

# Vapor-Liquid Equilibria for Eight Binary Mixtures

HOWARD E. JONES, Polychemicals Department, E.I. du Pont de Nemours and Co., Inc., Wilmington, Del.

VAPOR-LIQUID equilibrium data at normal atmospheric pressure were determined for the systems butadiene-chloroprene and acetic anhydride-methylene diacetate, and for several binaries involved in mixtures of acetic acid, acetic anhydride, and pyridine with acetone and cyclohexane. The data would be useful in the design of a distillation column for separating such mixtures. Equilibrium curves for the systems acetic acid-acetic anhydride and acetic anhydride-methylene diacetate were also obtained at a pressure of 100 mm. of Hg.

The binary systems: butadiene-chloroprene, cyclohexane-pyridine, and cyclohexane-acetic anhydride depart considerably from ideality. The other systems are either ideal or show relatively small deviations. Azeotropes were discovered for the system: cyclohexane-acetic anhydride and for the ternary system: pyridine-acetic acid-acetic anhydride.

## APPARATUS

Two modifications of the Othmer-type equilibrium still were used in these studies. The stills (Figure 1) were constructed of borosilicate glass. Each still included a boiler of about 200-ml. capacity which was heated by oil circulating in an electrically heated jacket. The oil-filled jacket extended up the entire height of the 10-inch high, disengaging column to prevent condensation and consequent fractionation. A dead vapor space between the rising vapor stream and the jacket further helped to achieve adiabatic conditions in the column. Both stills were provided with a thermometer well so that the temperature of the boiling liquid could be measured. A magnetic stirrer in the pot provided agitation to prevent bumping and superheating and to mix the returning condensate. The vapors upon leaving the column passed immediately through a downward sloping tube to the condenser.

From this point on, the two stills differed. In still A, the condensate passed through a 6-mm. tube to the bottom of a receiver of 25-ml. capacity. The receiver contents overflowed continuously and returned to the pot. After 1.5 hours of operation, the distillate had displaced itself about 10 times, the boiling liquid had reached a constant temperature, and equilibrium was, therefore, considered to have been reached. Samples of liquid phase and condensed vapor phase were taken simultaneously. With some mixtures there was a tendency toward a certain amount of stratification in the receiver. This was avoided by bubbling a slow stream of nitrogen through the distillate to provide agitation. This still was used for mixtures requiring fairly large samples for analysis. It was not suitable for mixtures of immiscible liquids such as cyclohexane and acetic anhydride. The rate of flow of nitrogen was very small compared to the boil-up rate and was estimated to have a negligible effect on the composition of the condensed vapor.

Still B differed from still A in that there was virtually no hold up of condensate. In operation, the condensate returned immediately to the boiler through the three-way stopcock. The distillate sample was taken by turning the stopcock 180° and collecting the sample running down from the condenser. The liquid-phase sample was taken simultaneously. This still was suitable for binary mixtures where only a few drops of sample were required for analysis and for immiscible systems. It had the advantage that with so little holdup in the return line, equilibrium could be reached

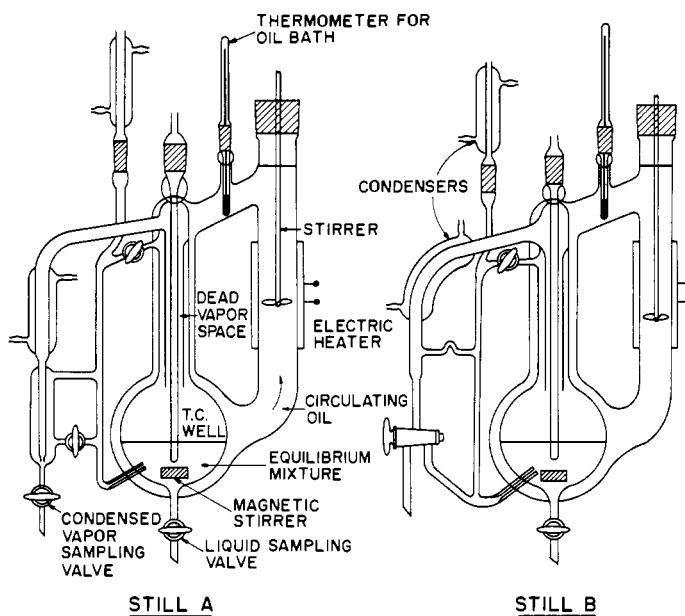


Figure 1. Vapor-liquid equilibrium stills

after only a few minutes of boiling. Atmospheric pressure equilibrium data were all obtained with the barometer reading in the range of 753 to 767 mm. of Hg.

