THE CONSTRUCTION AND OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL

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SUMMARY

In nearly all phases of chemical engineering education and research it is occasionally necessary to perform distillation calculations on a binary system for which equilibrium data are not available. For such occasions, the availability of apparatus with which equilibrium data may be easily and accurately determined is necessary to prevent unusual delays in important projects. The primary purpose of the present work was the construction of such apparatus.

The equilibrium still constructed was based on the design of Griswold, Andres, and Klein[1], and was a modification of an original design proposed by Othmer[2]. The apparatus was built as an entirely closed system with the condensed vapor being returned to the still pot. The steel construction permitted the attainment of high pressures but limited the systems to be used to those not corrosive to iron.

In order to determine the alterations in equipment or in procedure necessary for obtaining reliable data, the experimental work was confined to the determination of systems for which equilibrium data were available. The systems studied were carbon tetrachloride-toluene and trichloroethylene-toluene at 760 mm. pressure.

Equilibrium data were obtained which checked within approximately 0.5 per cent with available data. Operation of this apparatus following the procedure outlined should give satisfactory results for unknown systems at either high or low pressures.

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[1]Griswold, J., Andres, D., and Klein, J. A., Trans. AIChE, 39, 2, 171-8 (1943).

[2]Othmer, D. F., Ind. Eng. Chem., 20, 743-6 (1928).

In order to improve the operation of the equipment, it is specifically recommended that:

1. The present sample outlets be replaced by small diameter copper tubing.

2. A constant-head overflow tank be used to supply condenser water.

3. A more sensitive check valve be used in the condensate return line.

4. Apparatus for further cooling of the condenser water be included in the system if determinations are to be made using low-boiling mixtures.

INTRODUCTION

When a mixture of two liquids vaporizes, that component which has the highest partial vapor pressure tends to be distilled more rapidly and concentrates in the vapor. Thus a difference in composition will exist between a liquid and the vapor in equilibrium with it. The relation between the composition of a mixture and the composition of the vapor evolved when it is distilled is the basis for the calculation of equipment design for the industrial separation of the components of such mixtures. Equilibrium data may be calculated from Raoult's law for certain "ideal" systems but the greater proportion of such data must be determined experimentally.

Vapor-liquid equilibrium data have been determined by many investigators using widely varied methods. Data that have been presented often show extreme inconsistencies which are largely due to errors inherent in the type of apparatus being used. All investigations are based on the assumption that the bubbles of vapor given off are in equilibrium with an average sample of the liquid when formed or that they attain equilibrium before leaving the liquid surface[1]. It is generally agreed that true equilibrium is seldom established in the determination of "equilibrium" data.

In the simplest type of determination, a small sample of vapor is distilled from a large quantity of liquid, using an ordinary laboratory distillation unit. If the amount of liquid is 300 to 400 times as large as the sample of vapor distilled from it, this method is theoretically capable of good results[2]. However, the error introduced

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[1] Othmer, D. F., Ind. Eng. Chem., 35, 614-20, (1943).

[2] Othmer, D. F., Ibid., 20, 743-6, (1928).

by refluxing action above the still pot has generally led to inaccurate data.

Virtually all types of equipment currently in use in the determination of vapor-liquid equilibrium data are variations of a design first proposed by Othmer[3]. The original apparatus had as its distinguishing innovation the provision of a condensate return line between the condensate collection bulb and the still pot. This allowed continued operation of the system until equilibrium had been attained. An ingenious arrangement of traps enabled almost complete separation of entrained liquid from the vapor. Fractionation above the still pot was effectively prevented by a vapor-filled jacket which surrounded the tube carrying equilibrium vapor from the still pot to the condenser.

However, this improved form introduced further sources of error. The condensate returning to the still had a tendency to flash upon entering the still pot. Jones[4] partially corrected this tendency by providing an overflow trap in the return line for further cooling of the condensate and by providing for rapid mixing of the returned condensate with the still liquid. Gillespie[5] has developed a modified Othmer still wherein the liquid disengaged from the vapor in a Cottrell pump returns to the still pot in the condensate return line. At equilibrium, the return composition is the same as the pot composition and errors due to flashing or inhomogeniety in the still pot are eliminated.

The problem of fractionation has been solved by the application of external heating to the area above the still pot. However, it is

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[3]Othmer, D. F., Ind. Eng. Chem., 20, 743-6, (1928).

[4]Jones, C. A., Schoenborn, E. M., and Colburn, A. P., Ibid., 35, 666-72, (1943).

[5]Gillespie, D. T. C.., Ibid., 18 (Analytical Ed.) 575-7, (1946).

essential that the temperature of the vapor tube be but slightly above the boiling temperature of the liquid. If the tube becomes too hot, entrained liquid deposited on the walls will be completely vaporized and the condensate will be enriched in the less-volatile component. Carey and Lewis[6] surrounded the entire vapor chamber with an accurately heated jacket kept at a temperature only slightly above the boiling temperature of the liquid. However, it has been pointed out that the accuracy of their results was dependent upon strictly controlled operation of the jacket at a temperature that was only arbitrarily specified.

