ABSORPTION OF CARBON TETRACHLORIDE IN A LIGHT OIL

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INTRODUCTION

The Chemical Engineering Department of the University of Tennessee desires to find a system suitable for a laboratory experiment to illustrate the principles of absorption. Most absorption apparatus of the laboratory type are designed for the absorption of carbon dioxide in caustic solutions. This system, however, involves chemical reactions in addition to pure absorption. It is desired to find a noninflammable system which involves only pure absorption. The present work is an investigation of one such system on a small scale.

The purpose of the present work is to determine the equilibrium between various concentrations of carbon tetrachloride in a light oil (Atlantic Refining Co, Oil "A".#) and carbon tetrachloride in air at different temperatures. Since it was desired to determine the applicability of the system to a laboratory experiment, some minor consideration is given to the rates of absorption and of desorption.

For specifications of oil, see appendix.

GENERAL SURVEY OF FIELD

As in many chemical engineering operations, the theory of gas absorption was developed many years after its practical performance was started. Therefore, the design of absorption equipment has followed widely divergent lines. This variety is justified to some extent by the wide variations of purpose and specification of such equipment. However, since Whitman introduced the two-film theory in 1923, some progress has been made toward unifying gas absorption equipment. [1]

Theory

The literature contain several good discussions of the theory of absorption.[2] It is sufficient to state here that gas absorption is a diffusion process in which a gas passes through a film of an inert gas, enters a liquid at the liquid-gas interface, and then diffuses through a liquid film into the body of the liquid. The liquid and the gas at the interface are assumed to be in equilibrium with each other. The rate of absorption depends upon the thickness of the films, upon the concentration or partial pressure differences between the

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1. J.H. Perry, Chemical Engineers' Handbook, p. 1007 McGraw-Hill, 1934.
2. Cf. T.K. Sherwood, Absorption and Extraction, McGraw-Hill, 1937.

interface and the body of the fluids, and upon the physical properties of the fluids. When a gas and a liquid are in equilibrium, there is no concentration or partial pressure difference between the interface and the body of the liquid or gas and no absorption or desorption takes place.

Equipment

No information was found in the literature on the system used in the present work, but some studies of a similar nature were found. Much has been written on the absorption of carbon dioxide in caustic solutions, but this system is so unlike the one studied that it was not much help except for giving suggestions as to the general design of the equipment. The work of Simmons and Long[3] was more help in the design of the equipment. They studied the absorption of benzene in a light oil in a small absorption column. The benzene was added to the air by passing preheated air through a bubble tower, the amount of benzene in the air being controlled by regulating the temperature of the entering air. They did not mention the method used to analyze the liquid and their method of analyzing the gas was not applicable to the present case. The general design of the absorption tower was patterned after their equipment. Sherwood[4] used an apparatus similar to the one

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3. Simmons and Long, Ind. Eng. Chem. 22, 718-22 (1930)

4. Sherwood, Ind. Eng. Chem. 30, 765-9 (1938)

used in this work in studying flooding velocities. His work was helpful in redesigning the vents to give a closed system.

Chilton and Vernon[5] state that initial distribution of the liquid over the column packing is of prime importance and that the vapor velocity and minor changes in the liquid rate have little influence on distribution. For this reason some care was given to the design of the liquid distributor.

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5. Chilton and Vernon, Trans. Am. Inst. Chem. Engr., 31, 296-315 (1935)

GENERAL THEORY

Gas Absorption

Gas absorption in the usual sense involves the transfer of gas from the gas phase into a liquid in which it is more or less soluble. In the design of equipment one is concerned with two major aspects of the problem. First, if the gas and the liquid are left in contact with each other for such a time that equilibrium is obtained, what will be the resulting compositions of the liquid and gas phases? Second, if liquid and gas phases are brought into contact for a limited time, what will be the rate at which absorption will take place? In the present work the first question was studied. The rate of absorption in any system depends upon the thickness of a gas film and of a liquid film, and upon the differences in the concentrations of the phases and the concentrations at equilibrium. The equilibrium conditions are discusses more fully below.

Solubility of Gases

Different gases will exhibit very great differences in the partial pressures that their solutions exert at equilibrium. Three general cases may be distinguished as regards the nature of the gas and liquid involved:[6]

(a) a chemical reaction takes place such that the gas

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6. Perry, op. cit. p.1007-12.

will not exert an appreciable vapor pressure after absorption; (b) a chemical reaction takes place, but the compound formed is sufficiently unstable for the dissolved gas to exert an appreciable vapor pressure; (c) no chemical reaction takes place, and the liquid exerts a pressure of the gas dependent only on the temperature and the concentration of the gas in the liquid phase. Applications falling in case (c) are the easiest to handle, especially if the system is of such a nature that the solubility of the gas follows Henry's Law.

The solubility of gases in liquids is limited, the extent to which they dissolve depending upon the pressure, the temperature, and the nature of the gas and the solvent. The number of gas molecules entering a liquid at its surface is proportional to the concentration of the molecules in the gas phase, C_2, and the number of molecules leaving the liquid is proportional to the concentration of the dissolved gas, C_1, in the liquid. Then, at equilibrium in a saturated solution, the rate of escape of dissolved molecules from the liquid to the gas phase is equal to the rate at which molecules dissolve in the liquid from the gas phase and

$$K_1 C_1 = K_2 C_2 \qquad (1)$$

where K_1 and K_2 are proportionality constants.

Then $$C_2 = \frac{K_1}{K_2} C_1 = K C_1 \qquad (2)$$

Equation (2) is an expression of Henry's law. The concentration in the gas phase is usually expressed in terms of

partial pressure, and Henry's law may be written

$$P = KC \qquad (3)$$

Modifications of the form in which the concentration in the liquid phase is expressed will sometimes broaden the range over which Henry's law holds.[7]

Raoult's law states that the vapor pressure of a dissolved gas or vapor is equal to the vapor pressure of the gas times its mol-fraction in the liquid. Thus Raoult's law is the same as Henry's law for the special case where Henry's constant is equal to the vapor pressure of the pure solute. The mathematical expression of Raoult's law is as follows:

$$P = P_o \times \text{mol-fraction solute} = P_o N_1 \qquad (4)$$

where P is the vapor pressure of the solute from the solution, P_o is the vapor pressure of the pure solute and N_1 is the mol-fraction of the solute.