Still A was modified for reduced pressure operation by the addition of a mechanical vacuum pump, a manostat, a manometer, and cold traps. At the end of each equilibration period, the heat was turned off, the vacuum was released by admitting air through a drying tower containing Drierite, and the samples were withdrawn.

Another modification of still A was used for the low temperatures encountered with the butadiene-chloroprene system. The condenser had to be kept well below the boiling point of butadiene ( $-4^{\circ}\text{C}.$ ), the receiver cool enough to prevent the condensate from boiling, and the boiler warm enough to permit steady boiling. To satisfy these conditions, the apparatus was immersed in a methanol-water-ethylene glycol bath contained in a glass aquarium. A plastic insulating partition was placed across the tank to separate the boiling and condensing ends of the equilibrium still. The stopcocks for sampling shown in the diagrams were removed and replaced by capillary tubes bent so as to conduct the samples up to stopcocks located above the level of the bath. From there each sample passed through a short capillary tube into an evacuated sample bottle equipped with a stopcock and immersed in a cold bath when necessary to prevent flashing. Sampling was facilitated by applying about 50 mm. of nitrogen pressure to the still.

Each end of the bath was independently cooled by controlled circulation of the brine through copper coils immersed in methanol-dry ice mixtures. The circulating brine also provided cooling for the condenser.

Temperatures in the low range were measured by calibrated thermometers graduated to  $0.1^{\circ}\text{C}.$  In the higher temperature ranges, the stem corrections became appreciable and could not be estimated accurately. Therefore, an iron-constantan thermocouple and potentiometer were used which permitted readings to  $\pm 0.5^{\circ}\text{C}.$  accuracy. Millivolt values were converted to temperature values by means of a calibration curve obtained from boiling points of pure compounds.

Table I. Boiling Points and Refractive Indices of Reagents Used in Equilibrium Studies Compared with Literature Values

Component	B.P., °C.		$n_D^{25}$	
	Found	Literature	Found	Literature
Acetone	56.1	56.1-56.5	1.3561	1.35662
Cyclohexane	80.7	80.74	1.4234	1.42354
Pyridine	115.3	115.3	1.5073	1.50711
			1.50685	
Acetic acid	118.1	118.1	1.3698	1.3698
Acetic anhydride	139.5	139.55	1.3901 (20° C.)	1.3901 (20° C.)
			1.3878 (25° C.)	1.3878 (25° C.)
Methylene diacetate	170.0	170.0	1.4053 (20° C.)	...
			1.4030 (25° C.)	1.4025 (24° C.)

Table II. Sensitivity of Refractive Index Method of Analysis

Component	Pure Compd., $n_D^{25}$	$\Delta n_D^{25}$	$\frac{dn}{dc}$	Mole % Change Concentration Detectable
Cyclohexane	1.4235	0.0836	0.00084	0.06
Pyridine	1.5071			
Acetone	1.3561	0.1510	0.00151	0.03
Pyridine	1.5071			
Acetic anhydride	1.3878	0.0152	0.00015	0.3
Methylene diacetate	1.4030			

## REAGENTS

Reagent grade compounds were distilled through a 1 × 48 inch column packed with 1/8-inch glass helices. Only heart cuts with a boiling range of ±0.1° C. were used. The purity of the heart-cut materials was checked by their refractive indexes. The boiling points and refractive index values are shown in Table I.

Pure methylene diacetate was obtained by refluxing a mixture of paraformaldehyde in acetic anhydride followed by careful fractionation. The methylene diacetate cut (b.p. 169.8° to 170.2° C.) was redistilled at 100 mm. of Hg. Only the fraction with a boiling range of ±0.5° C. was used. The density of this material was measured as 1.1355 at 25.0° C. and compared to the literature value, 1.136 (1).

1,3-Butadiene was used as purchased. It analyzed 99.0 mole % of butadiene by mass spectrometry. The remainder consisted of various C<sub>4</sub> hydrocarbons.

β-Chloroprene was twice distilled and analyzed over 99 mole % by mass spectrometry.

## ANALYTICAL

In a case where a sufficient difference in the refractive indices of the two components existed, analyses of the mixtures were made with a Valentine refractometer which gave direct readings to the fourth decimal place and estimated values reproducibly to the nearest 0.00005. A sodium vapor lamp provided illumination. Circulating water from a constant temperature bath kept the temperature of the prisms between 24.95° and 25.05° C. For a given binary system, a curve relating refractive index to composition was prepared from the refractive indices of the two pure components and of at least three known mixtures. The accuracy of the method depended on the slope of these curves. The refractive indices of the components, the slopes, and the accuracies obtainable are shown in Table II.

Binary mixtures containing acetic anhydride and no interfering compound were analyzed by direct titration of the sample with standard, aqueous, 0.5*N* sodium hydroxide solution to a phenolphthalein end point.

