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Critical Phenomena in the Cyclohexane-Aniline System

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Abstract

It is now well-known that phenomena in the neighborhood of the critical point are not as simple as would be anticipated from a theory of the van der Waals type. In particular, the question has been raised as to whether the top of the coexistence curve (solubility curve in a binary liquid system) should have a flat horizontal portion, and as to whether there is a portion of the one-phase homogeneous region where the fugacity is independent of concentration. An attempt has been made to answer these questions for the cyclohexane-aniline system by measuring the coexistence curve, and by comparing the vapor pressures of mixtures of different composition, just above the critical temperature, by use of a differential manometer. Extreme purification of the materials has been found to be very necessary. The data are believed to show that the top of the coexistence curve is flat. Within the limits of experimental error, there is no region above the critical temperature where the fugacity is independent of concentration.

It has been realized for a considerable period of time that the phenomena which occur in the immediate neighborhood of the critical point of a one-component system are not as simple as might be anticipated from the van der Waals theory or similar theories of the equation-of-state. Though a number of experimenters had early pointed out some of the "anomalies", attention was most forcibly directed to them by the statistical theory of clusters as developed by Mayer and Harrison^(1,2). These authors concluded that the liquid-vapor coexistence curve in the p - V (pressure-volume) diagram, as determined by the observation of the meniscus, should have a flat horizontal section at the top, instead of being roughly parabolic as predicted by van der Waals. Thus instead of a single critical volume, there will be a range of critical volumes. There will be an isotherm having a portion which coincides with the horizontal part of the coexistence curve; the temperature of this isotherm will be designated as T_0 .

Partly from theoretical considerations and partly from intuition Mayer and Harrison inferred further that even for temperatures somewhat greater than T_0 the isotherms would have a horizontal portion, in spite of the fact that the ordinary type of condensation with formation of a visible meniscus could not be observed at these temperatures. These isotherms, however, would not have the discontinuities in slope which normally occur where the isotherm crosses the coexistence curve, but the portions with zero slope would be approached smoothly. They considered the last isotherm (highest temperature) for which a portion with zero slope occurs to be the true critical isotherm; this temperature we shall call T_0' .

More recently Rice^{3,4,5)} has developed a thermodynamic theory based on a consideration of the actual physical clusters of molecules (as contrasted to the mathematical clusters of Mayer and Harrison) which will form when a vapor is compressed. The critical temperature, T_0 , is defined as the temperature at which the surface tension vanishes, a meniscus presumably not being visible above this

temperature. Below T_0 the clusters will, at a certain pressure, tend suddenly to be infinitely large in size, thus giving ordinary condensation. But at T_0 , instead of a compact liquid, a large spongy mass will be gradually formed. The surface tension being zero it will not resist compression. Thus the critical isotherm in this theory, also, should have a finite horizontal portion, and in agreement with Mayer and Harrison the coexistence curve should be flat at the top. However, if the surface tension becomes negative above T_0 (and arguments in favor of this were given), the spongy coalesced cluster will then resist compression. Thus all isotherms above T_0 are expected to have a finite slope.

According to the theory of Rice there is only one characteristic temperature, T_0 . According to Mayer and Harrison there are two, T_0 and T_0' , and it would be a most unexpected coincidence if these two coincided. However, Zimm⁽⁶⁾ has recently suggested that the integrals which occur in Mayer and Harrison's theory may be consistent with the vanishing of all derivatives of p with respect to V , without discontinuities in any of the derivatives, at one single point in the p - V plane. This would be the critical point and T_0 and T_0' would coincide. The coexistence curve would be rounded at the top, but it would not be parabolic, as in van der Waals theory, where only $(\partial p / \partial V)_T$ and $(\partial^2 p / \partial V^2)_T$ vanish at a single point without discontinuities.

Despite a number of experiments intended to elucidate the questions raised by the above theories, the matter cannot be said to be settled. Observations of the meniscus in the critical region have led some authors to believe that the top of the coexistence curve is flat. [For a discussion and references, see (3)]. Recent work, however, has tended to show that the effect of gravity may be of importance in this phenomenon⁽⁷⁾, so that some of the results which lead to this conclusion may be spurious, though stirring or agitation should tend to minimize this effect.