Numerous problems have arisen in the taking of samples from this type of system. Othmer specified that no distillation or condensate return should take place during sampling. Before taking samples, he simultaneously removed the source of heat and closed the condensate return line. The thin-glass construction of the apparatus allowed rapid cooling and distillation was essentially instantaneously interrupted. Hence, the liquid and vapor composition did not materially change from equilibrium composition.

In the apparatus constructed by Langdon and Keyes[7] the heat reservoir of the system was large enough to continue distillation for some time after the heat source was removed. The procedure followed consisted in the removal of heat and closing of the condensate return line followed by the taking of one sample of condensate and four samples of still pot residue. By plotting still pot sample composition against the time of taking the sample and extrapolating to the time of heat removal,

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[6]Carey, J. S., and Lewis, W. K., Ind. Eng. Chem., 24, 882-3, (1932).

[7]Langdon, W. M., and Keyes, D. B., Ibid., 34, 938-42, (1942).

the equilibrium liquid composition was determined.

Gillespie[8] maintains that true equilibrium samples cannot be obtained by either of the above methods. In the use of his modified apparatus, the liquid and vapor samples are taken simultaneously without interrupting the distillation. If proper precautions are taken, the equilibrium will not be disturbed.

Virtually all investigators used constancy of the boiling temperature as the criterion for the attainment of equilibrium. It was also specified that samples should not be removed from the system until time had been allowed for a turnover of twenty to twenty-five times the original charge.

The apparatus of Griswold[9], on which the present apparatus is based, was designed primarily for high-pressure work. The all-metal construction permits the attainment of pressures and temperatures outside the range of glass apparatus. Its use is limited to systems which are not corrosive to the metal used in construction.

The distinguishing features are:

1. A circulation pipe and collar in the still pot to provide adequate mixing of the returned condensate with the liquid in the still pot.

2. A liquid sample outlet placed above the still pot proper so that the samples collected are of liquid which has percolated through the circulation pipe into the vapor space above the still pot. Prev-

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[8]Gillespie, D. T. C., Ind. Eng. Chem. (Analytical Ed.) 18, 575-7, (1946).

[9]Griswold, J., Andres, D., and Klein, J. A., Trans. AIChE, 39, 2, 171-8, (1943).

iously, sample outlets had been placed in the bottom of the still pot in such close proximity to the condensate return line that even vigorous mixing did not completely insure representative samples.

3. A large, electrically-heated vapor chamber above the still pot to minimize entrainment and fractionation.

4. A ball-check valve in the condensate return line to prevent surges of still pot liquid into the condensate chamber during the removal of samples.

5. A condenser constructed in several sections so that the amount of heat removed at the condenser may be adjusted for the system involved and for the pressure desired.

6. Provision for evacuation of the system to prevent the solution of air in the liquid and to provide for easier control of pressure.

Note: For complete description and dimensions, see Equipment section under numbers listed below.