The acetic acid-acetic anhydride binary mixtures were analyzed as follows: A sample was titrated with standard, aqueous sodium hydroxide, which reacted mole for mole with acetic acid and two moles for one of acetic anhydride. A second sample was titrated with standard methanolic

Table III. Equilibrium Still and Method of Analysis Used for Each System

System	Still Used	Method of Analysis
Cyclohexane-pyridine	B	Refractive index
Cyclohexane-acetic anhydride	B	Titration with NaOH
Pyridine-acetic anhydride	A	Titration with NaOH
Acetic acid-acetic anhydride	A	Titrations with NaOH and NaOCH <sub>3</sub>
Acetone-pyridine	B	Refractive index
Acetone-acetic anhydride	B	Titration with NaOH
Acetic anhydride-methylene diacetate	A	Refractive index
Butadiene-β-chloroprene	A	Mass spectrometry

sodium methylate which reacted mole for mole with either acid or anhydride. The per cent of each component in the mixture could then be calculated.

Equilibrium mixtures of butadiene and β-chloroprene were analyzed by mass spectrometry. The error in these analyses is believed to be less than 1% relative in the range of 90 to 99% of butadiene and less than 0.1% relative above 99% of butadiene. Table III summarizes the analytical methods used.

## RESULTS

The vapor-liquid equilibrium data are shown as data points in Figures 2 through 10. The activity coefficients were calculated for all points of each curve, using the equation of Benedict and others (2) to correct for gas law deviations. The corrected activity coefficients for the five nonideal systems are shown graphically as data points (Figures 11 to 15). The solid line plots in these figures were calculated from the Van Laar equations:

$$\text{Log } \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad (1)$$

and

$$\text{Log } \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (2)$$

The solid line plots in Figures 2, 4, 7, 8, 9, and 10 were obtained by back calculation using values of  $\gamma_1$  and  $\gamma_2$  from the Van Laar plots and the relationships:

$$y_1 = \frac{x_1 \gamma_1 P_1}{P} \quad (3)$$

and

$$y_1 = 1 - y_2 = \frac{x_2 \gamma_2 P_2}{P} \quad (4)$$

where

$P$  = total pressure

$p_1$  = vapor pressure of low-boiling component at boiling point of the mixture corresponding to  $x_1$

$p_2$  = vapor pressure of high-boiling component at boiling point of the mixture corresponding to  $x_1$

Generally, values calculated for  $y_1$  by Equations 3 and 4

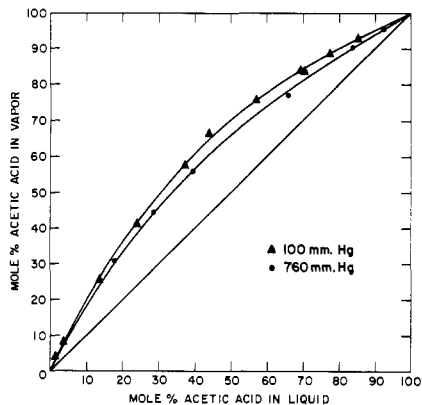


Figure 2. Vapor-liquid equilibrium diagram for the system acetic acid-acetic anhydride

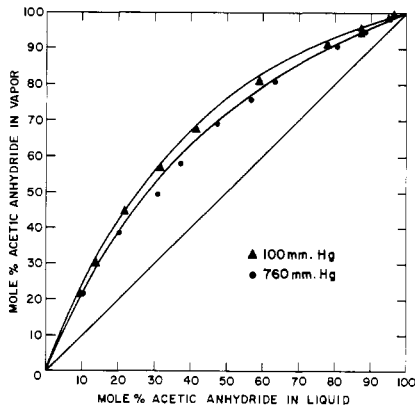


Figure 3. Vapor-liquid equilibrium diagram for the system acetic anhydride-methylene diacetate

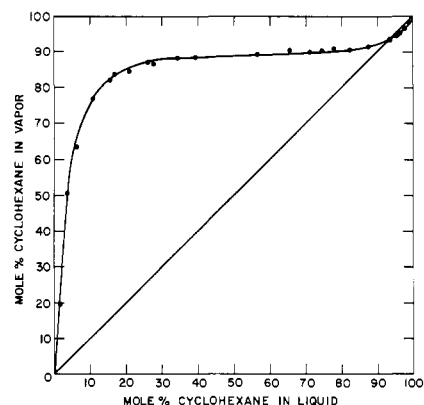


Figure 4. Vapor-liquid equilibrium diagram for the system cyclohexane-acetic anhydride