The question as to the shape of the isotherms in the critical region is also unsettled⁽³⁾, and here, too, gravity may have an influence⁽⁸⁾.

However, even the most elementary observations show that the van der Waals type of theory is in need of substantial modification. Guggenheim⁽⁹⁾ has collected a large amount of data on the coexistence curve from the literature, and has shown that the coexistence curve cannot be even approximately parabolic. It appears to be a curve of the third-degree rather than of the second degree. Such a curve is very nearly flat on the top, and it may be expected that it will be exceedingly difficult to decide experimentally whether there is actually a finite horizontal portion.

Any situation which can arise in a one-component system could have its counterpart in the behavior of a binary liquid system in the neighborhood of its consolute or critical solution temperature, and very similar theoretical considerations can be applied^(4,10). Usually somewhat different methods of plotting are used. Thus the coexistence curve is plotted in a diagram of temperature vs. concentration. In such a diagram we may still ask whether there is a finite horizontal portion at the critical temperature. And we may ask whether there is a range of concentrations and temperatures just above the critical temperature (or below if it is a lower consolute temperature), that is, in the homogeneous one-phase region of complete mutual solubility, where the fugacity of each component at a given temperature is independent of concentration.

Experimental answers to these questions are certainly not unequivocally provided in the literature [for references and summary see (4)]. From the data given in the Landolt-Bornstein Tables one gets the impression that more accurate data might show many of the coexistence curves to have flat tops. Some of the more accurate data do appear to indicate a flat horizontal portion, notably in the systems phenol-water, acetic hydride-cyclohexane, acetone-carbon disulfide, methyl acetate-carbon disulfide (in the latter two the flat portion is unusually

long), and a number of organic mixtures studied by Woodburn, Smith, and Tetewsky. On the other hand, the coexistence curves for the systems acetic anhydride-carbon disulfide and perfluoromethylcyclohexane-carbon tetrachloride appear to be rounded at the top. The coexistence curves for liquid pairs show a great variety of forms, and they may well differ in this respect. However, it is to be noted that liquid systems are extremely sensitive to minute quantities of impurities, and it seems probable that these are more likely to make a curve with a flat top seem rounded than the reverse.

There are no data which can be used to calculate fugacities in the critical region which are of sufficient accuracy except those of Zimm⁽¹¹⁾ on the perfluoromethyl cyclohexane-carbon tetrachloride system, obtained from measurements of light scattering. These indicate that in this system there is no portion of the homogeneous region where the fugacities are independent of concentration.

Despite their sensitivity to impurities, binary liquid systems offer certain advantages for this type of investigation. Effects of gravity will be practically negligible, since direct effects of pressure of the order of magnitude involved will not be appreciable. Only if gravity could cause concentration gradients could it be of importance, but gravity-caused concentration gradients are always small and can be practically eliminated by stirring. Also liquid pairs with convenient critical temperatures can be found and it is unnecessary to work at elevated pressures.

The cyclohexane-aniline system, measurements of which we will report here, has a very convenient critical temperature (values ranging from 30.2 to 31.3°C have been reported in the literature⁽¹²⁾). It further has the advantage that most of the vapor pressure is due to cyclohexane and so a measurement of the total vapor pressure gives approximately the fugacity of one of its components. If both components had comparable vapor pressures an increase in the partial vapor pressure of one of them with concentration could well be almost compensated

by a decrease in the partial pressure of the other, thus masking changes in the fugacity, and making use of the total vapor pressure as a measure of fugacity impracticable.

