THE OPERATION OF A VAPOR - LIQUID EQUILIBRIUM STILL AT ELEVATED PRESSURES

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FOR THE DEGREE OF

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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THE OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL AT ELEVATED PRESSURES

SUMMARY

In recent years, a demand for equilibrium data at elevated pressures has arisen. Equilibrium relationships for most of the more common binary systems are available in technical publications. However, these data are usually restricted to operation at atmospheric pressure. Thus, a need for a reliable method of obtaining such data is desirable.

The purpose of the present work was to collect equilibrium data at elevated pressures and to check the accuracy of these data. A vapor-liquid equilibrium still constructed by R.E. Cates[1] based on a design by Griswold, Andres, and Klein [4], as modified by Othmer [6] was used for this work.

The system trichloroethylene-toluene was investigated at pressures of 14.7 and 100 psia (pounds per square inch absolute). From the data taken, equilibrium curves were drawn and compared with curves calculated by Raoult's law. Agreement between the experimental and calculated data was found to be very good; the composition not varying over one per cent in the extreme cases. Hence, it was concluded that the system tends to approach Raoult's law at pressures of 14.7 and 100 psia.

INTRODUCTION

The separation of the components of a binary system is usually effected by taking advantage of the difference in the vapor pressures of the components. The component having the higher vapor pressure is more readily vaporized; thus, a vapor enriched with this component is obtained. From an examination of the statement above, it is seen that the composition of the vapor is a function of the vapor pressures of the pure components. Raoult's law predicts that for certain ideal systems, the partial pressures of the components is equal to the product of their respective vapor pressures and mol fractions in the liquid. For ideal gases, the pressure per cent is numerically equal to the mol per cent; thus, the composition of the vapor can be determined by calculating the partial pressures of the components. This statement becomes apparent if Dalton's law of partial pressures is remembered. This law stated that the total pressure of a gas is equal to the sum of the partial pressures of the components.

In actual practice, very few systems follow Raoult's law exactly, but many systems have been found to approach the predictions of this law to a degree where it is safe to assume the law is valid.

Theoretical values of X and Y used for comparison were calculated using a form of Raoult's law given by Dodge [3].

$$X = \frac{P - P_B}{P_A - P_B} \qquad Y = \frac{\alpha X}{1 + (\alpha - 1)X}$$

where,

X = mol fraction of A in the liquid

Y = mol fraction of A in the vapor

P = total internal pressure

P_A = vapor pressure of A

P_B = vapor pressure of B

α = relative volatility $= \frac{P_A}{P_B}$

For solution of these formulae, the vapor pressures of the components must be known. For many materials, including trichloroethylene and toluene, a plot of log P versus the reciprocal of the absolute temperature results in a straight line. The equation of this line is of the form,

$\log P = \frac{A}{T}$ plus B

By taking reference data from the literature for any two temperatures, two equations may be written and the constants in these equations determined. When this general equation is known, vapor pressures at any temperatures may be calculated. An alternative method is to plot available data on a log P vs $\frac{1}{T}$ graph and extrapolate to the desired temperature. The accuracy of this method is limited to the size of the plot, hence the former method is usually the more reliable.