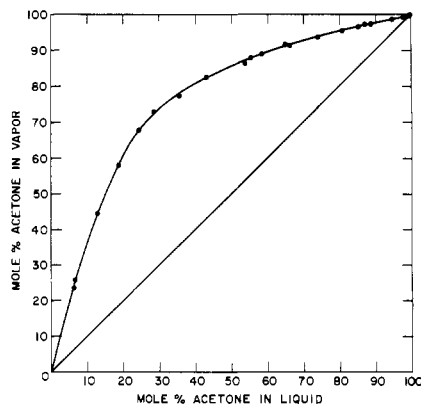


Figure 5. Vapor-liquid equilibrium diagram for the system acetone-acetic anhydride

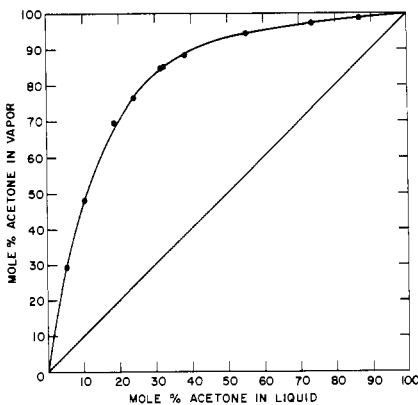


Figure 6. Vapor-liquid equilibrium diagram for the system acetone-pyridine

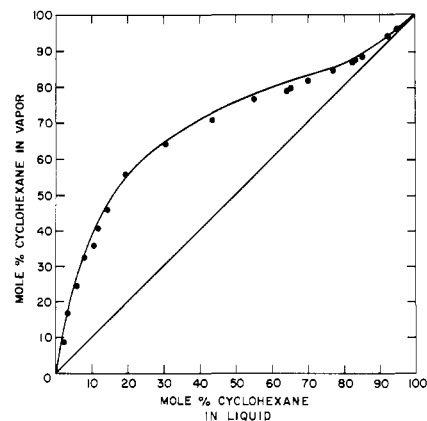


Figure 7. Vapor-liquid equilibrium diagram for the system cyclohexane-pyridine

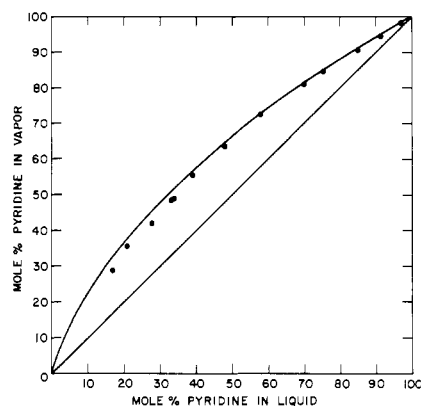


Figure 8. Vapor-liquid equilibrium diagram for the system pyridine-acetic anhydride

Figure 9. Vapor-liquid equilibrium diagram for the system 1,3-butadiene-chloroprene

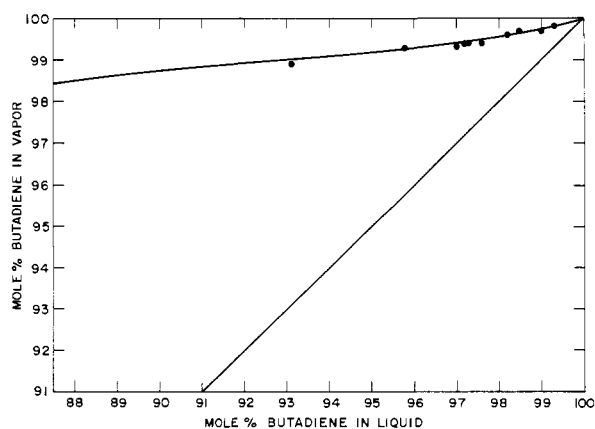
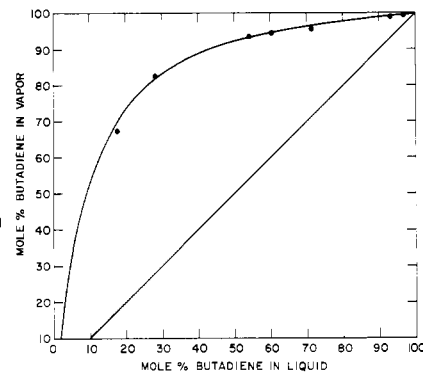


Figure 10. Detailed vapor-liquid equilibrium diagram for the system 1,3-butadiene-chloroprene

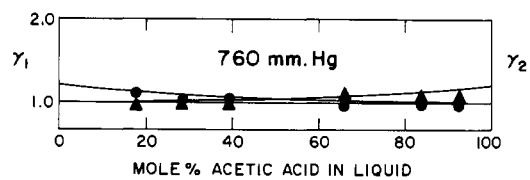


Figure 11. Activity coefficients vs. composition for the system acetic acid-acetic anhydride  
● Acetic acid      ▲ Ac<sub>2</sub>O