Apparatus and Materials

Purification of Materials. In view of the sensitivity of binary liquid systems to impurities, great precautions were taken in the purification of our materials. The anilins used was a special sample, kindly supplied by Dr. A. T. Schramm of National Aniline Division of Allied Chemical and Dye Corporation of Buffalo, New York. This aniline was first placed in 500-ml. ground-stopper Erlenmeyer flasks (about 200 ml. aniline per flask) each containing approximately 50 grams of KOH pellets (Merck, reagent grade). The flasks were stored in a dark cupboard for about two weeks and thoroughly shaken several times each day. This aniline was then distilled from zinc dust (Merck, reagent grade) at atmospheric pressure, rejecting the first few milliliters and leaving a few milliliters residue. The sample was next distilled three times from zinc dust at 5 mm. Hg pressure. A vacuum-jacketed column, 1.5 x 30 cm., packed with glass helices, reflux ratio about 8 to 1, was used for rectification. The middle cut of approximately 75% was saved; dry nitrogen was bled into the receiver prior to its removal from the distillation apparatus. The aniline was then fractionally crystallized twice. The top of the cold trap was kept in an atmosphere of dry nitrogen, and reducing adapters were used so that the size of the opening was large enough only for the stirring rod. The freezing mixture was dry ice-acetone, and the freezing period was approximately six to eight hours, with frequent stirring. After approximately 90% of the aniline had been frozen, the top 10% was removed by suction. The top portion of the remaining aniline was then melted and that portion removed. The aniline was fractionally distilled once more. The samples were stored in small glass-stoppered flasks in a dark cupboard in a nitrogen atmosphere. Several months elapsed before the final runs were made and during this period the aniline had taken on a very slight color, so it was again fractionally distilled from zinc dust and finally from ignited CaO. The usual precautions to keep out oxygen and moisture were observed. The melting point showed no discernible range when checked with a Beckmann thermometer.

The cyclohexane was obtained from the National Bureau of Standards, sample 209a-25; impurity mole percent 0.010 ± 0.006 . It was opened in an atmosphere of dry nitrogen and kept in closed sample tubes. No attempt was made to purify the sample as it was believed that it already had the highest purity obtainable.

The Sample Tubes. It was at first hoped that we could introduce mixtures of two different known concentrations into two tubes which were connected through a sensitive differential manometer. Thus minute differences in vapor pressure between the two mixtures could be measured, and it could be determined whether there was any range above the critical temperature where the difference in vapor pressure between two such mixtures would vanish. At the same time the point on the coexistence curve could be determined. These early attempts were unsuccessful. This may have been because it was necessary to use stopcock grease in the apparatus. Also some moisture may have been present, in spite of the fact that all transfers of liquid were carried out in an atmosphere of dry nitrogen.

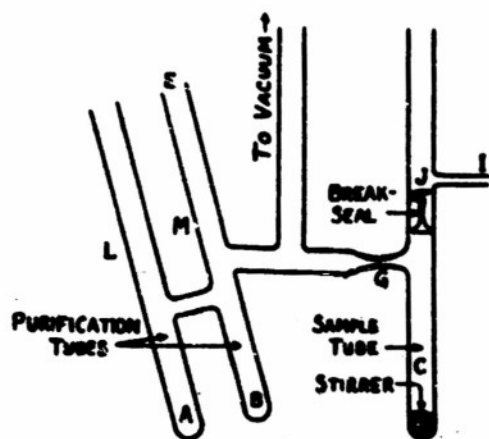


Fig. 1.

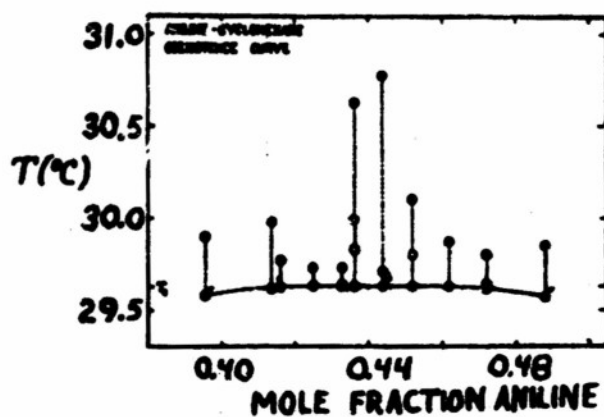


Fig. 2.

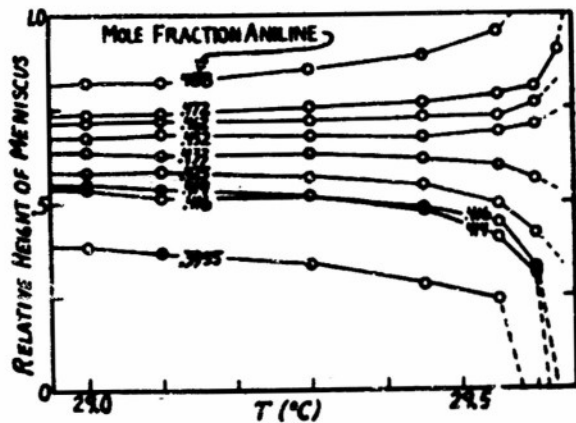


Fig. 3.

