct the measurements on the top phase for the pressure effect on the critical temperature as the meniscus changes position, which has been done. The calculated bottom phase densities can also be corrected to test the consistency of this picture with the data by taking into consideration the density gradient in the bottom phase.

To make this correction we assume that the behavior of the system is properly described by the measurements on the top phase and this knowledge in combination with the measured effect of pressure on the critical temperature will determine the density gradient in the bottom phase for each density measured in the top phase. Since the calculated density in the bottom phase is the average density, and since the density gradient turns out to be nearly linear with the distance below the liquid-liquid meniscus, we need only calculate the difference in density between the point just below the meniscus and that at the midpoint of the bottom phase, then subtract these values from the previously calculated values.

At any point below the meniscus the density,  $D$ , is given by

$$D = D_c + k(T_c' - T)^{1/4} \quad (5)$$

where  $D_c$  is the critical density,  $k$  is a proportionality constant for density,  $T_c'$  is the critical temperature at the point in question, and  $T$  is the temperature of the sample. The variation of  $T_c'$  with the distance below the meniscus can be obtained from eq. 4. The value of  $k$  may be estimated from data on the density of the pure liquids and the mixture. The densities at 25° are as follows:  $\text{CCl}_4$ ,<sup>10</sup> 1.5844; mixture<sup>11</sup> ( $x = 0.7149$ ), 1.6433;  $\text{C}_7\text{F}_{14}$ ,<sup>6</sup> 1.7878. From the difference of densities of the pure substances one would conclude that the change of density per unit mole fraction is 0.2034, and the density of the mixture lies close to what would be expected from a linear interpolation. Assuming that the rate of change of density with mole fraction remains at 0.2034 at the critical temperature, we can combine eq. 5 with eq. 1 to find  $k = 2.34 \times 10^{-2}$ , and eq. 5 becomes, with numerical evaluation of the coefficient of  $l$  in eq. 4

$$D = D_c + 2.34 \times 10^{-2}(T_c - T + 6.12 \times 10^{-5}l')^{1/4} \quad (6)$$

(10) Landolt-Börnstein, "Physikalisch-Chemische Tabellen, 3. Ergänzungsband," Julius Springer, Berlin, 1935, p. 332.

(11) From Table IV.

where here  $T_c$  is the critical temperature at the liquid-liquid meniscus, and  $l'$  is the distance below that meniscus.

$D - D_c$  was calculated for  $l'$  equal 0 and  $l'$  equal to one-half the length of the bottom phase for each measurement and the magnitude of the difference between these two values was subtracted from the previously calculated density,  $D_b$ , in Table V. (For the lowest values of  $T_c - T$  a more accurate average was obtained.) The results of these calculations are given in Table V and the corrected densities are plotted in Fig. 4.

The values of  $k$  for the two lines shown in Fig. 4 are  $2.44 \times 10^{-2}$  for the top,  $\text{CCl}_4$ -rich phase, and  $2.23 \times 10^{-2}$  for the bottom,  $\text{C}_7\text{F}_{14}$ -rich phase. Thus the coexistence curve, in contrast with the conclusion drawn from Table II, seems not to be quite symmetrical (not sufficient to warrant further correction in  $D$ ). This lack of symmetry seems to be slightly beyond the limits of the experimental error, especially when it is considered that any change in the choice of  $T_c$  or any error in the temperature measurements would affect the corresponding points of the two branches of the curve, as derived from Table V, in the same way. However, it is not certain that the difference between Table II and Table V is beyond the combined error in the two tables. Nor is it absolutely certain that the rate of change of density with mole fraction is entirely constant, though from the fact that the density of the mixture is almost linearly placed between the densities of the pure constituents, we would assume any deviation from linearity to be small.

The general conclusion is that the density in this system is a linear function of  $(T_c - T)^{1/4}$  to within 0.0001° of the critical temperature, there being, thus, no flat portion of the coexistence curve unless it lies within 0.0001° of  $T_c$ . The first of these conclusions would be slightly modified if there is some remnant of a density gradient in the upper phase, but in view of the self-consistency of the results obtained on the basis of our interpretation this seems highly unlikely. There recently have been some speculations, based on theoretical considerations,<sup>12</sup> that the density should be linear to  $(T_c - T)^{3/16}$  rather than  $(T_c - T)^{1/4}$ . We have tried replotting the results of Table V on this basis, using a slightly different value of  $T_c$ , but, unfortunately, it appears, these functional forms are so closely similar that, even with the degree of precision we have obtained, it is impossible to distinguish between them.

(12) J. W. Essam and M. E. Fisher, *J. Chem. Phys.*, **38**, 802 (1963).