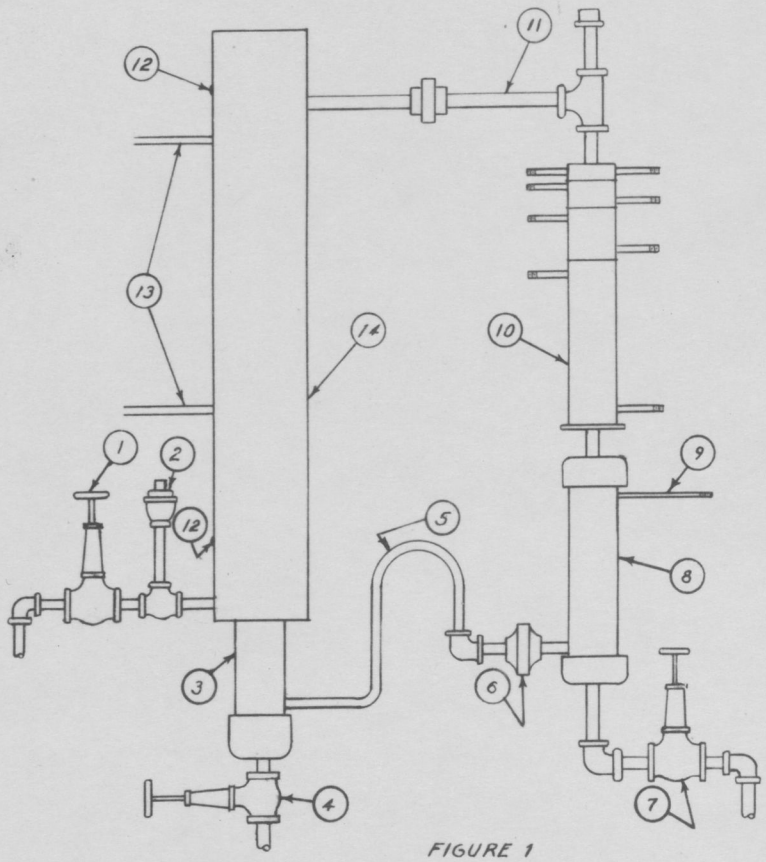


FIGURE 1
SKETCH OF APPARATUS

THE OPERATION OF A VAPOR-LIQUID EQUILIBRIUM STILL AT ELEVATED PRESSURES

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MATERIALS AND EQUIPMENT

The still used in obtaining the data in this work is based on a design proposed by Griswold, Andres, and Klein [4] and modified by Othmer[6]. The still was built at the University of Tennessee in 1948 by Robert E. Cates[1], and the construction of same is well covered in his thesis. Figure 1 is a sketch indicating the important parts of the apparatus.

The distinguishing features of this still are:

1. A ball check valve in the vapor return line to prevent surge of the liquid into the condensate collection chamber.

2. A variable condenser built in four sections of progressive lengths to permit variation in condensation rates.

3. Provisions for heating the vapor column to prevent condensation on the walls of the column.

4. A liquid sample trap to insure a representative sample.

In the present work, a constant head overflow tank was installed to give an even flow of cooling water to the condenser. This tank furnished water to the condenser with a potential head of approximately ten feet. Glass laboratory condensers were installed in the liquid and vapor sample lines to prevent "flashing" during sampling. Since it was necessary to remove the insulation from the still in order to reweld some of the joints, the 1/4 inch lagging was replaced by lagging approximately 1 inch thick. During tests at 14.7 psia, the pressure was determined by means of a standard U-tube manometer using Meriam

red oil (Specific Gravity 0.827) as the manometer fluid. At 100 psia, it was necessary to replace this manometer with a 160 psi Ashcroft American pressure gage. All valves in the system were replaced by 1/4 inch, 125 psi needle valves in order to eliminate leakage.

All materials used for the tests were analytical grade procured from the Chemistry Department. To prevent decomposition, 0.75 per cent pyridine was added to the trichloroethylene.

PROCEDURE

Somewhat different operating techniques were necessary in operating the still at the two pressures.

In operating at 100 psia, the still was charged by venting through the vapor sample tap and introducing the charge through the charging port. The system was operated using the largest section of the condenser in order to obtain more rapid condensation of the vapors. The pressure was adjusted to the desired value by manipulation of the variacs controlling voltage input to the base and column heaters. During the tests, the column wall was kept approximately 5° F above the temperature of the still pot to eliminate any condensation on the walls. When the desired pressure had been reached, the still was allowed to remain at this pressure for a minimum of thirty minutes before samples were taken. A potentiometer used in conjunction with the thermocouples was used to ascertain if the system was in equilibrium during this period. If only minor deflections were noted on the galvanometer during this period, samples were taken at the end of thirty minutes. The procedure in sampling was to open the sample valves slightly, allowing the sample to "bleed" into the laboratory condensers which were cooled by circulating water from the mains.

In tests at 14.7 psia, it was found that insufficient cooling water was supplied from the constant head tank to condense the vapors rapidly enough to maintain the low pressure. For these tests cooling water to the variable condenser was supplied directly from the mains. After charging, the still was evacuated to a total pressure of approximately 10 psia, removing the bulk of the air and making control

of pressure easier. This was affected very simply by building up a pressure of approximately 30 psig, decreasing the pressure rapidly by opening the vapor sample valve and closing immediately. When the still was allowed to cool, a partial vacuum was created by the contraction of the cooling gases. This method proved very satisfactory.