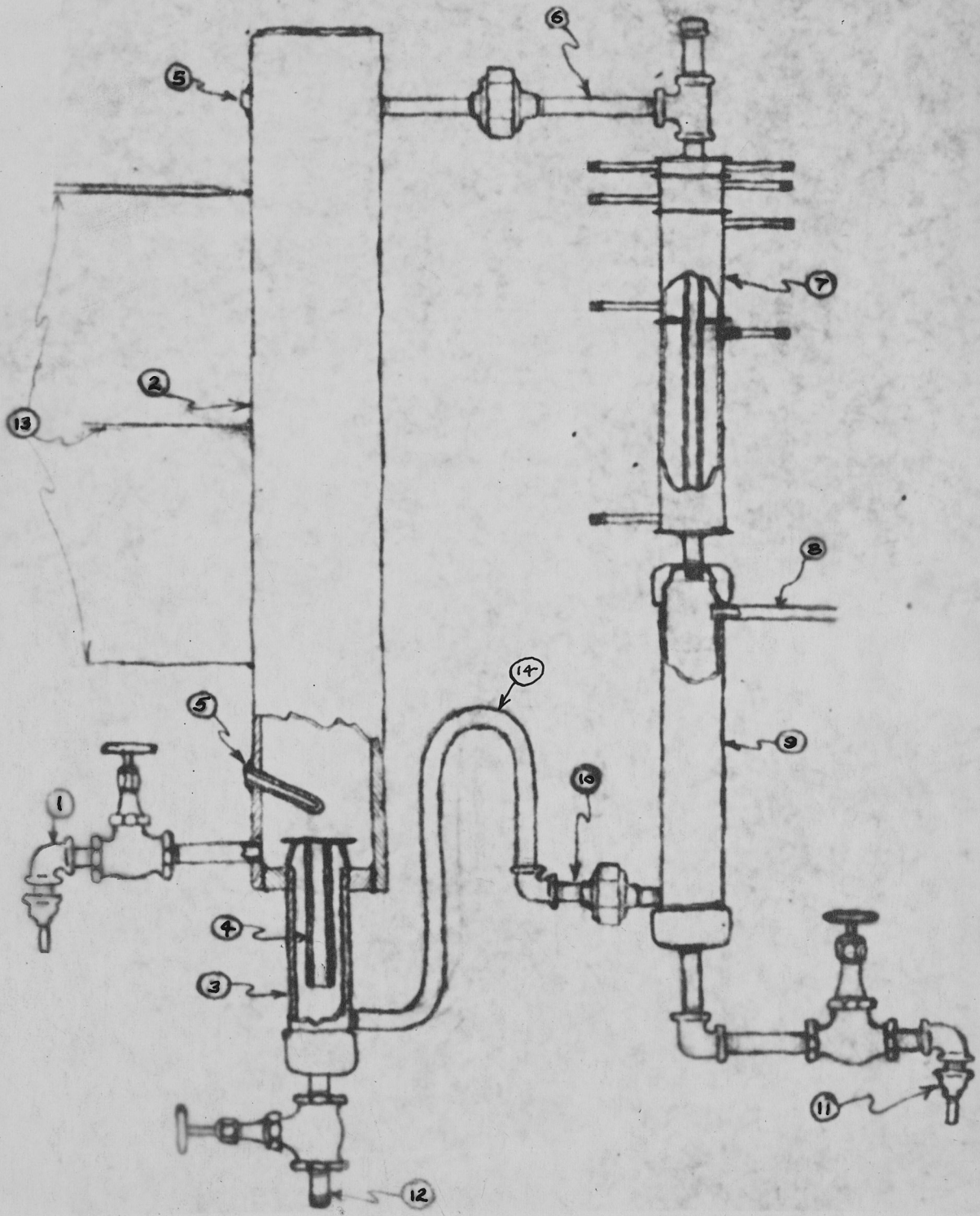

Fig. 1

SKETCH OF APPARATUS

THE CONSTRUCTION AND OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL

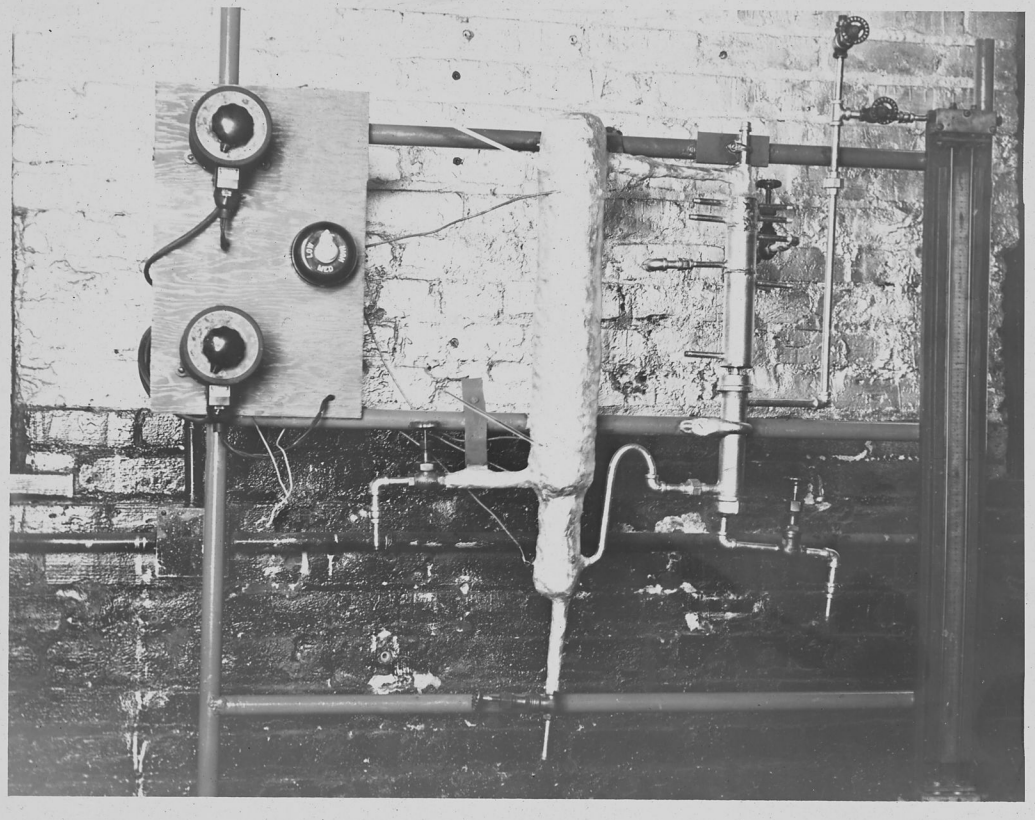

Fig. 2

PHOTOGRAPH OF APPARATUS

THE CONSTRUCTION AND OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL

The vapor chamber (2) was constructed of a 22-1/2-inch length of extra-heavy iron pipe, 3-5/8-inch outside diameter by 3-inch inside diameter. The end plugs were made of 3/8-inch steel plate and were welded to the main body. Constantan wires (13) were spotted to the outside wall of the vapor chamber at three points. One common iron thermocouple wire was fastened to the upper constantan wire. Two thermometer wells (5) were brazed to the vapor chamber. These wells were constructed of 2-inch lengths of 1/4-inch pipe. The lower ends were closed with brass. The liquid sample outlet (1) was constructed of 1/4-inch extra-heavy iron pipe equipped with a 125-pound globe valve. The outlet assembly was brazed into place on the lower portion of the vapor chamber, the opening flush with the bottom plug.