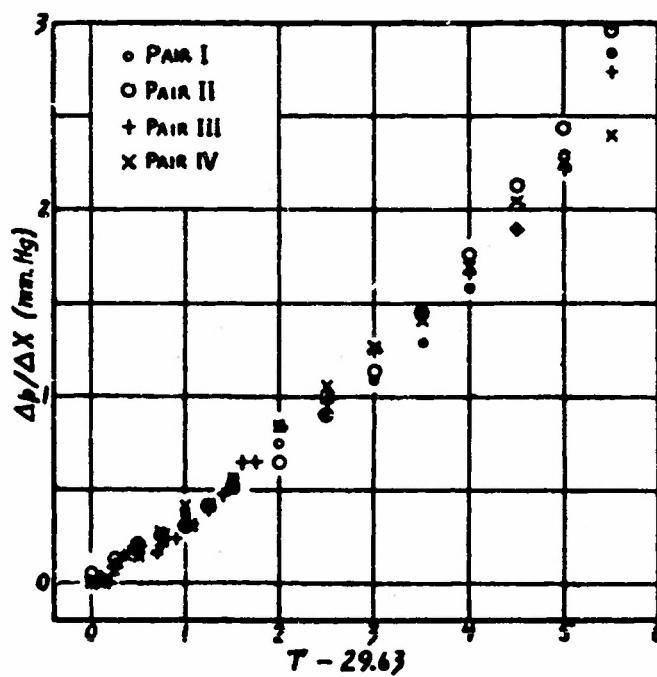


Fig. 4.

It was finally decided to make up mixtures of varying compositions in separate tubes, in which the transition temperatures from two-phase to one-phase mixtures could be observed. Afterward certain pairs could be attached to differential manometers and pressure differences measured. The apparatus used is shown in Fig. 1. The portion to the right of G is the sample tube. A magnetic stirrer was placed at the bottom of this tube. It consisted of a piece of iron covered with roughened glass, which could be moved by means of a solenoid. Adequate stirring was provided when the solenoid switch was very quickly closed and opened twice for each sample. Excessive operation of the switch caused a noticeable change in temperature of the bath and was avoided.

The portion of the apparatus to the left of G was used for purification. The vacuum system used to evacuate this apparatus could be cut off with a mercury cut-off, and all stopcocks were behind a cold trap. The first mixtures were prepared in a purification and sample tube having only one purification chamber (B) on the left. A rubber stopper was placed in the tube at E and the apparatus was evacuated and flamed intermittently for two hours. Nitrogen was then bled into the entire system, and allowed to pass through it at a rate of several ml. per minute after the rubber stopper was removed and during the filling procedure; in addition a "dry box" containing an atmosphere of dry nitrogen was placed around the apparatus. The aniline and then the cyclohexane were introduced into chamber B by the use of calibrated micro-pipets. The nitrogen was then turned off, a stopper was inserted in the tube at E, and the dry box removed. The mixture was immediately frozen with liquid air to prevent loss of the cyclohexane, the purifying chamber sealed at H and the system evacuated.

After evacuation the mixture was melted to let dissolved gas escape, refrozen with liquid air, and evacuated. This melting, freezing, and pumping procedure was repeated two more times. With the vacuum system out off, the mixture was distilled from purification chamber B to the sample chamber C, which was cooled with dry ice-acetone. An ice-alcohol bath was used on chamber B to prevent too rapid distillation; it had to be removed, however, before the aniline would distill. The mixture in the sample tube, C, was melted twice, and each time refrozen with liquid air and pumped off at 10^{-6} mm. Hg. With the mixture frozen the sample tube was then sealed off at constriction G.