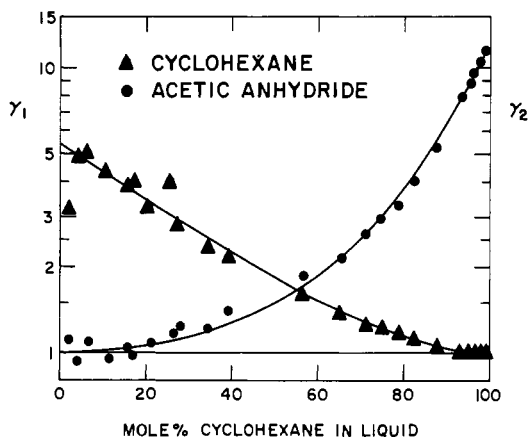


Figure 12. Activity coefficient vs. composition for the system cyclohexane-acetic anhydride

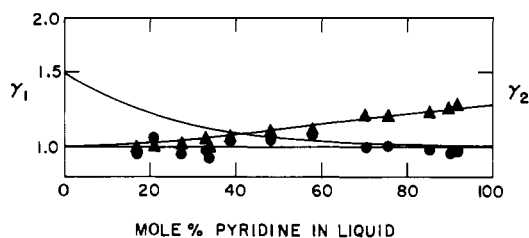


Figure 14. Activity coefficient vs. composition for the system pyridine-acetic anhydride

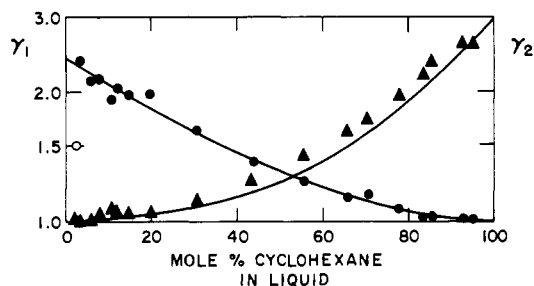


Figure 13. Activity coefficient vs. composition for the system cyclohexane-pyridine

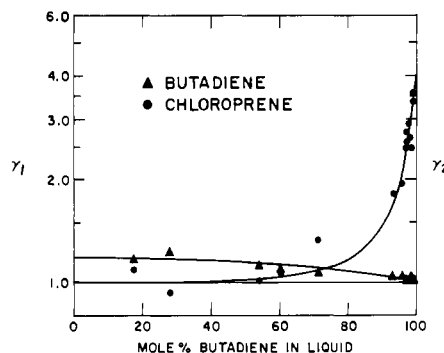


Figure 15. Activity coefficient vs. composition for the system 1,3-butadiene-chloroprene

were in good agreement. Thus, thermodynamically consistent sets of boiling points, liquid and vapor composition, and activity coefficients were obtained. The smoothed, thermodynamically consistent data for these five systems are given in Table IV. A summary of the Van Laar constants is given in Table V.

Plots of the activity coefficients for acetic anhydride and methylene diacetate indicated that the mixtures were essentially ideal at the pressures investigated. Acetic acid and acetic anhydride mixtures appeared to be ideal at 100 mm. of Hg, but departed slightly from ideality at 760 mm. of Hg.

Data for the acetone-pyridine system and the acetone-acetic anhydride system could not be correlated satisfactorily by the Van Laar method. This difficulty is undoubtedly attributable at least in part to the wide range of boiling points of the components in each system, since the Van Laar equations are strictly valid only for isothermal data. The experimental vapor-liquid equilibrium curves for these two systems are shown in Figures 5 and 6, and the smoothed, experimental boiling point, activity coefficients, and X-Y data are given in Table IV.

Boiling point diagrams are presented in Figures 16 to 22.

The equilibrium curve for the system acetic acid-acetic anhydride at 760 mm. of Hg (Figure 2) differs considerably from that given by Othmer (5). The curve found in the present investigation approximates that of an ideal system, whereas Othmer's data indicate a higher relative volatility than that of an ideal system. An apparent higher relative volatility for this system could result from any of several factors, such as fractionation during operation of the still, moisture in the samples, or analytical error. The author believes that these factors were under control in the present investigation, and favors the resulting equilibrium curve, which is in closer agreement with the curve predicted by Raoult's law.

The equilibrium curve for the system pyridine-acetic

anhydride agrees fairly well with that reported by Nelson and Markham (4) and is nearly that expected of an ideal mixture.

#### AZEOTROPES

For the system cyclohexane-acetic anhydride an azeotrope containing 93.5 mole % of cyclohexane with a boiling point of 80.12° C. is found.