The still pot (3) was constructed of extra-heavy 1-1/2-inch iron pipe, 5-1/2 inches in length. It was brazed into the lower end plug of the vapor chamber. The cap on the lower end was a standard fitting, screwed into place to allow for removal. All small pipe connections were brazed in place. The drain pipe (12) was brazed to the cap.

The circulation pipe (4) was 4-1/2 inches in length and was constructed of 1/2-inch standard iron pipe. To the upper end a 1-3/4-inch diameter, 1/16-inch thick steel collar was brazed. The collar was supported above the end plug of the vapor chamber by three equally spaced legs, each 1-inch long, brazed to the plug and to the collar.

The vapor line (6) connecting the vapor chamber to the condenser was made of 1/4-inch extra-heavy iron pipe and had an overall length of 9-inches. Four condensers (7) were provided, having lengths of 1/2-inch, 3-inches and 6-inches. The outer shell was made of 1-3/4-inch standard

iron pipe and the inner shell of 1/4-inch extra-heavy iron pipe. The coolant connections were 2-1/2-inch lengths of 1/8-inch standard iron pipe. All joints were brazed.

The condensate collection chamber was made from a 9-inch length of 1-1/2-inch extra-heavy iron pipe. The caps on both ends were standard screwed fittings. The vapor sample outlet (11) was made in the same manner as the liquid sample outlet and was brazed to the lower cap. The manometer and vacuum line (8) and the condensate return line (14) were brazed in place. The condensate return line was constructed of extra-heavy 1/4-inch iron pipe and standard fittings. The bend in the line had a radius of 2-1/2-inches. The point of connection to the condensate collection chamber was 5-inches above the point of connection to the still pot.

The condensate return line was equipped with a ball-check valve (10) which checked flow from the still pot to the condensate collection chamber. The outside dimension of the check valve was that of 1/4-inch extra-heavy iron pipe. The seat was 1/8-inch in diameter and ground to fit a 3/16-inch ball. The ball was held in place by a short length of welding rod inserted through the valve and brazed in place.

Two separate electrical heating circuits were used. The still pot was wrapped with approximately 15-feet of 26-gauge Nichrome resistance wire, insulated from the iron with asbestos paper and a coat of Glyptal paint. The vapor chamber heater consisted of approximately 10-feet of 26-gauge Nichrome wire. The heat input to the circuits was controlled by 110 v., 7.5 amp. "Powerstat" rheostats, type 116, manufactured by the Superior Electric Company, Bristol, Connecticut. As

mounted on the control panel, the upper rheostat (U.T. Ch. E. 660) controls the vapor chamber heating element and the lower rheostat (U.T. Ch. E. 661) controls the still pot heater.

Also mounted on the control panel was a three-way switch to provide thermocouple-potentiometer connections. The "high" and "low" positions connected respectively to the top and bottom thermocouples on the vapor chamber. Because of duplication of connections in the "medium" and "high" positions, the switch was not used for all three thermocouples.

The still pot, vapor chamber, condensate return line, and the vapor line to the condenser were covered with a 1/2-inch layer of molded asbestos lagging. The entire apparatus was mounted on a stand made of iron pipe and was located on the south side of Chemical Engineering Laboratory No. 1 during operation.

A charge of approximately 500 cc. was introduced into the apparatus through the liquid sample outlet. This was accomplished by turning the elbow of the pipe until the opening faced upward and attaching a funnel made of a large coupling and reducer. During the introduction of the charge, the apparatus was vented through the vapor sample outlet.

The rheostats were then adjusted to give approximately 85 volts drop through the still pot heater and 70 volts drop through the vapor chamber heater. The system was evacuated using the laboratory vacuum pump connected to the vent. Since water was being used in the manometer, the valve connecting the manometer to the system was closed during evacuation to prevent drawing the water into the system.

After evacuation, the system was completely closed and the condenser water turned on. When the apparatus had reached operating temperature, the internal pressure was adjusted to the desired value. During the present work, the internal pressure was maintained at the difference between barometric pressure and 760 mm. Best control of pressure was obtained using the water flow rate for coarse adjustment and the heat input to the still pot for fine adjustment. The heat input to the vapor chamber was regulated to give an upper wall temperature approximately 4°C. above the observed boiling temperature.

After the proper adjustments had been made, the pressure in the system remained constant except for minor variations due to fluctuating water pressure. The boiling temperature became constant after ten to fifteen minutes operation. The system was operated at constant boiling temperature for a minimum of one-half hour before taking samples.