The solubility of a gas is changed by the total pressure when the latter is large. This effect is small below about five atmospheres and is neglected in all but high pressure work.[8]

Influence of Temperature on Equilibrium

The following theoretical equation has been derived

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7. Walker, Lewis, McAdams, and Gilliland, Principles of Chemical Engineering, p.434, 3rd. ed. McGraw-Hill (1937)

8. Badger and McCabe, Elements of Chemical Engineering, p.386, 2nd. ed. McGraw-Hill (1936)

to show the influence of temperature on chemical equilibrium:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \qquad (5)$$

This van't Hoff equation is a very important relationship which is used for calculating heats of reaction from chemical equilibria and for calculating equilibrium constants at different temperatures. "In fact, the equilibrium constant, K_p, can be extended to include any type of equilibrium, such as reactions of gases or solutes, vaporization of liquids, and solubility or sublimation of solids."[9]

Over small temperature changes, ΔH can be assumed to be constant, and the integration of the above equation gives

$$\ln K_p = \frac{-\Delta H}{R}\left(\frac{1}{T}\right) + C \qquad (6)$$

If the values of $\ln K_p$ are plotted against $1/T$, a straight line results. The heat of reaction, ΔH, can be calculated from the slope of the line as follows

$$-\Delta H = \text{slope} \times R \qquad (7)$$

The value of the integration constant, C, in equation (6) can be determined from experimental values of K_p at definite temperatures.

Methods of Obtaining Equilibrium Data

Bottle method: When a solution is placed in a closed vessel with a gas above it, the volatile parts of the solu-

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9. Getman and Daniels, Outlines of Theoretical Chemistry, pp.278-80, 6th, ed. John Wiley (1937)

tion will vaporize until the space above the liquid is in equilibrium with the liquid. If a solution of a gas is placed in a closed container and allowed to stand long enough under a given set of conditions, it should come to equilibrium. If the solution and the gas above it are then sampled and analyzed, the equilibrium point should be established for those conditions. This method was tried in the present work, but was found to be unsatisfactory.

Columns: Industrial apparatus for gas absorption may usually be classified as one of three quite different types, each having as a principal objective the promotion of interphase contact between the gas and the liquid.[10] These types are (a) packed towers, (b) bubble cap or plate towers, and (c) miscellaneous, including spray towers. The various forms of bubble towers are particularly suited for cases where the liquid film resistance is the controlling factor, since the liquid film resistance is greatly reduced by the motion of the bubbles upward, but the gas film resistance is relatively great because of the lack of turbulent mixing within the bubble. The spray towers are best suited for use in cases where the gas film normally controls. The drops falling and spinning through the gas attain a fairly high velocity relative to the gas, making

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10. Sherwood, Absorption and Extraction, p.68, McGraw-Hill, (1937)

the gas film resistance low. The movement of the solute within the drop is by diffusion since the liquid in the drop is almost stationary. Therefore, the liquid resistance is high. Packed towers may be used where the gas film, the liquid film or both control, since both the gas and the liquid are in violent turbulence. However, the interfacial area per unit tower volume is much less than for the other types. Since it was thought that both films would be important in this work, a packed tower was used.

DESCRIPTION OF THE METHOD AND APPARATUS USED

Packed Tower Method

Since the Chemical Engineering Department is planning to erect a packed tower absorption system, a packed tower was chosen for this work. It was hoped that the information obtained would be of value in designing the large absorption tower. Primary consideration was given to the determination of the equilibrium points between the carbon tetrachloride in the oil and that in the air. At first, it was intended to make an absorption and a desorption run under the same set of conditions and extrapolate the curves obtained until they crossed, the point of crossing being taken as the equilibrium point for those conditions. Later it was found that the air leaving the column was practically in equilibrium with the oil entering the column. The larger part of the equilibrium data was obtained from the assumption that equilibrium existed at the top of the column.

Apparatus

A flow sheet of the apparatus is given in the appendix, figure 7. The apparatus consisted of a packed tower (14), liquid circulation system, air circulation system, gas and liquid heaters (10 & 18), bubble tower (8), wicks (9), thermometers (11, 20 & 23), Westphal balance, and Orsat apparatus (12).

The packed tower was 1-13/16 inches I.D. by 60 inches long and was packed to a height of 46½ inches with ¼ inch raschig rings.

The liquid circulation was maintained by a positive displacement gear pump (17). The liquid head was maintained constant by a constant head tank (19). The liquid distributor (21) was made from an ordinary glass funnel, the sides of which were cut down to about two-thirds the diameter of the column. The liquid rate was determined by catching the liquid leaving the column for a definite time and weighing it on a Fairbanks scales (25), (0 -21 pound range, 0.01 pound graduations).

The gas circulation system was maintained by a water cooled air pump (2). The rate of flow was determined by a calibrated orifice (5). A large bottle (4) was placed between the air pump and the orifice to eliminate small variations in the air rate. The outlet gas was recirculated through the system.

The oil heater (18) was made of number 22 nickel-chromium resistance wire wound around ¼ inch glass tubing. It was 25 inches long and wound with just sufficient pitch for the wire not to touch. The gas heater (10) was made of the same wire, but the coil was placed inside of a 5/8 inch glass tube which was 28 inches long.

The bubble tower (8) was 1-13/16 inches inside diameter and 15¾ inches long. An ordinary test tube (6) was

inverted over the gas inlet tube to make the gas bubble through the carbon tetrachloride. Later it was found sufficient merely to let the air pass over a wick (9) wet with CCl_4. This was done by placing the wick on the lower end of a separatory funnel (13) and allowing it to extend into the bubble tower. It was found necessary to equalize the pressure by connecting the top of the funnel to the bubble tower.

The temperature of the system was determined by 0 - 220°F. thermometers (11, 20, 23) placed in small bottles in the lines. The specific gravity of the oil-carbon tetrachloride solutions was determined with a Westphal balance. The Orsat apparatus was connected to the gas inlet and outlet lines by a two-way stop cock.

DIFFICULTIES OF THE WORK

The chief problems arising in this work were those of producing and maintaining the desired compositions in the gas entering the column, maintaining the constant liquid and gas rates, analysis of the gas and oil, and producing and maintaining the desired temperatures.

Liquid Flow

The oil was fed to the column from a constant head tank and distributed at the top of the column by a cone-shaped distributor (an inverted funnel) which gave a ring of liquid falling at about three-fourths distance from the center of the column. Trouble was encountered in the air blowing back through the liquid inlet at the top of the column. At first, this was overcome by carefully regulating the liquid and gas rates. Later, the constant head tank was vented to the discharge line at the top of the column. Before venting the tank to the discharge line, small changes in back pressure had an appreciable effect on the liquid rate. The venting practically eliminated this effect. The most serious changes in the liquid rates were cause by bubbles collecting in the liquid feed line. These bubbles partially obstructed the line and on several occasions completely stopped the liquid flow.

At first, considerable difficulty was experienced in maintaining a constant level in the bottom of the tower,

due to the syphon effect of the liquid seal. A vent was placed at the top of the liquid seal to break the syphon, and this trouble was eliminated. However, because of the pressure in the bottom of the column, it was necessary to place a control valve on the liquid outlet line.

Air Flow

The air rate was measured by a calibrated orifice and maintained by a water cooled pump. The air flow had to be constant to eliminate changes in the liquid rate and in the amount of carbon tetrachloride in the air.