Swearingen and Ross (6) found that acetic acid and pyridine form a high-boiling azeotrope (b.p. = 138.40° C.). This seems to be true generally with aliphatic acids and tertiary amines (3). The author has found, furthermore, that with the addition of acetic anhydride a ternary azeotrope is formed. This azeotrope has a boiling point of 134.4° C. and a composition of 55% of acetic anhydride, 23% of acetic acid, and 22% of pyridine by weight.

#### VAPOR PRESSURE DATA

The vapor pressure data necessary for computing the activity coefficients are generally available in the literature, except for methylene diacetate, for which only the boiling point is given (1). The temperature-vapor pressure relationship was, therefore, determined experimentally as follows: A sample of pure methylene diacetate was charged to the pot of a small, packed, glass laboratory still. The still was equipped with condensing head, receiver, vacuum pump, manostat, absolute mercury manometer, and a series of interchangeable calibrated thermometers graduated in 0.1° C. The sample was brought to a boil at atmospheric pressure. The still was operated at a reflux ratio of 10 to 1 in order to remove any traces of low boiling compounds produced by hydrolysis. After a constant vapor temperature was obtained, the manometer reading was taken. Pressure was then reduced intermittently and new vapor temperatures were obtained. The manometer readings were

Table IV. Smoothed Vapor-Liquid Equilibrium Values, Boiling Points, and Activity Coefficients

System, x	Pyridine-Acetic Anhydride			Acetone-Pyridine			Acetic Acid-Acetic Anhydride			Ac <sub>2</sub> O-Methylene Diacetate				
	760 Mm. Hg <sup>a</sup>			760 Mm. Hg <sup>a</sup>			100 Mm. Hg, (Ideal)			100 Mm. <sup>a</sup> (Ideal)				
	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.		
10	0.225	1.32	134.7	0.367	1.22	102.5	0.199	79.3	0.243	166	107.0	0.470	0.88	119.0
20	0.365	1.20	131.2	0.609	1.16	91.0	0.360	76.9	0.421	162	103.2	0.705	0.92	103.0
30	0.480	1.14	128.5	0.740	1.11	83.0	0.495	74.8	0.525	158.2	99.5	0.832	0.95	91.5
40	0.580	1.09	126.0	0.809	1.07	76.5	0.610	72.9	0.633	154.8	96.2	0.896	0.98	82.5
50	0.665	1.05	124.0	0.858	1.05	72.0	0.703	71.1	0.721	151.5	93.4	0.932	0.98	76.5
60	0.740	1.025	122.0	0.897	1.03	68.0	0.780	69.3	0.795	148.7	90.8	0.953	0.99	71.0
70	0.815	1.02	120.5	0.929	1.02	64.8	0.845	67.6	0.857	146.0	88.2	0.969	1.00	66.5
80	0.880	1.01	118.6	0.953	1.01	62.0	0.902	65.9	0.911	143.7	86.0	0.981	1.00	62.5
90	0.940	1.005	117.0	0.977	1.01	59.0	0.953	64.2	0.958	141.5	84.0	0.991	1.00	59.5
95	0.970	1.002	116.3	0.989	1.00	57.5	0.978	63.4	0.979	140.5	83.0	0.996	1.00	57.7
97.5	0.985	1.001	116.0	0.994	1.00	57.0	0.989	63.0	0.990	140.0	82.5	0.998	1.00	57.0

1,3-Butadiene-Chloroprene

x	1,3-Butadiene-Chloroprene			Acetic Acid-Acetic Anhydride			Cyclohexane-Pyridine			Cyclohexane-Acetic Anhydride				
	760 Mm. Hg <sup>a</sup>			760 Mm. Hg <sup>a</sup>			760 Mm. Hg <sup>a</sup>			760 Mm. Hg <sup>a</sup>				
	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.	y	γ <sub>1</sub>	T, °C.		
10	0.520	1.178	1.000	0.180	1.12	100.5	0.380	2.10	1.01	102.0	0.750	4.3	1.01	101.5
20	0.732	1.175	1.001	0.330	1.09	101.0	0.555	1.84	1.03	94.8	0.850	3.45	1.05	87.5
30	0.833	1.16	1.004	0.460	1.07	101.5	0.845	1.625	1.075	90.8	0.878	2.78	1.14	84.0
40	0.889	1.15	1.007	0.566	1.05	102.0	0.710	1.45	1.14	88.0	0.885	2.22	1.28	82.7
50	0.922	1.14	1.02	0.660	1.025	102.5	0.785	1.31	1.25	86.0	0.890	1.82	1.50	81.8
60	0.947	1.13	1.03	0.740	1.020	105	0.800	1.20	1.38	84.2	0.892	1.51	1.88	81.3
70	0.963	1.10	1.08	0.815	1.015	107	0.832	1.11	1.58	82.8	0.899	1.30	2.54	81.0
80	0.978	1.08	1.16	0.880	1.010	109	0.866	1.05	1.88	81.8	0.903	1.13	3.8	80.6
90	0.9874	1.04	1.45	0.940	1.005	112	0.920	1.015	2.32	81.1	0.922	1.04	6.5	80.4
95	0.9918	1.001	1.95	0.970	1.002	113	0.960	1.005	2.63	80.8	0.944	1.01	8.7	80.2
97.5	0.9947	1.000	2.65	0.985	1.001	114	0.980	1.002	2.90	80.8	0.967	1.005	10.4	80.4