Samples were removed from the system without disturbing the operation. Before removing the samples, the heat input to the still pot

was increased approximately 10 volts to compensate for the pressure drop that tends to occur when liquid is removed. Approximately 20 cc. of liquid were first drawn off from each sample tap and discarded before taking the actual samples. When sample removal was properly carried out, the pressure in the system changed but slightly over the sampling period. Analysis of the 25 cc. samples was by density, using the Westphal balance. Density data are included in the Appendix.

All materials used in the present work were C.P. or purified reagents.

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LABORATORY DATA

TABLE I

THE SYSTEM CARBON TETRACHLORIDE-TOLUENE

Run No.	Boiling Temp. (°C.)	Manometer Reading (Cm. H_2O)	Bar. Pressure (mm. Hg.)	Total Internal Pressure (mm. Hg.)	Density of Liquid (32°C.)	Density of Vapor (32°C.)	Mol % CCl_4 in Liq.	Mol % CCl_4 in Vapor
1	92.5	19.0	745.7	760	1.093	1.144	35.6	42.9
2	93.1	18.0	745.7	759	1.099	1.164	36.4	45.8
3	86.8	17.5	745.7	759	1.233	1.326	55.1	68.0
4	86.8	19.1	745.7	760	1.217	1.369	53.0	73.6
5	91.1	20.0	745.7	761	1.173	1.325	46.9	67.7
6	93.8	19.5	745.7	760	1.096	1.255	36.0	58.0
7	83.0	19.9	745.4	760	1.342	1.433	70.0	82.0
8	84.1	19.8	745.4	760	1.335	1.451	69.0	84.5
9	98.8	19.8	745.4	760	0.983	1.086	19.8	34.5
10	104.8	17.2	747.2	760	0.906	0.956	8.3	15.9
11	78.4	19.7	745.5	760	1.480	1.526	88.2	94.2
12	97.0	20.0	745.5	760	1.027	1.170	26.2	46.0
13	101.9	19.9	745.5	760	0.947	1.040	14.5	28.1

THE CONSTRUCTION AND OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL

LABORATORY DATA

TABLE II

THE SYSTEM TRICHLOROETHYLENE-TOLUENE

Run No.	Boiling Temp. (^{o}C.)	Manometer Reading (Cm. H_2O)	Bar. Pressure (mm. Hg.)	Total Internal Pressure (mm. Hg.)	Density of Liquid (32°C.)	Density of Vapor (32°C.)	Mol % C_2HCl_3 in Liq.	Mol % C_2HCl_3 in Vapor
1	104.6	20.2	745.0	760	0.936	0.988	16.5	26.3
2	102.1	21.0	744.6	760	1.035	1.116	34.8	49.4
3	95.0	18.0	746.7	760	1.139	1.243	53.5	70.4
4	93.5	18.2	746.7	760	1.194	1.288	62.6	77.3
5	88.7	18.1	746.7	760	1.335	1.384	85.0	92.2
6	92.2	18.4	746.5	760	1.246	1.321	71.0	82.6
7	97.5	18.3	746.5	760	1.092	1.193	45.0	62.4
8	102.5	18.5	746.5	760	0.988	1.061	26.3	38.8
9	106.6	18.5	746.4	760	0.903	0.939	10.2	17.0