Feeding Carbon Tetrachloride to Air

Feeding carbon tetrachloride to the air at a constant rate was one of the major problems of the work. At first, a small electric evaporator was thought sufficient, but this gave much too large a rate. Next a bubble tower was used. The amount of carbon tetrachloride added was to be regulated by adding sensible heat to the air and by varying the level in the tower. It was found that no sensible heat was required to give the desired amount of carbon tetrachloride in the air. In fact, part of the air had to be by-passed around the column. By by-passing part of the air, the carbon tetra chloride partial pressure could be lowered as desired, but could not be maintained constant because of the fact that a very small change in the air velocity or in the carbon tetrachloride level upset the

balance. The method finally used was an arrangement of wicks on the carbon tetrachloride feed line. The CCl_4 was added as desired from a separatory funnel which was connected to the bubble tower in such a way as to equalize the pressure. By this method it was possible to hold the carbon tetrachloride percentage near a constant value by regulating the amount added to the wick. However, as equilibrium was approached, it was found necessary to run part of the air in the return line into the atmosphere. On desorption runs the concentration in the air was regulated by changing the amount of the gas recirculated.

Analysis of the Oil

It was first attempted to determine the concentration of the CCl_4 in the oil from the refractive index of the solution, but it was found that the oil had practically the same refractive index as carbon tetrachloride. The method used for the analysis was the determination of the specific gravity of the solutions with a Westphal balance. By this method the concentration could be determined within about 0.3%.

Analysis of the Air

The concentration of the CCl_4 in the air was determined at first from a system of wet and dry bulb thermometers. The method was found to be inaccurate because the partial pressure of the CCl_4 in the relatively small amount

of air passing through the system was appreciably changed by passing over the wet bulb. The method used consisted of absorption of the CCl_4 in oil in a standard Orsat apparatus. Each sample of gas was run through two bulbs and as soon as the oil in the second bulb began to absorb CCl_4 the oil in the first bulb was changed. The Orsat apparatus was such that the concentration in tha air could be determined only to $\pm 0.1\%$.

Temperature Regulation

To find true equilibrium points it was necessary to regulate the temperature rather carefully. All runs were made at room temperature or above. In those runs made above room temperature, the oil was heated by a coil of resistance wire wound around a glass tube. This coil was covered by asbestos paper held in place by friction tape. The current flowing in the coil was regulated by changing the voltage with a Variac auto-transformer. The air was heated by a similar coil placed within a glass tube. Again the current was regulated with a Variac.

Vents

At first, the vents were all open to the air and it was noticed that much CCl_4 escaped through them. This was remedied by connecting all vents to the outlet line and recirculating this gas.

OPERATION

Preliminary Preparations

Oil was added to the resirvoir and the circulation pump started. The inlet line to the column was then opened and oil was allowed to flow through the column for some time before the air flow was started. While the oil was thus circulating, carbon tetrachloride was added to the CCl_4 reservoir and the Orsat apparatus checked for leaks. The entire system was brought to the desired temperature by regulating the current in the heating coils. After the oil had circulated for some time, air was started and regulated to the desired rate. Carbon tetrachloride was then started into the air stream and regulated according to Orsat analysis (rough analysis at first — correct analyses as desired regulation was approached). The flow of carbon tetrachloride from the storage tank had a tendency to decrease gradually with time, thus requiring close attention by the operator.

Making of Run

At the beginning of a run analyses of the inlet air and the inlet and outlet oil were made. An analysis of the outlet air was made 15 minutes after the run was started. The analyses were repeated at 30 minute intervals. The liquid rate was checked at the start of the run and at 30 minute intervals thereafter. Rough inlet air analyses

were run between the recorded analyses as was thought desirable to maintain the correct gas concentration. The run lasted for three to five hours, until equilibrium was approached as evidenced by the small change in concentration in the oil between analyses. As each analysis was completed, the log of the concentration was plotted against the log of the time (See figures 1 and 2).

Desorption runs were similar to absorption runs except that no addition of carbon tetrachloride to the air was required until equilibrium was approached. The gas concentration was regulated by by-passing part of the returning gas to the atmosphere. As equilibrium was approached, leaks in the system necessitated the addition of a small amount of carbon tetrachloride.

All runs in this investigation were made with the inlet gas containing 4% CCl_4 by volume. The temperature ranged form 81°F to 115°F. The gas leaving the column contained from 3 to 6% carbon tetrachloride by volume. On the assumption that equilibrium existed at the top of the column, equilibrium data were obtained for CCl_4 concentrations in air of from 3 to 5%.

OBSERVATIONS

Temperature Drop

Near the start of an absorption run at 100°F. the temperature drop through the column was only about one or two degrees. As the equilibrium was approached the temperature drop increased to about five degrees. At the start of a desorption run the temperature drop was about eight degrees and this decreased to about five degrees as the equilibrium was approached. This change in the temperature drop could be due to nothing but the heat of absorption of CCl_4 in oil. The heat of absorption was calculated from the equilibrium data and found to be 7160 calories per gram-mol or 84.0 B.t.u. per pound.# The heat of vaporization of CCl_4 is 7120 calories per gram-mol (83.5 B.t.u. per pound).

Oil Color Change

The color of the oil became darker on heating even to moderate temperatures. A sample of the oil heated to approximately 150°C (300°F.) became almost black. A noticeable color change took place at the low temperatures (115°F) used in this experiment.

Packing Material

The packing material used seemed not very well suitted

See "Correlation of Data"

for the system. An oil film formed on the end of the rings, thus preventing gas from passing through them. This film was formed because of the small opening in the rings.

SOURCES OF ERROR

Irregularity of Per Cent Carbon Tetrachloride in Air

Even with the most careful regulation, the per cent carbon tetrachloride in the air could not be kept absolutely constant. This was more evident as smaller amounts were required. However, it is believed that the partial pressure of CCl_4 over an entire run was practically the required value. This variation would not effect the final equilibrium point, but it would effect the rate of approaching equilibrium.

Variations of Oil Rate

The oil rate showed wide variations in any particular run. Changes in the oil rate did not effect the final equilibrium, but they did effect the rate of approaching equilibrium. Combined with the irregularities in the air partial pressures, they throw strong doubt on the accuracy of the equilibrium points obtained from the rate of absorption and desorption curves.

Limit of Analyses

The recorded concentrations of the gas is subject to an error of ± 0.1%. The graduations on the gas burette were 0.2% and the 0.1% readings were estimated. This estimation was hard to make on the zero readings because of the shape of the burette.

The oil analysis is subject to an error of ± 0.3%. The gravity of the solution changed so much with the temperature that it was difficult to obtain the gravity exactly.

Assumption of Equilibrium at Top of Column

The assumption that equilibrium existed at the top of the column may not be entirely justified where there was a large concentration change in the gas passing through the column. As the entire system approached equilibrium there was a small concentration change through the column and it is likely that the gas leaving the column was in equilibrium with the oil entering. For this reason the curve of figure 3 was not drawn according to the best line indicated by the points, but was rotated enough for it to pass through the origin. It is thought that this line gives the approximate value of the equilibrium.