<sup>a</sup> Pressure absolute

x = mole % low-boiling component in liquid phase.

y = mole % low-boiling component in vapor phase.

γ<sub>1</sub> = activity coefficient of low-boiling component.

γ<sub>2</sub> = activity coefficient of high-boiling component.

Table V. Van Laar Constants

System	Pressure, Mm. Hg	A	B
Acetic acid-acetic anhydride	760	0.061	0.061
Cyclohexane-acetic anhydride	760	0.732	1.097
Cyclohexane-pyridine	760	0.380	0.477
Pyridine-acetic anhydride	760	0.176	0.097
1,3-Butadiene-β-chloroprene	760	0.0719	0.602

Table VI. Temperature-Vapor Pressure Data for Methylene Diacetate

T, °C.	P, Mm. Hg Abs.	T, °C.	P, Mm. Hg Abs.
61.0	10.0	118.3	139.0
74.4	20.0	127.9	199.0
81.9	29.5	145.2	361.0
88.0	38.0	161.9	616.0
105.0	81.5	170.0	760.0
109.9	100.5		

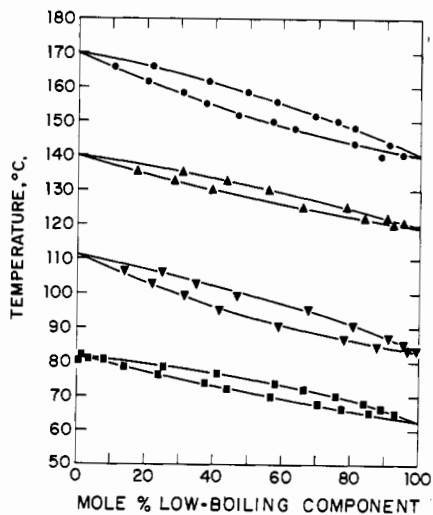


Figure 16. Boiling point diagrams

- Acetic anhydride-methylene diacetate, 760 mm. Hg
- ▲ Acetic acid-acetic anhydride, 760 mm. Hg
- ▼ Acetic anhydride-methylene diacetate, 100 mm. Hg
- Acetic anhydride-acetic acid, 100 mm. Hg