This procedure is essentially the one outlined by Cates[1], with modifications which were found to facilitate operation.

The samples were analyzed by determining the buoyancies of the samples relative to that of water at 32° C using a chainomatic balance and the float from a Wesphal balance. From these data the specific gravities of the samples were calculated. The composition - specific gravity curve in Appendix C was used to determine the composition of the samples. These data were obtained from Cates'[1] thesis.

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LABORATORY DATA

TABLE I

THE SYSTEM TRICHLOROETHYLENE-TOLUENE AT 14.7 PSIA

Run No.	Manometer Reading (Cm. of oil)	Barometric Pressure (psia)	Total Internal Pressure (psia)	Density of Liquid (32°C)	Density of Vapor (32°C)	Mol % C_2HCl_3 in Liquid	Mol % C_2HCl_3 in Vapor
1	25.6	14.40	14.7	1.305	1.365	81	90
2	25.6	14.40	14.7	1.142	1.240	54	71
3	29.8	14.35	14.7	1.010	1.105	31	48
4	29.8	14.35	14.7	0.915	0.965	12	22

THE OPERATION OF A LIQUID-VAPOR EQUILIBRIUM STILL AT ELEVATED PRESSURES

TABLE II

THE SYSTEM TRICHLOROETHYLENE-TOLUENE AT 100 PSIA

A. LABORATORY DATA

Run No.	Gage Reading (psi)	Barometric Pressure (psi)	Total Internal Pressure (psi)	Density of Liquid (32°C)	Density of Vapor (32°C)	Mol % C_2HCl_3 in Liquid	Mol % C_2HCl_3 in Vapor
1	86	14.4	100.4	0.950	1.012	19	31
2	86	14.4	100.4	1.031	1.111	34	49
3	86	14.3	100.3	1.135	1.210	52	66
4	86	14.3	100.3	1.325	1.382	84	92

B. CALCULATED DATA

Temperature °R	$P_{tol.}$ (psi)	$P_{tri.}$ (psi)	$\frac{P_{tri.}}{P_{tol.}}$	X	Y
777	51.4	100	1.945	1	1
790	60.4	115	1.908	0.725	0.834
800	69.2	129	1.865	0.515	0.665
805	70.9	138	1.945	0.434	0.598
810	75.9	144.8	1.908	0.350	0.507
815	81.4	155	1.905	0.253	0.394
825	91.3	170	1.862	0.1105	0.188