CORRELATION OF DATA

It was found that by plotting the logarithm of the per cent carbon tetrachloride in the oil against the logarithm of the time, a straight line was obtained for both the absorption and the desorption runs. The data were plotted in this manner as shown in figures 1 and 2. It was assumed that the absorption and desorption runs at one temperature would cross at the equilibrium point. As seen from the curves, this method did not give consistant results. This variation is probable due in part to the variations in the concentration of the entering gas and in the liquid and gas rates. Because of the large temperature drop through the column, there is some doubt as to the correct temperature to use in these data. The conjecture as to the correct temperature to use was eliminated in the method described below.

After investigating the data taken in the above runs, it was found that a plot of the gas concentration against the liquid concentration at the top of the column gives a straight line, both the absorption and desorption data falling on the same line (figure 3). This was taken as convincing proof that the system follows Henry's law. This line did not go through the origin as would be expected. However, the best line indicated by the experimental points was turned so as to go through the origin and the point

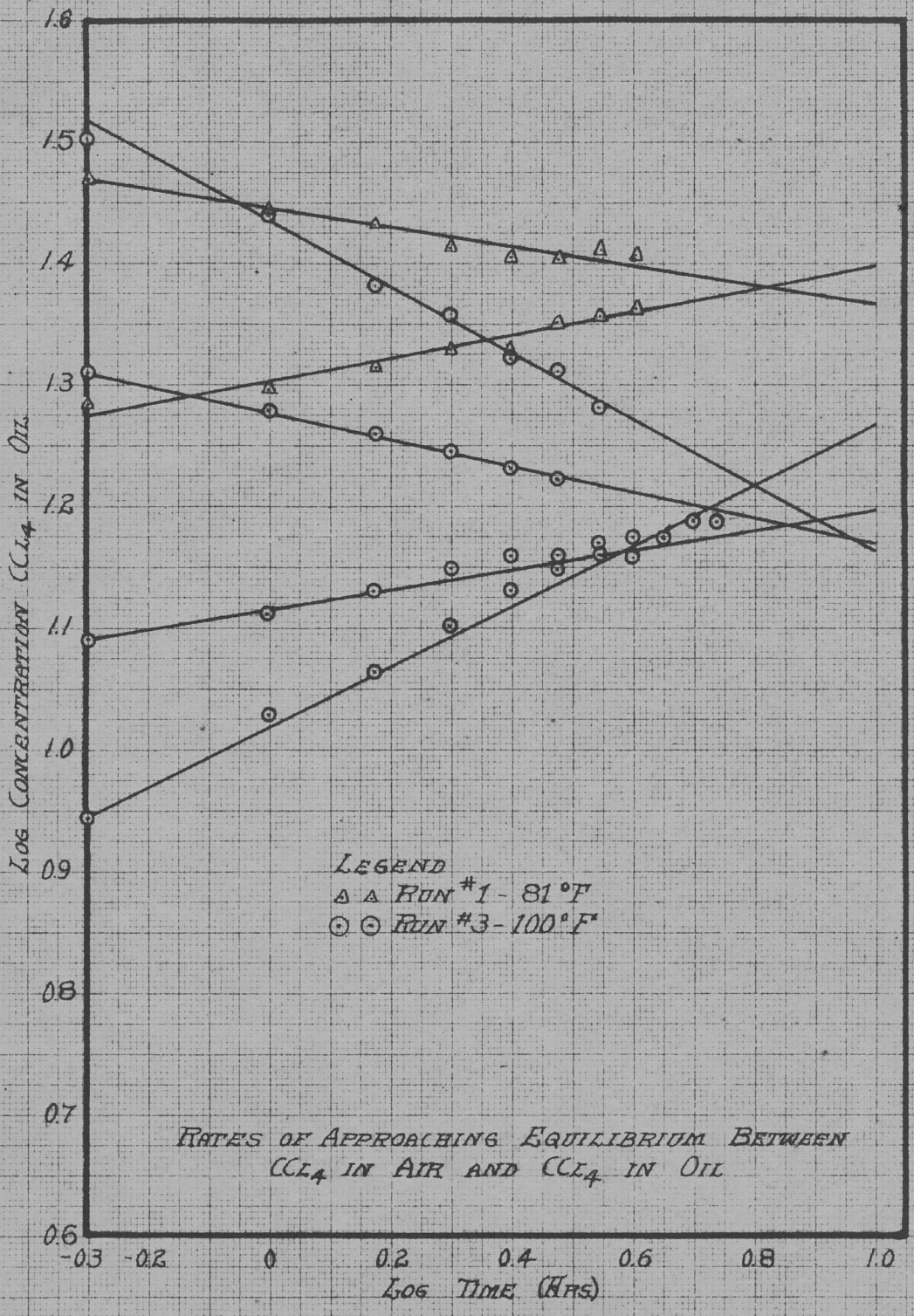

Fig. 1 Equilibrium Data for Oil-CCl_4 Solutions

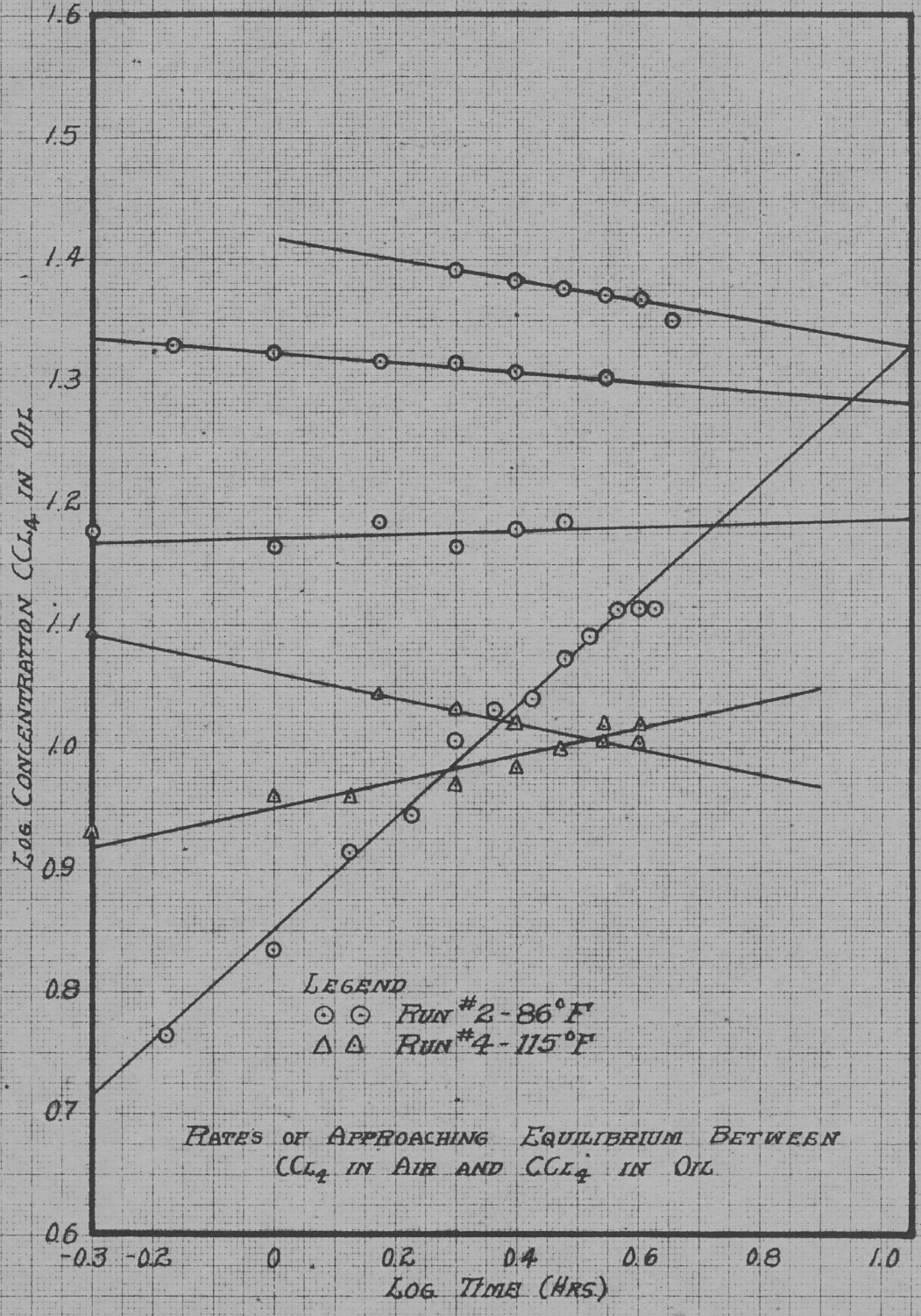

Fig. 2 Equilibrium Data for Oil-CCl_4 Solutions