In later samples and for repurification of earlier samples, the apparatus used was as shown in Fig. 1. The procedure was the same except that freshly ignited CaO was put into purification chambers A and B and the tube sealed off at L prior to the initial pumping and intermittent flaming. The distillation was from B to A to C. The liquid mixture remained in contact with the CaO of each chamber for at least two hours. The liquid air was kept on the receiving chamber for approximately thirty minutes after the CaO in the distilling chamber appeared to be dry to insure complete transfer of the mixture. The distilling chamber was not heated as this might have driven off some of the water taken up by the CaO. After the sample tube had been removed the purification chambers were heated to see whether any liquid could be driven off and the color of the liquid was noted. Should any aniline have been left in the CaO the liquid would be dark red since air had been let into the vacuum system. Nothing was observed other than very small quantities of moisture, except that in four of the mixtures, generally in early stages of the purification, a very slight reddish-brown coloration was noted. The amount of material involved was perceptible but believed not measureable.

Purification of the samples could be continued by attaching the sample tube at I (Fig. 1) to a new purification apparatus of the type of Fig. 1. The latter was then closed, evacuated, and flamed; then the break seal at J was broken by an iron pellet enclosed in glass, the material transferred by distillation in vacuum to the new purification apparatus, and the purification process carried on as before.

Pressure Measurements. When the samples were sufficiently purified, and after the measurements on the transition temperatures were completed, two of the sample tubes could be sealed at I to the two ends of a differential manometer. The differential manometer was then carefully filled with the manometer fluid, closed off, outgassed and evacuated. With the cyclohexane-aniline mixtures frozen out the break seals were opened. In warming up the mixtures it was necessary to take care not to drive the manometer fluid out of the manometer tube, though traps were provided to catch the manometer fluid in case of accident. In all cases except the first one, the manometer was provided with break seal to permit further repurification of the mixtures if desirable.

The manometer fluid used was polyethyleneglycol, it being the best of several tested. It did not dissolve the cyclohexane, but after a long period did appear to react with the aniline, turning yellow in so doing. The vapor pressure of aniline was very small under the conditions of our experiments, and there was sufficient time to make the measurements required before any reaction took place. It was rather obvious when reaction had occurred, because of difficulty in obtaining equilibrium in making the pressure measurements; in any event, the appearance of the yellow color served as a warning. The polyethyleneglycol that was used was pumped on the vacuum system for a week with a hot-air blower keeping its temperature around 75°. The last three days of this pumping the pressure was less than 10^{-5} mm. Hg.

A scale taken from a broken Beckmann thermometer was placed behind the manometer, and the height of the liquid in the two arms was read on it with a telescope. The smallest divisions on the scale were 0.3715 mm. apart, and, using polyethyleneglycol, density 1.12 g. per ml., were equivalent to 0.0306 mm. Hg.

Thermostat. The thermostat used was capable of being regulated as closely as the temperature could be read with a Beckmann thermometer, and the temperature could be changed as slowly or as rapidly as desired. The water was vigorously stirred to avoid temperature gradients. The temperature was measured by two Beckmann thermometers which had been checked against a thermometer standardised at the Bureau of Standards.

Transition Temperatures and Related Observations

Transition Temperatures. For the experiments in closed tubes the eleven mixtures of Table I were prepared. When these were first placed in the tubes the transition temperatures shown as black circles in Fig. 2 were obtained. Their extreme irregularity indicates that some impurity was introduced in making the mixtures, since the same aniline and cyclohexane was used in all cases. This

Table I

Compositions and Transition Temperatures

Millimoles aniline	Mole fraction Aniline		Transition Temperature °C	
	A	B	Cooling	Heating
5.89	0.395 _g	0.398	29.58	
6.35	.414	.416	29.61 _g	29.61
6.42	.416	.419	29.62 _g	29.62
6.65	.425	.427 _g	29.63	
6.88	.433	.436	29.63	29.63
6.97	.436 _g	.439	29.63	29.63
7.20	.444	.447	29.63	29.63
7.43	.452	.455	29.63	29.63
7.78	.462	.465	29.63	29.63
8.05	.472	.475	29.61	
8.58	.488	.491	29.57	

Note: To the number of millimoles of aniline given was added in each case 9.04 millimoles of cyclohexane. When corrected for distillation of cyclohexane into the space (approximately 7 ml. in all tubes) between the liquid and the break seal this became 9.00 millimoles, giving mole fraction, column A, to be used for coexistence curve measurements. When corrected for distillation into the space (approximately 23 ml in all tubes) between liquid and manometric fluid this became 8.90 millimoles giving mole fractions, column B, to be used for pressure-differences measurements. The vapor pressure of all mixtures was approximately 113 mm Hg at 30°C; variation with temperature (about 25% in 5°) can be neglected. Partial pressure of aniline is negligible.