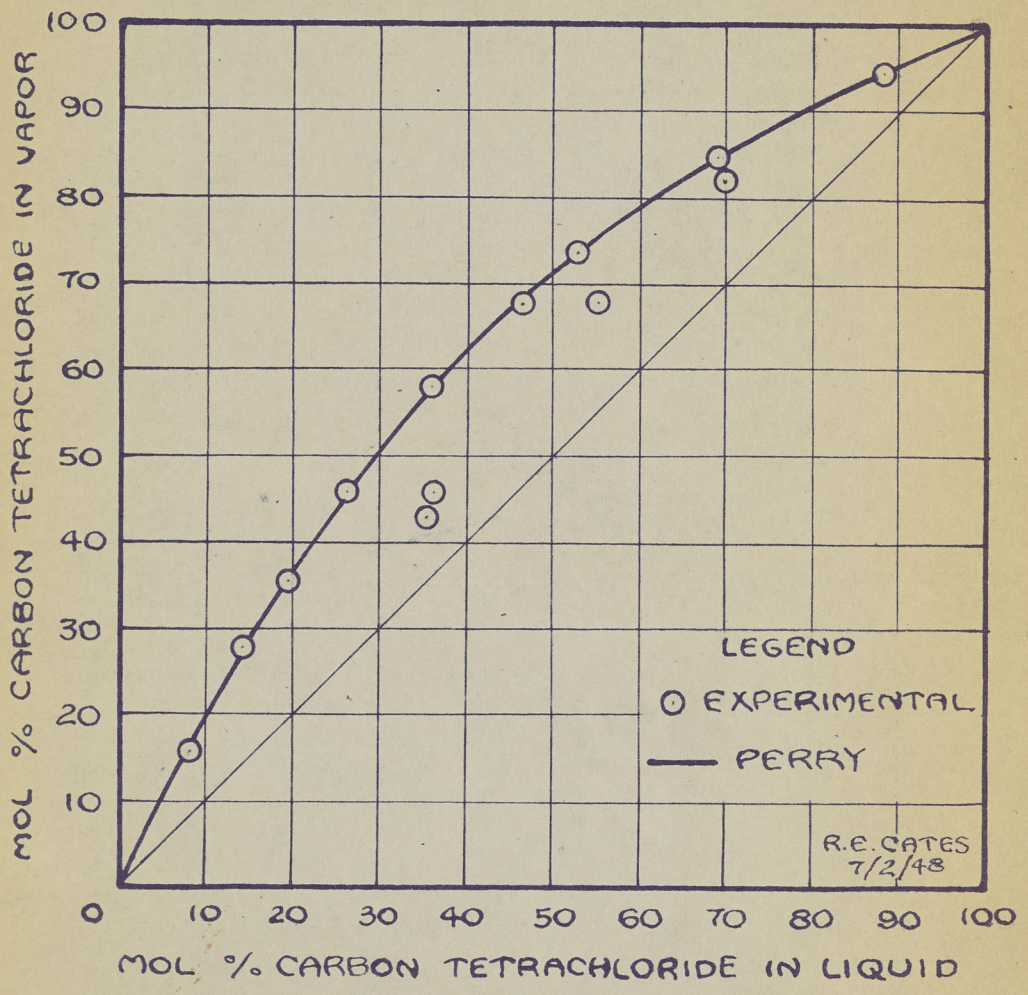

FIG. 3

EQUILIBRIUM DIAGRAM

SYSTEM CARBON TETRACHLORIDE-TOLUENE

AT 760 M.M.

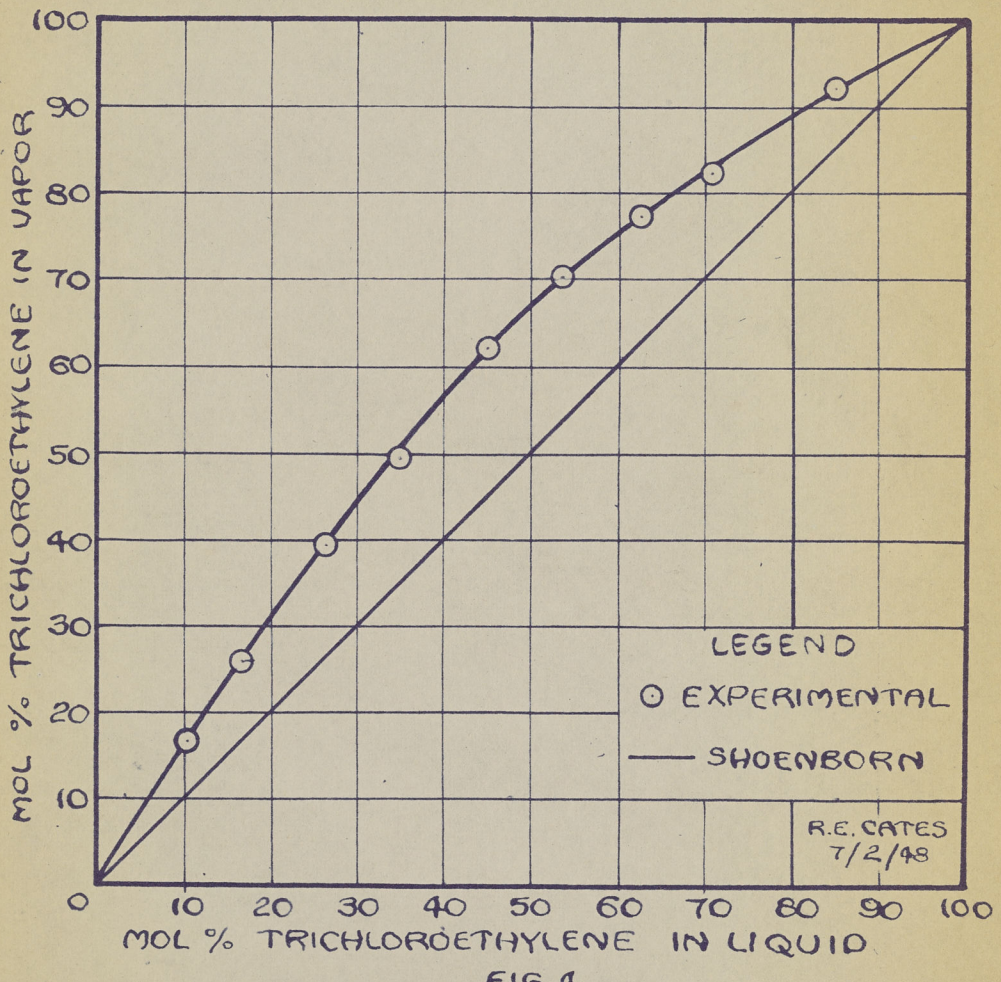

FIG. 4

EQUILIBRIUM DIAGRAM
SYSTEM TRICHLOROETHYLENE-TOLUENE
AT 760 M.M.