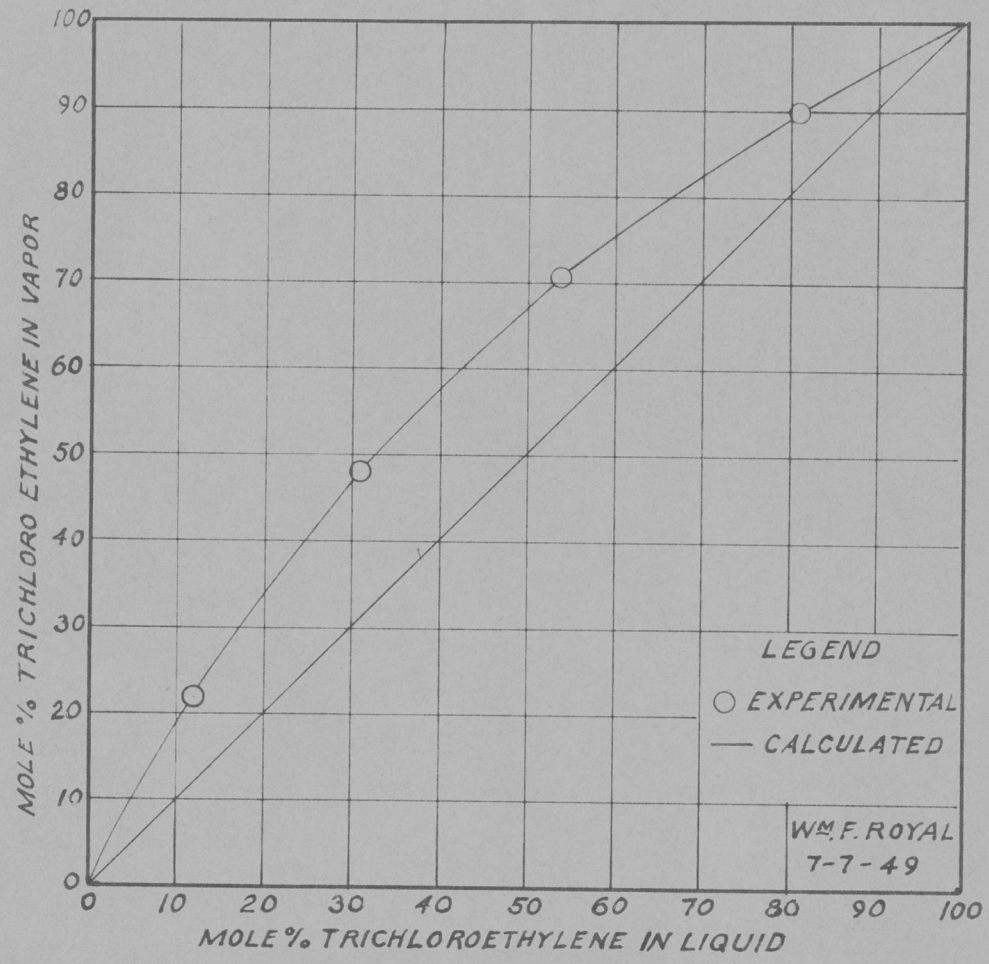


FIGURE 2

EQUILIBRIUM DIAGRAM

SYSTEM TRICHLOROETHYLENE-TOLUENE

AT 14.7 P.S.I.A.

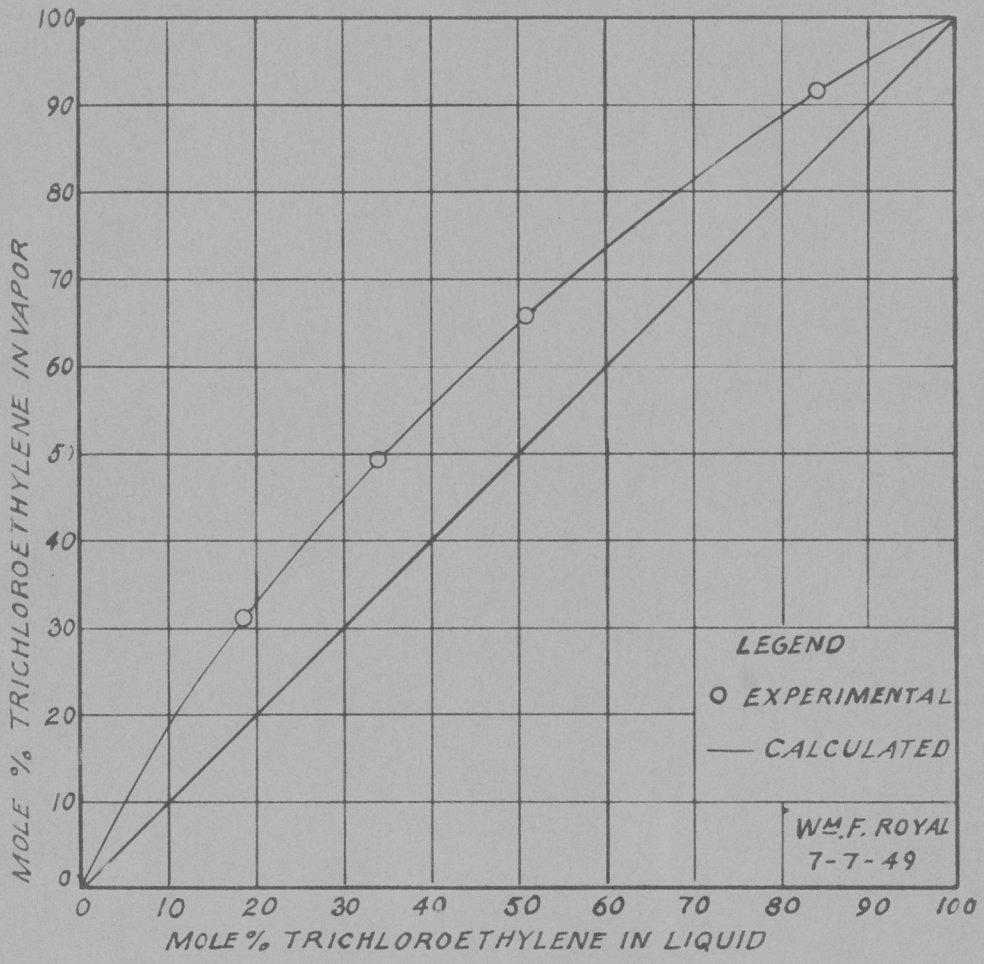


FIGURE 3

EQUILIBRIUM DIAGRAM

SYSTEM TRICHLOROETHYLENE-TOLUENE

AT 100 P.S.I.A.