0.414 sample) a whitish cast appeared. (The 0.395g and 0.488 samples did not show this blue-white opalescence). The stirrer could still be seen very clearly, but as the temperature was decreased still further a distinct very intense white cloudiness appeared quite suddenly and the stirrer was no longer visible. This occurred in all the mixtures except in the 0.395g and 0.488 samples (in the 0.414 sample it was considerably less intense). It was believed that the cloudiness was caused by the intimate dispersion and intermingling of tiny droplets of two distinct phases, and so when this cloudiness was present the temperature of its appearance was taken as the transition point. In the case of the six "critical mixtures" whose transition point was 28.63° the meniscus did not appear until the temperature was 0.015 lower. The meniscus of the 0.416 mixture appeared at the same temperature as the meniscus of the critical mixtures. In the case of the 0.414 mixture the meniscus appeared 0.008° below the onset of the cloudiness, and since this cloudiness was not as dense and had a different appearance than in the case of the critical mixtures, the appearance of the meniscus was assumed to give the transition temperature.

The changes appeared in essentially the same way and at the same temperatures, but in reverse order, if the mixtures were heated slowly instead of being cooled.

Behavior of the Meniscus. In the 0.488 and probably in the 0.472 mixtures (column A, Table I) the meniscus disappeared out of the top of the tube on heating, while in the 0.395g, the 0.414, and possibly the 0.416 mixture it seemed to disappear at the bottom, though in the latter cases it was rather difficult to observe because of the stirrer resting on the bottom of the tube. In the six "critical mixtures" the meniscus seemed to disappear in the center of the tube. Some measurements of relative height of the meniscus (i.e., height of the meniscus divided by the total height of the liquid column) were made at various temperatures. The results for some of the mixtures are shown in Fig. 3. In interpreting these measurements, especially for the three mixtures least rich in aniline, the effect of the stirrer resting on the bottom, and occupying a

considerable fraction of the cross section of the tube, must be borne in mind. These measurements were all made on mixtures in their final state of purity except for the 0.425 and 0.472 samples, whose transition temperatures changed only by 0.005° and 0.03° on further purification. Extrapolations (broken lines) were carried to the observed transition points of mixtures in the actual state of purification used, and are actually merely guesses based on general observations.

Conclusions and Discussion. The conclusion that we have drawn from these observations is that the coexistence curve has a flat, horizontal portion on the top, extending approximately over the range of concentrations, of the six mixtures we have called critical mixtures. This is based not merely on the results shown in Table I, but principally upon the fact that when the temperature of the thermostat was lowered at the rate of 0.01° per hour the extreme cloudiness which we believed marked the transition appeared, as nearly as could be judged, simultaneously in all six of these tubes; also the meniscus appeared simultaneous in all of them, as well as in the 0.416 mixture. On the basis of these observations we believed that we could state unequivocally that the transition temperature was the same for all six "critical mixtures" within 0.003°⁽¹³⁾.

Our conclusion that these are all critical mixtures has been questioned by Zimm⁽¹⁴⁾, because he has shown that a smooth curve of the form

$$T_0 - T = 60 (X' - X'')^2$$

where X' and X'' are the mole fractions of aniline of the two phases coexisting at the temperature T , passes through our six critical points within 0.003° and comes nearly as close to our other points. He therefore states that within limits of error, our curve is a smooth curve, of the same type, and with very nearly the same quantitative characteristics as the curve used by Guggenheim⁽⁹⁾ for the liquid-vapor equilibrium of one-component systems, and the curve used by Zimm⁽¹¹⁾ to fit his own data on the perfluoromethylcyclohexane-carbon tetrachloride system.

It is, of course, and always will be, impossible to prove experimentally that a given curve is a true straight line over any portion of its length. We may call attention to the qualitative fact that our six "critical mixtures" do appear to be critical because the meniscus disappears within the body of the liquid. However, if, as we suppose, the true transition temperature is 0.015° higher, this may not be convincing evidence. The state of extreme cloudiness appears to be characteristic of the critical mixtures, which may be significant. However, it did appear in at least one non-critical mixture, the one with 0.472 aniline mole fraction, but this sample is a little hard to compare; it was (the only one) not observed simultaneously with the others in its final state of purity.