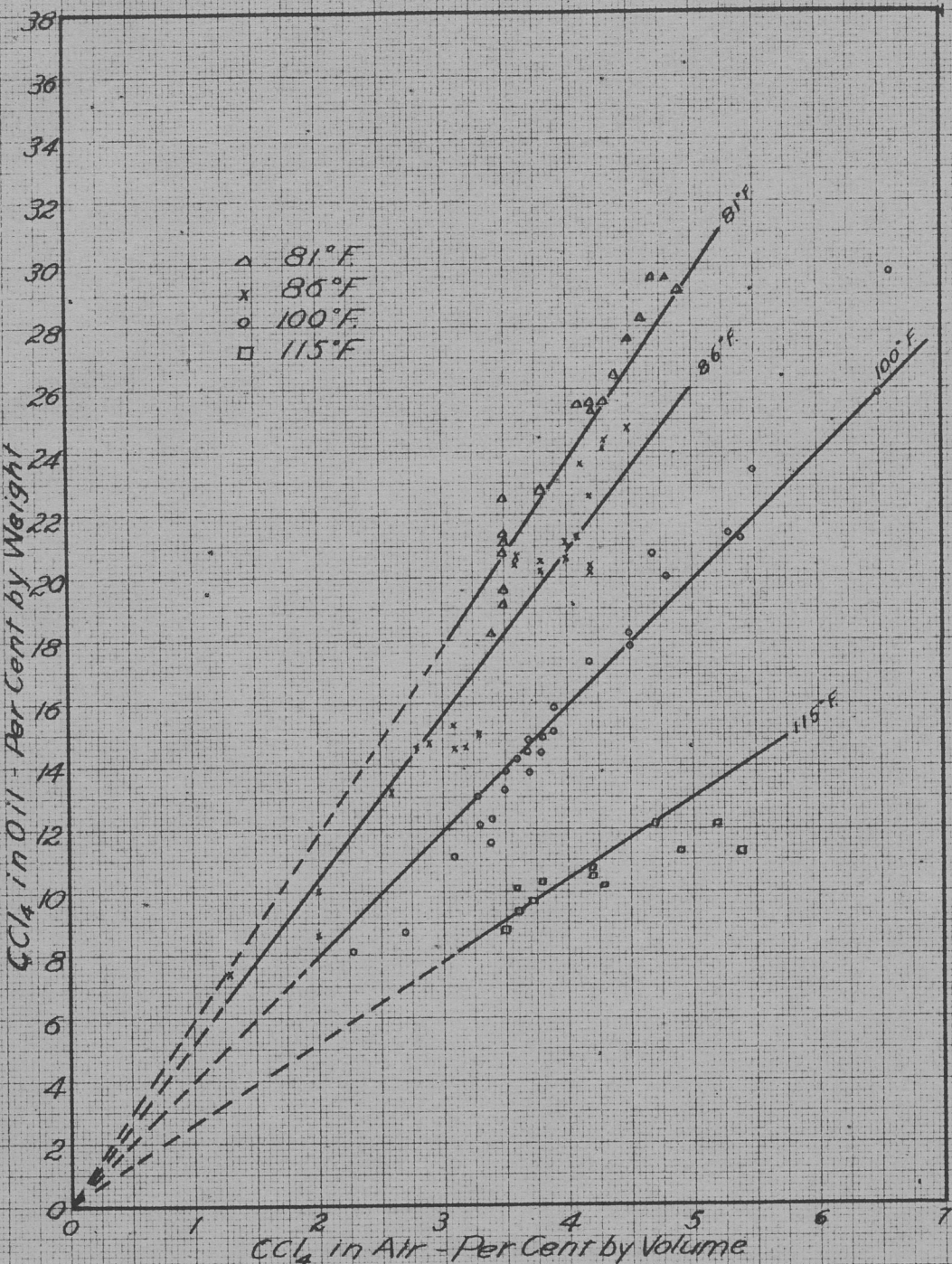

FIG. 3 EQUILIBRIUM BETWEEN CCl_4 IN OIL AND AIR

Based on Conditions at Top of Column

corresponding to 4% CCl_4 in the air which was known to be at equilibrium. This line was slightly above the absorption and slightly below the desorption data, indicating that the entering oil and outlet air at the extreem ends of the runs were not quite in equilibrium. By plotting all the data on the assumption that the entering oil and the leaving gas were in equilibrium, equilibrium points were established for a limited range. Figure 3 shows these data.

Data were taken from figure 3 and used to plot figure 4. From this curve it is possible to read the equilibrium gas and oil concentrations at various temperatures. The most accurate part of these curves is from 80° to 115°F. with gas concentrations ranging from 3.5 to 4.5%.

Equilibrium data were found for various temperatures and it was desired to establish some theoretical correlation. Some chemical equilibria follow the van't Hoff equation (Equation 6). This formula applies to other equilibria when K_p is properly evaluated. The best way to test this formula is to plot log K_p vs. 1/T. If this gives a straight line, the formula holds. When the logarithm of K_p was plotted against the reciprocal of the absolute temperature (Figure 6), a straight line was found to correlate the points as well as any other curve. However, the experimental data are too meager to furnish conclusive proof.