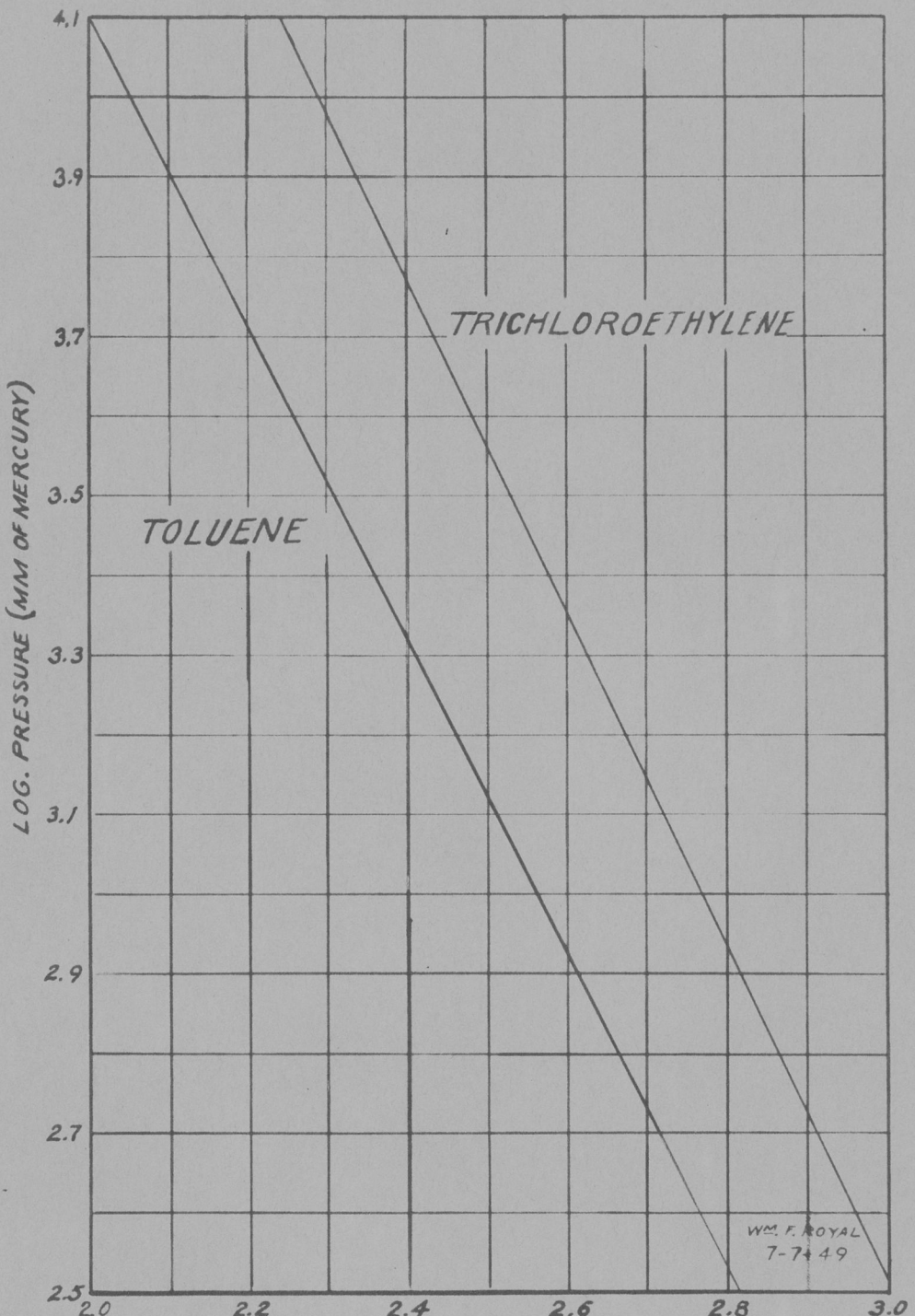


FIGURE 4

VAPOR PRESSURES OF THE PURE COMPONENTS

DISCUSSION OF RESULTS

Data obtained in the present work, both calculated and experimental, are tabulated in Tables I and II. Values of X and Y used for comparison were calculated by Dodge's[3] modification of Raoult's law, at 14.7 psia. The calculated values were found to be in agreement with experimental data determined by Schoenborn, Koffolt, and Withrow[7]. Maximum deviation of experimental data determined in this work did not exceed one per cent.