On the other hand, we wish to point out one pertinent fact. The observations were repeated several times, with the tubes in different positions in the rack in the thermostat. If there had been any systematic differences of as much as 0.003° or even 0.002° we believe that we would have detected them. This seems to be confirmed by the fact that the transition temperature of the 0.416 mixture was definitely lower than that of the six critical mixtures. Yet when it was attached to the differential manometer along with the 0.452 mixture (which became the 0.455 mixture) and became the 0.419 mixture, the tubes now underwent their transitions simultaneously at 29.63° . Thus the 0.416 mixture appeared to have become a critical mixture, and this small change was detected. We therefore believe that the evidence does favor the conclusion that there is a range of critical mixtures.

Furthermore, we may point out that there is actually a considerable difference between our results and those of Zimm. Zimm finds that the critical mixture for the perfluoromethylcyclohexane-carbon tetrachloride system has a volume fraction of carbon tetrachloride of 0.551. Mixtures with volume fractions

of 0.531 and 0.571 have a transition temperature 0.007° lower. This range of concentrations is quite comparable to our "critical" range. Zimm did not take precautions to exclude dissolved air and atmospheric moisture. While it is quite possible that his system was not as sensitive as ours to traces of moisture, our results suggest that his work ought to be repeated with precautions similar to those we used. This might result in a flattening of his curve.

Results of Vapor Pressure Measurements

Differences in vapor pressure between pairs of mixtures, aniline mole fractions shown in parentheses in Table II, were measured by the method described above. Two of these pairs involved critical mixtures; in the other cases the mixtures were outside the critical range. The pressures shown in Table II are the vapor pressure of the other phase. The pressure unit is 0.0506 mm. Hg (see above, section on "Pressure Measurements").

Care was used in making these measurements to see that equilibrium had been attained by waiting until the measurements remained constant for at least five minutes (in later runs, for ten minutes).

When the two mixtures of a pair both show two liquid layers, the pressure difference between them should, of course, be zero. However, it was almost always found, that there was a small residual pressure difference under these conditions. As long as the temperature was low enough so that there were two layers in both tubes, however, this difference remained almost constant, and it decreased only a little if the mixtures were frozen out with liquid air. It, therefore, appeared to be permanent gas, undoubtedly driven off from the glass in sealing it off from the vacuum system, even though the glass was flamed before these seals were closed. This residual pressure, which is recorded in Table II as the "Correction" was subtracted from the actual pressure difference

Table II

Pressure Differences
as Measured on the Polyethylene Glycol Manometer

	Pair I		Pair II		Pair III		Pair IV	
Temp. °C	(0.398 and 0.491) Heating	(0.398 and 0.491) Cooling	(0.416 and 0.475) Heating	(0.416 and 0.475) Cooling	(0.419 and 0.455) Heating	(0.419 and 0.455) Cooling	(0.4275 and 0.447) Heating	(0.4275 and 0.447) Cooling
26.88			0.0					0.1 ^a
27.88	0.0	0.0	0.0		-0.1 ^a			0.0 ^f
28.88	-0.1		0.0	0.0	0.0 ^b			0.0 ^g
29.38	0.0				0.0 ^c	0.0 ^d	0.0 ^e	
29.58	0.0							
29.63	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
29.73	0.1				0.1	0.0	0.0	0.0
29.88	0.3	0.3	0.3	0.2	0.1		0.0	0.1
30.13	0.6	0.7	0.4	0.4	0.2	0.2	0.1	0.1
30.38	0.8	0.9	0.5	0.5	0.2	0.3	0.2	0.2
30.63	1.1	1.2	0.6	0.6	0.4	0.4	0.3	0.3
30.88	1.3	1.3	0.8	0.8	0.4	0.6	0.3	
31.13	1.6	1.7	1.0	1.0	0.7	0.7	0.4	0.4
31.63	2.3	2.4	1.3	1.2	1.0	1.1	0.6	0.6
32.13	2.8	2.8	1.8	1.7	1.2	1.2	0.8	0.7
32.63	3.4	3.4	2.2	2.2	1.4	1.7	0.9	
33.13	4.0	4.1	2.8	2.8	1.7	1.9	1.0	1.0
33.63	4.9	5.0	3.4	3.4	1.9	2.2	1.2	1.2
34.13	5.9	6.0	4.0	4.2	2.2	2.5	1.4	1.5
34.63	7.2		4.6	4.8	2.4	3.1	1.6	
35.13	8.9		5.7		3.3	3.5	1.7	
Cor- rection	10.0	10.0	0.0	0.0	7.7	7.6	9.0	9.0