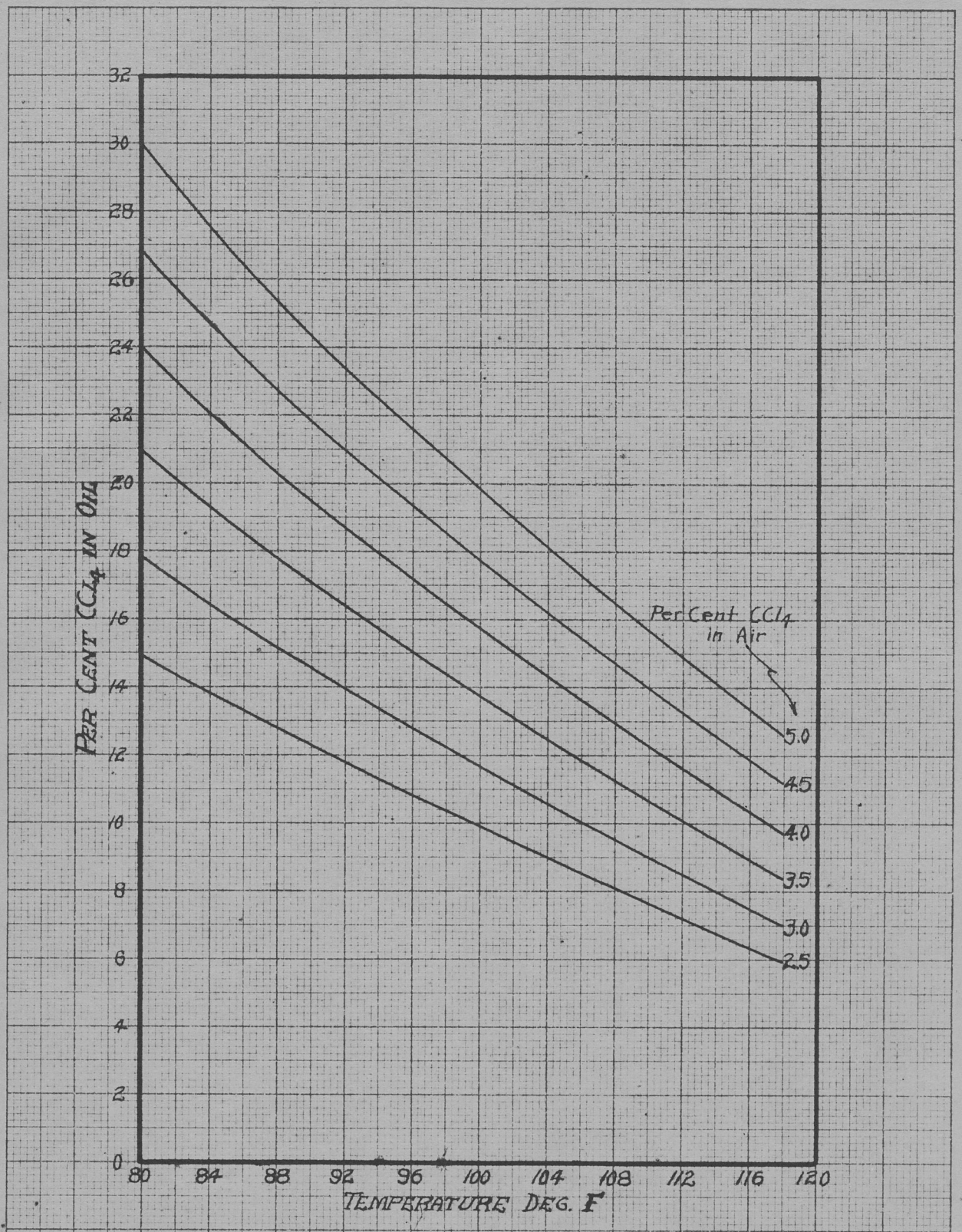

FIG. 4 VARIATION OF EQUILIBRIUM WITH TEMPERATURE OIL-CCl_4 SOLUTIONS

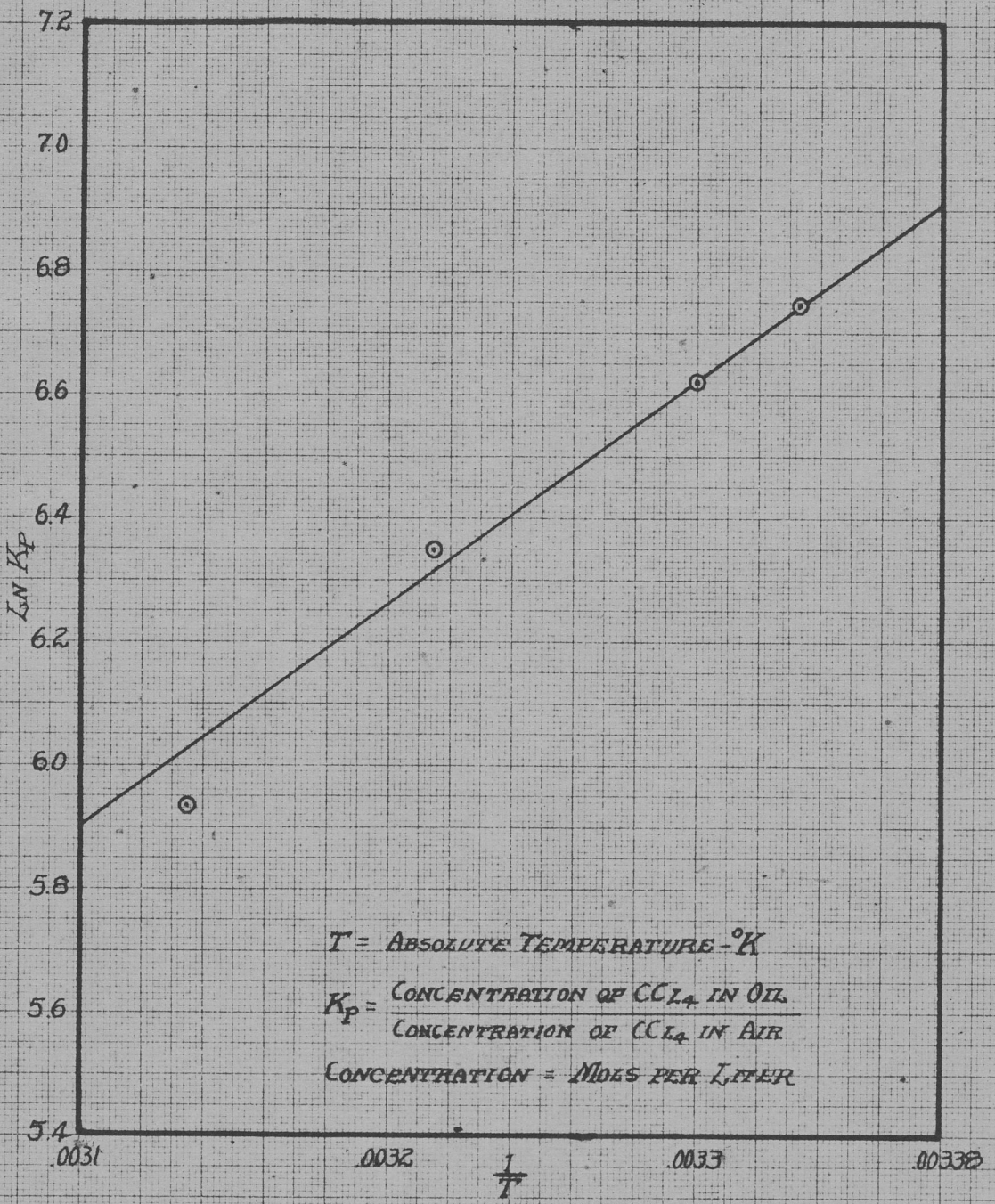

Fig. 6 Application of Data to Van't Hoff Equation

The heat of absorption of carbon tetrachloride in oil was calculated from the slope of the line in figure 6. The heat of absorption was found to be 7,160 calories per gram-mol as compared to 7,120 calories per gram-mol for the heat of vaporization of carbon tetrachloride.

The equilibrium constant, K_p, was obtained by dividing the concentration (mols/liter) of the carbon tetrachloride in the liquid by that in the air.

CONCLUSIONS

1. Air passing through the column comes very close to reaching equilibrium with the oil entering the column.

2. The vapor pressure of CCl_4 in solution in Atlantic Refining Co. oil "A" follows Henry's law over the range investigated (Figure 3).

3. The concentration of CCl_4 in air in equilibrium with 14% CCl_4 in oil ranges from 2.5% at 83°F. to 5.0% at 114°F.

4. The concentration of CCl_4 in oil in equilibrium with 4% CCl_4 in air ranges from 24% at 80°F. to 10% at 117°F.

5. Calculated from the van't Hoff equation (Equation 6), the heat of absorption of CCl_4 in oil (7160 cal/g.-mol.) is practically the same as the heat of condensation of CCl_4 (7120 cal./g.-mol).

APPLICATION OF CONCLUSIONS

Since one of the purposes of the present work was to test the applicability of the system to a laboratory experiment, the following advantages and disadvantages have been noted.

Advantages

1. It is a noninflammable system.

2. It involves only pure absorption.

3. Seemingly easy application of theoretical equations (Henry's law and van't Hoff's law).

4. There is an appreciable shift of the equilibrium point with the temperature. This shift makes it possible to carry out absorption and desorption at not too widely different temperatures.

5. The gravity analysis of the oil is easy to perform and is moderately accurate. However, changes in the physical properties of the oil would effect the analysis.

Disadvantages

1.. The Orsat apparatus used for the gas annalysis is not overly accurate and requires too much time for easy application. A wet and dry bulb temperature determination might be used to advantage on a large apparatus with an appreciable air rate.

2. There is a high concentration of CCl_4 in oil as compared to a low partial pressure in the air.