DISCUSSION OF RESULTS

The data obtained are given in Tables I and II and plotted in Figures 3 and 4 for comparison with known data. The known data for the system carbon tetrachloride-toluene were obtained from Perry[1] and for the system trichloroethylene-toluene from experimental data presented by Shoenborn, Koffolt, and Withrow[2]. The data obtained for both systems compare very favorably with the known data.

Figure 3 shows that runs No. 1 and 2 were in error by approximately 30 per cent. These runs were made using an original charge of 650 cc. and the system was not evacuated before heating. As a result of the enclosed air, the pressure in the system fluctuated widely and required constant adjustment of the heat input and water flow rate. Run No. 3 was made using the same size original charge but the system was evacuated before the run. It was immediately noted that the ease of control of pressure greatly increased. The error found for this determination was approximately 10 per cent.

Before making run No. 4, the system was drained and the charge re-introduced into the system with the vapor sample tap left open. It was noted that after approximately 500 cc. of charge had been introduced, siphoning action occurred through the condensate return pipe and the liquid flowed into the condensate collection chamber and out through the vapor sample outlet. Apparently, under the small pressure differential involved, the ball-check valve did not seat properly and permitted

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[1]Perry, J. H., Chemical Engineers Handbook, McGraw-Hill Co., New York, p. 1363. (1941).

[2]Shoenborn, E. M., Koffolt, J. H., and Withrow, J. H., Trans. AIChE, 37, 1003. (1941).

the flow to occur. Since a more sensitive check valve was not available, the size of the charge was reduced to 500 cc. Runs No. 4, 5, and 6 were made using the smaller charge and using a vacuum on the system. The data for these runs were found to give close correlation with known data.

It had originally been assumed that it was necessary to drain off the holdup in the sample lines before taking the actual samples. This procedure had been followed during the first six runs. Run No. 7 was made and samples were taken from the taps without draining off and discarding the holdup. The results for this run were approximately 3 per cent in error. Hence, the original assumption that the holdup in the sample lines was slow to reach equilibrium composition was proved to be correct and drainage of the taps before sample removal was carried out during the remainder of the determinations.

It was originally planned to determine equilibrium data for the unknown system toluene-ether after completing the evaluation of the system carbon tetrachloride-toluene. However, the use of this low-boiling system would have necessitated the addition of condenser-water cooling equipment to the apparatus. Due to the time involved, it was decided to determine data for another known system.

A run was made using the system acetone-water. Operation of the apparatus with this mixture was complicated by violent fluctuations in pressure, so extreme that equilibrium could not be attained. The liquid drained from the still was less than half of the initial charge and contained large quantities of a suspended brown solid, which later proved to be ferric hydroxide. The violent fluctuations in pressure

were apparently caused by decomposition of the acetone. No further runs were made using this system.

The system trichloroethylene-toluene proved to be non-corrosive to the still and a second set of determinations were made. No further difficulty was encountered in the use of the apparatus.

During the present work, the still was operated at distillation rates ranging from 130 to 150 cc. per minute. This corresponded to a complete turnover of the 500 cc. charge approximately every 3-1/2 minutes. If determinations were carried out according to Othmer's specification that the apparatus should be operated at equilibrium until time had been allowed for a turnover of 20 to 25 times the original charge, the time of operation at constant boiling temperature would be approximately 1-1/2 hours. Determinations were made in which equilibrium operation was maintained for periods as short as 15 minutes with no appreciable error in results. However, it was specified in the procedure that the apparatus should be maintained at equilibrium for at least 30 minutes before samples are taken.

The apparatus was constructed for a maximum pressure of 125 pounds per square inch, and by the use of high-pressure fittings the pressure range may be greatly increased. Although no determinations were made in the present work at pressures above 760 mm., it is believed that high-pressure operation of the system using the procedure outlined should give satisfactory results.

RECOMMENDATIONS

From experience gained in the use of the apparatus, the following recommendations are made:

1. The present large sample outlets should be replaced by small diameter copper tubing so that the holdup in the tubing will be negligible. This will eliminate draining of the sample outlets before samples are taken. If high-pressure work is anticipated, the present sample outlets should be left in place, since they are designed for the attachment of sample bombs.

2. A constant-head overflow tank should be added to the system to prevent fluctuations in the rate of water flow through the condenser. For low-boiling systems, this tank can be supplied with ice for cooling of the condenser water.

3. The present ball-check valve should be replaced by a check valve that is more sensitive. This is particularly necessary for high-pressure work to prevent surges of still pot liquid into the condensate collection chamber during the removal of samples.

4. The three-way switch now used for potentiometer-thermocouple connections should be replaced by a multi-point switch so that the wall temperature in the middle of the vapor chamber can be determined. If a multi-point switch is not available, two double-pole, double-throw switches may be used.