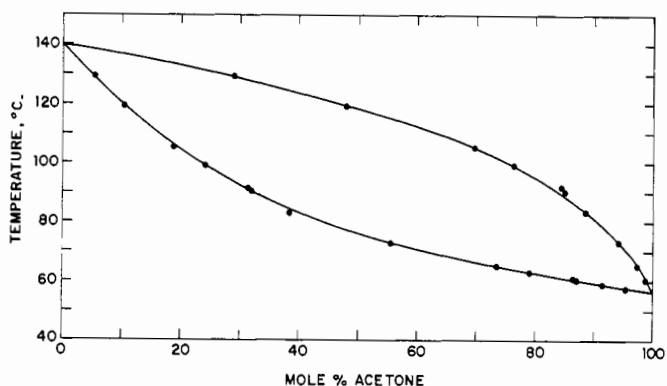


Figure 18. Boiling point diagram for the system acetone-acetic anhydride

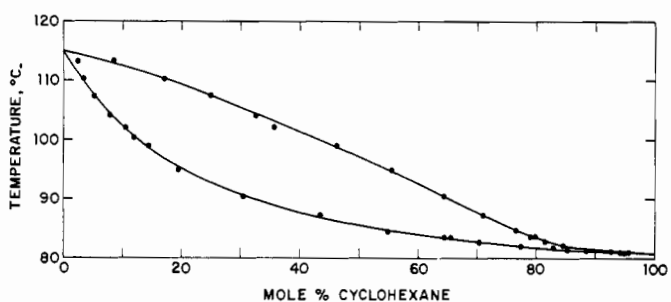


Figure 20. Boiling point diagram for the system cyclohexane-pyridine

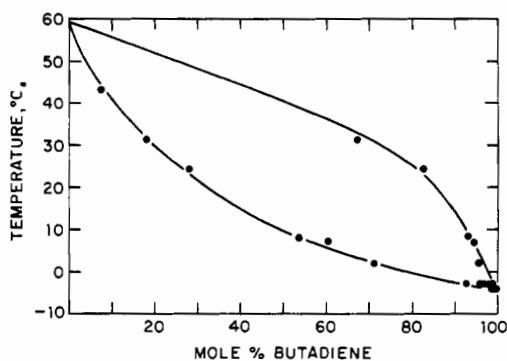


Figure 22. Boiling point diagram for the system 1,3-butadiene-chloroprene

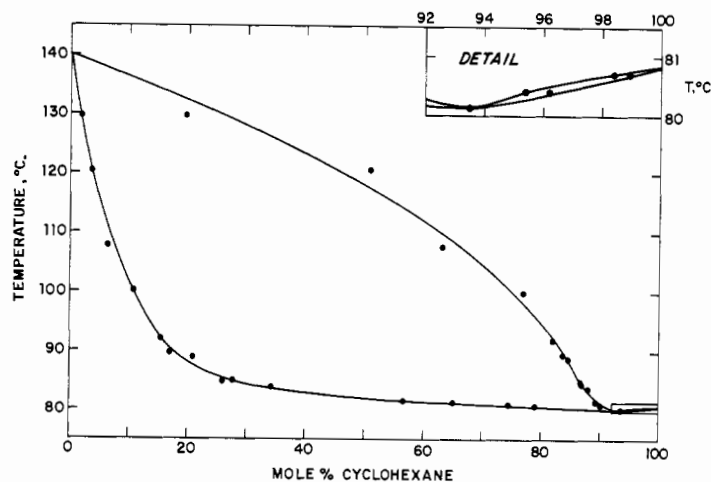


Figure 17. Boiling point diagram for the system cyclohexane-acetic anhydride

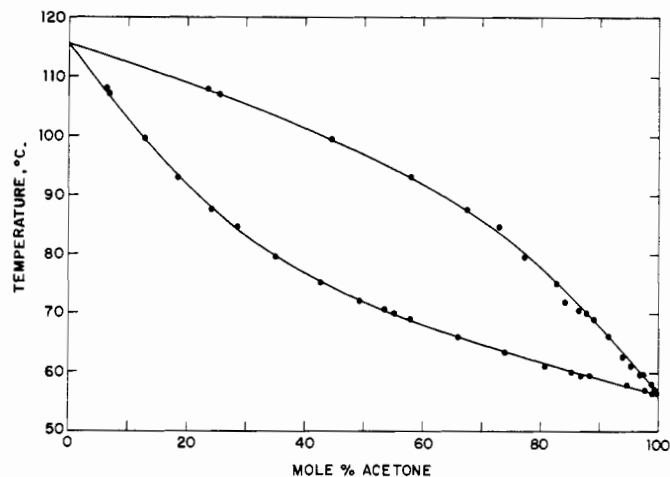


Figure 19. Boiling point diagram for the system acetone-pyridine

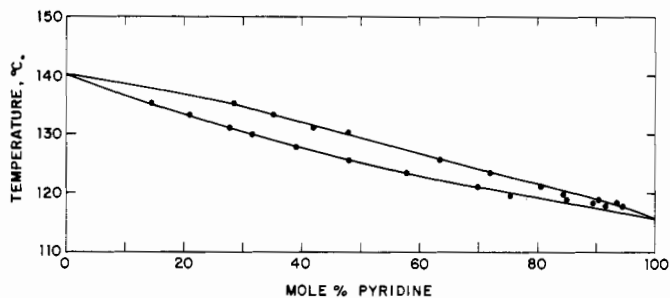


Figure 21. Boiling point diagram for the system pyridine-acetic anhydride

corrected for capillary depression and thermal expansion. Data thus obtained are presented in Table VI.

#### LITERATURE CITED

- (1) Beilstein, F.K., "Organische Chemie," Vol. II, p. 152, Julius Springer, Berlin, Germany, 1920.
- (2) Benedict, M., Johnson, C.A., Solomon, E., Rubin, L., *Trans. Am. Inst. Chem. Engrs.* 41, 371-92 (1945).
- (3) Hansley, V.L. (to E.I. du Pont de Nemours & Co.), U. S. Patent 2,452,460 (1948).
- (4) Nelson, P.A., Markham, A.E., *J. Am. Chem. Soc.* 72, 2417 (1950).
- (5) Othmer, D.F., *Ind. Eng. Chem., Anal. Ed.* 4, 232-4 (1932).
- (6) Swearingen, L.E., Ross, R.F., *J. Phys. Chem.* 39, 821 (1935).

RECEIVED for review April 11, 1961. Accepted May 26, 1961.