4. Much difficulty was encountered in adding the CCl_4 to the air uniformly. The method used is sufficient for a small apparatus, but would not be applicable for use on a large scale. The bubble tower method would probably be suited for a large scale apparatus since the regulation could be maintained by by-passing air around the tower.

5. Carbon tetrachloride is rather expensive ($0.0525 per pound in drums).

6. Carbon tetrachloride is rather volatile. The high vapor pressure at ordinary temperatures make its vapors rather difficult to separate from air.

7. Carbon tetrachloride vapors in the atmosphere are disagreeable to the operators.

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APPENDIX

RUN NUMBER 1-A

Time (min)	Temperature Bottom of Column Oil	Air	Temperature Top of Column Oil	Air	Liquid Rate lbs/hr.
0:0	80° F	78° F.	83 F	82 F	4.8
0:30	80	78	82	82	10.4
1:00	80	77	81	81	5.2
1:30	80	77	81	80	9.8
2:00	79	76	81	80	9.0
2:30	78	76	81	80	15.6
3:00	79	76	81	80	12.6
3:30	79	76	80	80	12.0

Time (min.)	Specific Gravity of Oil Top	Bottom	%CCl_4 in oil Top of Column	Bot. of Col.	% CCl_4 in air Into Col.	Out of Column
0	0.892	0.899	18.2	20.0	4.0	3.4
0:30	.896	.899	19.1	20.0	4.1	3.5
1:00	.898	.902	19.7	21.0	4.0	3.5
1:30	.901	.905	20.6	21.9	4.0	3.5
2:00	.903	.906	21.2	22.2	4.2	3.5
2:30	.903	.908	21.2	22.8	4.0	3.5
3:00	.907	.910	22.5	23.5	4.2	3.5
3:30	.908	.911	22.8	23.8	4.1	3.8
					4.1	

N.B. The per cent CCl_4 in the air into the column was run on the quarter hours.

Air velocity in all runs was 0.61 ft/sec based on empty tower.

Run Number 1-B

Time (min.)	Temperature Bottom of Column Oil	Air	Temperature Top of Column Oil	Air	Liquid Rate lbs/hr.
0	81 F	80 F	81 F	82 F	14.0
0:30	79	79	80	80	10.0
1:00	79	79	81	81	8.0
1:30	79	79	81	81	13.0
2:00	80	78	81	81	9.8
2:30	80	78	81	81	--
3:00	79	78	81	81	15.0
3:30	80	78	81	81	11
4:00	79	78	81	80	12

Time (min.)	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl in Air Into Col.	Out of Column
0	0.930	0.925	30.5	28.7	4.1	
						4.7
0:30	.925	.923	28.7	28.0	3.8	
						4.6
1:00	.923	.920	28.0	26.9	4.1	
						4.5
1:30	.921	.919	27.2	26.6	4.0	
						4.4
2:00	.917	.916	25.9	25.4	4.0	
						4.3
2:30	.916	.915	25.9	25.2	4.3	
						4.2
3:00	.916	.916	25.4	25.4	3.9	
						4.2
3:30	.917	.917	25.9	25.9	4.3	
						4.1
4:00	.915	.913	25.2	24.5	3.9	

N.B. The percent CCl_4 in the air out of the column was run on the quarter hour.