In preliminary tests, difficulty was encountered while trying to correlate the experimental data with known data. On continued operation the samples showed a marked turbidity, which proved to be due to a suspension of ferric chloride. An investigation showed that the trichloroethylene was decomposing at the higher pressures, liberating hydrochloric acid which attacked the still forming ferric chloride. The apparatus was flushed well and charged with a saturated solution of soda ash. This charge was allowed to boil for forty-eight hours. The still was then flushed with running water for one hour and boiled with water for another forty-eight hours. Following a final flushing and drying, the still was again placed in operation. Analytical grade reagents were procured from the Chemistry Department for all remaining tests. It was observed that if more than two tests were made without recharging the still with fresh materials, the samples again became turbid; thereafter, the still was drained and recharged after each test. No further contamination was observed.

In the operation of the still, it was found that the temperatures recorded for liquid and vapor were unreliable. It appears that heat is conducted quite readily from the walls of the column to the thermometer wells; thus, a temperature which is approximately the temperature of the walls is observed.

A constant head tank was installed to supply cooling water to the variable condenser. This tank was found to be inadequate for work at atmospheric pressure. The maximum cooling water rate furnished by this tank would not condense the vapors rapidly enough to prevent an excessive pressure build-up. It was necessary to obtain cooling water directly from the water mains, which have a pressure of 120 psig.

By comparing Figure 2 and 3, it is observed that increasing the pressure tends to depress the equilibrium curve very slightly. This phenomenon is best explained by Figure 4. Plotting log P versus $\frac{1}{T}$ for the pure components, it is observed that the lines are almost parallel. Since the rates of increase are approximately the same, it follows that the ratios of the individual pressures to the total pressures would change very slightly as the pressure is raised. In general, an increase in pressure tends to decrease the spread of composition between the vapor and liquid phases. Data for Figure 4 was obtained from Lange[5], and from an E.I. Dupont Bulletin entitled "Chlorinated Hydrocarbons"[2].

RECOMMENDATIONS

From observed operating characteristics of the still, the following recommendations are made:

1. Before any further work is done, the still should be decontaminated by boiling in caustic until no traces of ferric chloride are observed.

2. The constant head tank should be eliminated, or provisions made to supply water from the tank under pressure.

3. A recent bulletin from the E.I. Dupont DeNemours and Company[2] states that trichloroethylene should not be used at temperatures above 248°F, if decomposition is to be avoided. Future work should meet this limitation.

4. In all cases where tests are being made on the system trichloroethylene-toluene, approximately one per cent pyridine should be added to the trichloroethylene to prevent decomposition.

5. The thermometer wells should be reconstructed so that true liquid and vapor temperatures may be read.

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APPENDICIES

APPENDIX A

SAMPLE CALCULATIONS

(1) Calculation of vapor-liquid equilibria by Dodge's[3] modification of Raoult's law.

$$X = \frac{P - P_B}{P_A - P_B} \qquad Y = \frac{\alpha X}{1 + (\alpha - 1)X}$$

where,

P = Total internal pressure

P_A = Vapor pressure of trichloroethylene

P_B = Vapor pressure of toluene

X = Mol fraction of trichloroethylene in liquid

Y = Mol fraction of trichloroethylene in vapor

α = Relative volatility = $\frac{P_A}{P_B}$

EXAMPLE: At temperature of 800° R and total pressure of 100 psia,

P_A = 129 psi

P_B = 69.2 psi (from Figure 4)