^aTemperature, 28.40°

^bTemperature, 28.80°

^cTemperature, 29.30°

^dTemperature, 29.60°

^eTemperature, 26.63°

^fTemperature, 27.63°

^gTemperature, 28.63°

^hTemperature, 29.08°

Note: In the case of Pair III readings were also made at some intermediate temperatures, as follows:

Temp.	29.62	29.68	29.83	29.93	30.03	30.33
Heating	0.0	0.0	0.0	0.2	0.2	0.2
Cooling			0.0	0.1	0.2	
Temp.	30.43	30.53	30.73	31.03	31.23	31.38
Heating	0.3	0.3	0.4	0.6	0.8	0.6
Cooling						0.8

readings to get the values shown in Table II. In one case, the correction seemed to have changed very slightly between the readings which were made with rising and with falling temperatures.

In Fig. 4, we show the average slope, $\Delta p / \Delta X$, of the vapor pressure curves, for the temperatures above 29.63. Here Δp is the corrected pressure difference as given in Table II, and ΔX is the difference in mole fractions of aniline, for example, $0.491 - 0.398 = 0.093$ for Pair I. These pressure differences have been averaged for rising and falling temperatures where both readings are available, and have been converted to mm Hg. An additional correction has also been made. The corrections shown in Table II, arising from inert gas pressures, should not be constant with temperature, but should be proportional to absolute temperature, T . This was not taken into account in Table II. Since the change in the correction is proportional to $T - T_0$ and $\Delta p / \Delta X$ is also approximately proportional to $T - T_0$, the percentage change caused in $\Delta p / \Delta X$ will be approximately constant. To take this effect into account the results, as calculated directly from Table II, have been further multiplied by the following factors: Pair I, 0.97; Pair II, 1.00; Pair III, 0.95; Pair IV, 0.90.

In the case of Paire I and IV the results shown in Table II are the second sets of readings obtained. In the other cases all the data are shown. In the case of Pair IV there was an unusually large amount of inert gas in the first trial, so the correction was inordinately large. Therefore, the mixtures were frozen out with liquid air, evacuated through the emergency break-seals above the two sides of the manometer, and the tubes resealed just below the break-seals. The first runs on Pair I were the first ones made, and they seemed to be rather irregular, though the pressure differences when heating and when cooling agreed fairly well. The values of $\Delta p / \Delta X$ were only about 0.75 to 0.9 (in the first degree above the transition temperature, where the ratio is naturally much less

accurate, 0.5 to 0.7) as great as those shown in Fig. 4, which were obtained after repurification*. The cause for this discrepancy is not known, especially

* As no break-seals had been provided above the manometer arms in this case, a special procedure had to be used to attach the repurification apparatus, so as to introduce a minimum of moisture. The repurification over fused CaO then proceeded as usual.

as the repurification caused no change in the transition temperatures, but we feel that the values given in Table II and Fig. 4, obtained after some familiarity with the procedure was attained, are the most reliable, and they certainly fit in better with the other pairs.

Conclusions. From Fig. 4 we conclude that if there is a region above the critical temperature for which $\Delta p / \Delta X$ is zero it must either lie within 0.2° or 0.3° of the transition temperature or must be confined to a narrow range of concentrations. There is no evidence for any such region. The values of $\Delta p / \Delta X$ in the critical region are certainly extremely small, considering that the total vapor pressure is over 100 mm, but $\Delta p / \Delta X$ begins to deviate from zero, however slightly, at the critical temperature and increases approximately linearly with temperature from that point on. Within the limits of error, the experimental results seem to agree with the theoretical predictions of Rice, but more work along these lines is undoubtedly desirable.

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