ACKNOWLEDGMENT

To Mr. Ben Thomas and to many others associated with the Chemical Engineering Department, for their helpful assistance and advice during the construction of the apparatus involved, grateful acknowledgment is hereby rendered.

APPENDIX

APPENDIX A

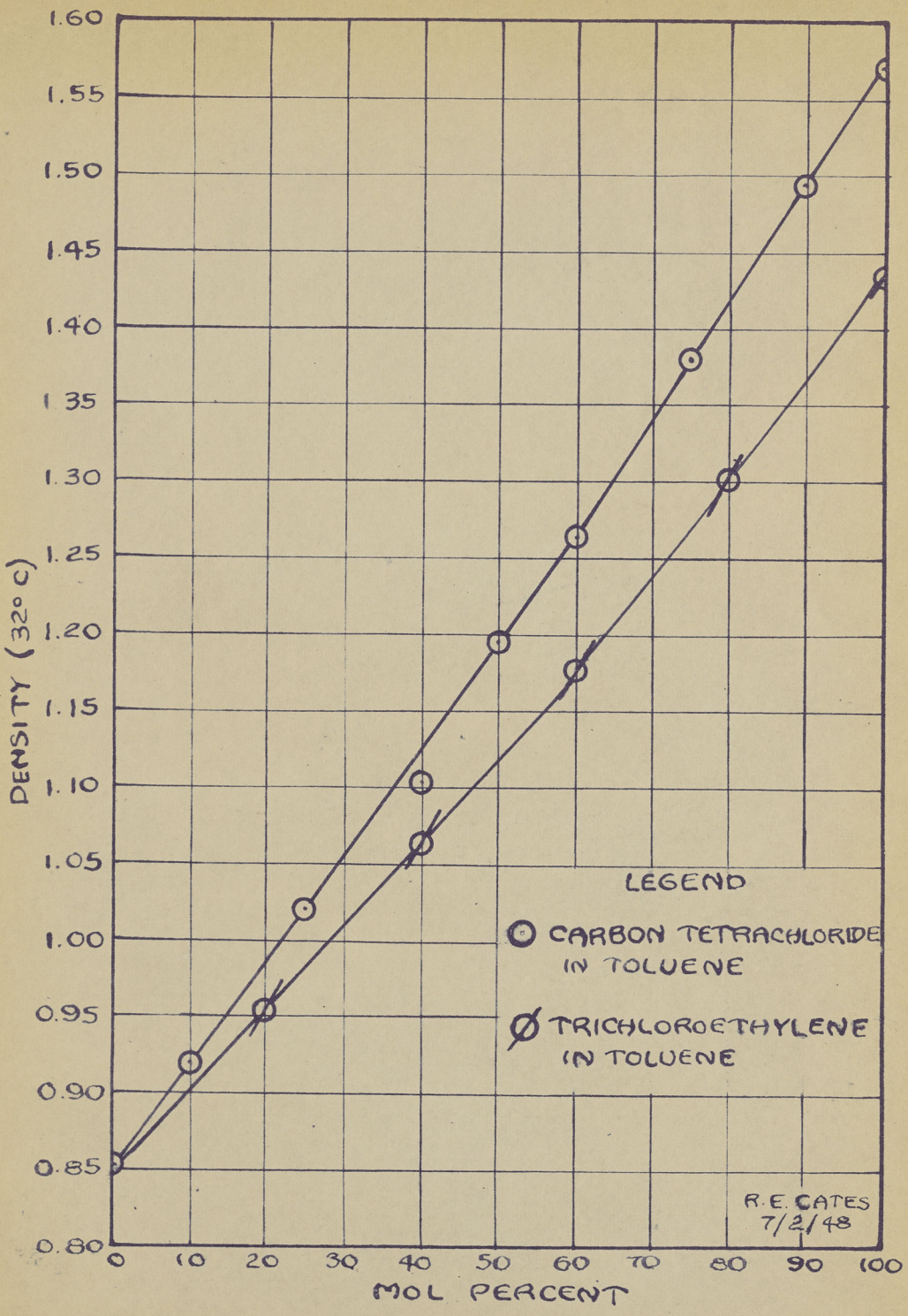
DENSITIES OF MIXTURES

a. Carbon tetrachloride-toluene

Mol % CCl_4	Volume % CCl_4	Density (32°C.)
0	0.0	0.852
10	9.1	0.920
25	23.34	1.021
40	37.5	1.104
50	47.4	1.196
60	57.5	1.263
75	73.0	1.380
90	89.0	1.494
100	100.0	1.572

b. Trichloroethylene-toluene

Mol % C_2HCl_3	Volume % C_2HCl_3	Density (32°C.)
0	0.0	0.852
20	17.5	0.955
40	36.2	1.063
60	56.0	1.177
80	77.25	1.302
100	100.0	1.435



DENSITIES OF MIXTURES

APPENDIX C

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

Name J. L. Oglesby

Title Instructor

Date August 6, 1948