$$\alpha = \frac{P_A}{P_B} = \frac{129}{69.2} = 1.865$$

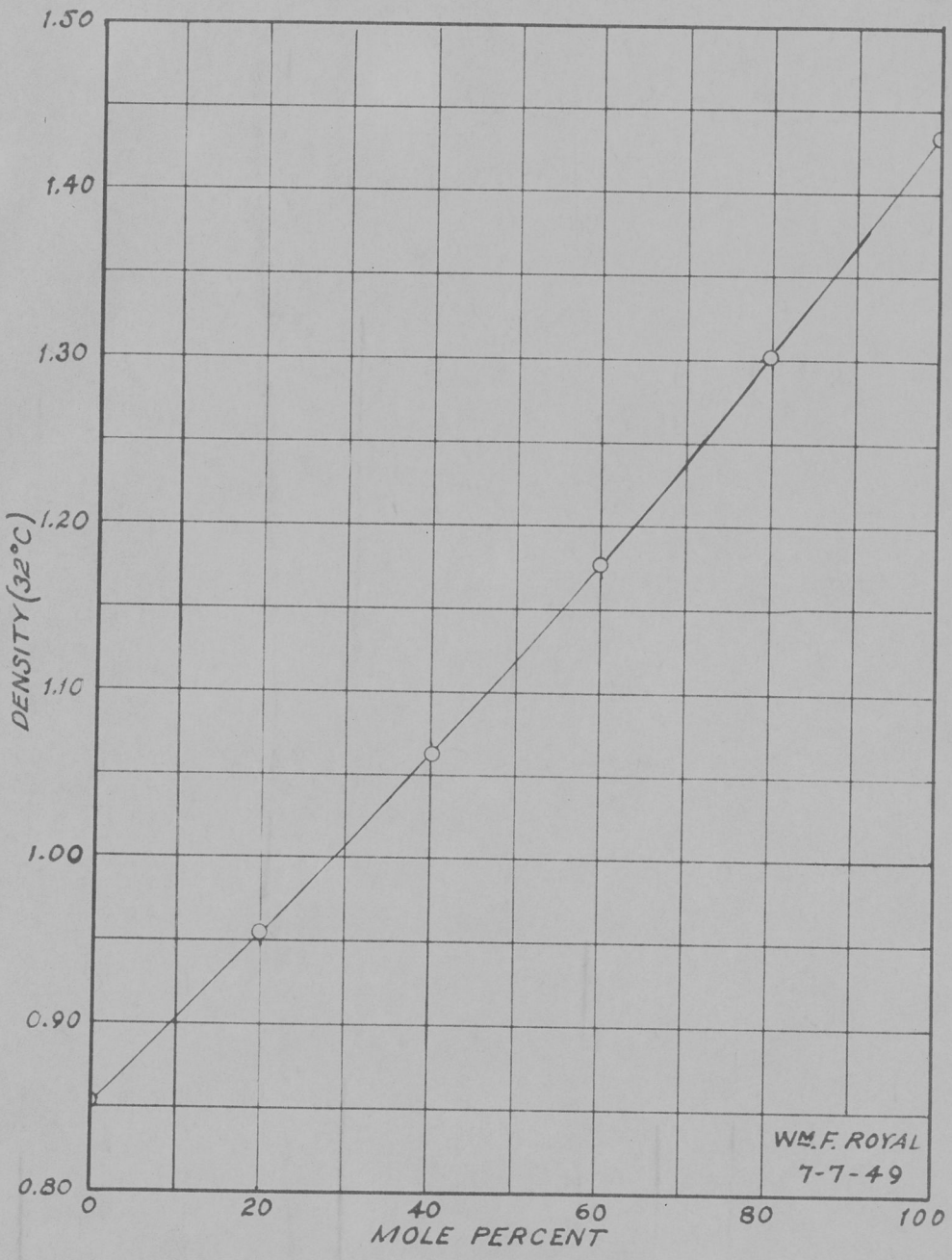
$$X = \frac{P - P_B}{P_A - P_B} = \frac{100 - 69.2}{129 - 69.2} = \frac{30.8}{59.8} = 0.515$$

$$Y = \frac{\alpha X}{1 + (\alpha - 1)X} = \frac{(1.865)(0.515)}{1 \quad (1.865 - 1)\ 0.515} = \frac{0.961}{1.445} = 0.665$$

APPENDIX B

DENSITIES OF TRICHLOROETHYLENE IN TOLUENE (1)

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 TRICHLOROETHYLENE IN TOLUENE

APPENDIX D

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.

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Date 23 July 1949