Run Number 2-A

Time (min.)	Temperature Bottom of Col. Oil	Air	Temperature Top of Column Oil	Air	Liquid Rate lbs./hr.
0	84 F	84 F	88 F	88 F	4.0
0:20	90	82	88	86	12.7
0:40	84	82	88	84	10.6
1:00	86	80	86	84	8.8
1:20	86	82	85	84	12.5
1:40	86	82	86	84	10.9
2:00	86	82	86	84	5.9
2:20	82	80	83	82	9.0
2:40	84	82	84	84	11.3
3:00	84	82	85	84	11.0
3:20	85	82	86	85	13.3
3:40	85	80	86	86	14.0
4:00	84	80	86	86	12.0
4:20	85	80	86	86	8.9

(Continued)

Run Number 2-A (Continued)

Time (min)	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Col.	Bot. Of Col.	% CCl_4 in Air Into Col.	Out of Col.
0	0.838	0--	2.8	--	--	--
0:20	.841	0.856	3.6	7.7	--	--
0:40	.849	.856	5.8	7.7	5.4	--
1:00	.853	.866	6.8	10.4	4.0	1.3
1:20	.858	.866	8.2	10.4	4.0	2.0
1:40	.860	.869	8.8	11.3	--	--
2:00	.865	.857	10.1	12.9	4.3	2.0
2:20	.867	.868	10.7	10.9	2.7	--
2:40	.868	.874	11.8	12.7	3.8	--
3:00	.871	.877	12.3	13.7	4.0	--
3:20	.873	.879	13.2	14.1	3.5	3.2
3:40	.876	.878	13.2	13.8	--	
4:00	.876	.880	13.2	14.4	3.8	
4:20	.876	.881	13.2	14.6	3.7	2.6

Run Number 2-B

Time (min.)	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid Rate lbs/hr.
0	80 F	94 F	90 F	87 F	14.2
0:30	83	83	85	84	10.6
1:00	82	84	85	84	8.6
1:30	82	84	91	88	10.2
2:00	84	84	86	85	10.2
2:30	82	84	85	84	9.6
3:00	82	84	85	84	10.3

Time (min.)	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl_4 in Air Into Col.	out of Column
0	0.882	0.880	14.0	15.0	4.0	3.2
0:30	.882	.882	15.0	15.6	3.8	
1:00	.883	.881	14.6	15.3	3.4	2.8
1:30	.884	.883	15.3	15.6	4.0	2.9
2:00	.884	.881	14.6	15.6	3.7	3.1
2:30	.884	.882	15.0	15.6	3.8	3.3
3:00	.886	.883	15.3	16.1	4.0	3.1

Run Number 2-C

Time (min.)	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid Rate lbs./hr.
0	80 F	78 F	90 F	86	11.0
0:20	82	82	86	85	10.4
0;40	81	84	86	84	10.4
1:00	80	84	85	83	11.9
1:30	80	84	86	85	9.7
2:00	80	84	86	84	10.7
2:30	80	84	87	85	12.0
3:00	80	84	86	84	11.4
3:30	80	84	86	85	13.8
4:00	81	84	86	85	13.1
4:30	80	84	88	86	13.8

Time (min)	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl_4 in Air Into Col.	out of Column
0	0.899	0.892	20.0	17.9	4.0	4.2
0:20	.903	.902	21.2	21.0	4.4	4.0
0:40	.902	.902	21.0	21.0	4.5	5.0
1:00	.901	.902	20.6	20.6	3.7	4.0
1:30	.914	.913	24.9	24.6	4.2	4.5
2:00	.913	.913	24.6	24.2	4.2	4.4
2:30	.912	.912	24.2	23.6	4.0	4.3
3:00	.911	.910	23.8	23.2	4.0	4.3
3:30	.910	.909	23.6	22.9	4.0	4.2
4:00	.909	.908	23.2	22.4	4.1	--
4:30	.907	.907	22.4	22.4	4.0	4.2

N.B. CCl_4 was added to the oil after one hour.

Run Number 2-D

Time (Hrs & Min.)	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid Rate lbs/hr.
0	79 F	84 F	85 F	--	--
0:20	79	84	84	84	7.1
0:40	80	84	85	85	11.2
1:00	80	84	86	84	10.7
1:30	80	84	85	84	9.4
2:00	80	84	86	83	11.6
2:30	80	84	86	84	11.6
3:30	80	84	99	92	13.4

Time Hours & min.	Specific Gravity Of Oil Top	Bottom	% CCl_4 in oil Top of Col	Bot. of Col.	% CCl_4 in Air Into Col.	Out of Column
0	--	0.901	20.6	20.6	3.7	--
0:20	0.901	.905	21.3	21.9	4.4	3.8
0:40	.903	.902	21.0	21.0	3.7	4.1
1:00	.902	.901	20.6	20.6	3.8	--
1:30	.901	.901	20.6	20.6	4.2	3.6 3.6
2:00	.901	.901	20.3	20.6	3.9	
2:30	.900	.899	20.0	20.0	4.2	4.2
3:30	.899	.899		20.0	--	4.8

RUN NUMBER 3-A

Time Hours & Min.	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid Rate lbs/hr.
0	92 F	98 F	102 F	96 F	18.0
0:30	92	99	100	96	16.8
1:00	89	99	102	96	16.1
1:30	92	100	100	94	18.0
2:00	91	100	99	94	16.8
2:30	90	99	102	96	16.3
3:00	90	100	102	96	16.0

Time Hours & Min.	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl_4 in Air Into Col.	out of Column
0	0.904	0.902	21.5	20.8	3.7	5.4
0:30	.900	.898	20.3	19.6	3.8	5.0
1:00	.896	.893	19.0	18.2	3.7	--
1:30	.893	.893	18.2	18.2	4.1	4.5
2:00	.891	.888	17.6	16.7	4.1	4.5
2:30	.889	.887	17.0	16.4	3.8	4.2
3:00	.888	.889	16.7	17.0	4.2	3.8

RUN NUMBER 3-B

Time Hours & Min.	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid Rate lbs/hr.
0	97 F	98 F	102 F	99 F	11.6
0:30	98	99	100	99	14.8
1:00	97	100	100	98	15.2
L;30	97	100	100	98	10.0
2:00	98	100	100	98	16.0
2:30	97	100	100	98	13.4
3:00	96	98	99	97	17.0
3:30	96	101	100	98	17.6
4:00	96	101	100	98	17.0

Time Hours & Min.	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl_4 in Air Into Col.	Out of Column
0	0.869	0.872	11.3	12.1	4.3	3.4
0:30	.871	.876	11.8	13.2	4.2	3.4
1:00	.875	.875	12.9	12.9	4.0	3.5
1:30	.877	.879	13.5	14.4	3.8	3.6
2:00	.879	.880	14.1	14.4	4.4	3.7
2:30	.880	.882	14.4	15.0	4.4	
3:00	.880	.881	14.4	14.7	4.0	
3:30	.880	.882	14.4	15.0	4.1	
4:00	.880	.881	14.4	14.7	4.0	3.7

RUMN NUMBER 3-C

Time Hours & MIN	Temperature Bottom of Col. Oil	Air	Temperature Top of Col. Oil	Air	Liquid R Rate lbs/hr.
0	92 F	101 F	100 F	97 F	17
0:30	90	100	99	97	15
1:00	91	99	100	97	15
1:30	91	100	99	97	17
2:00	93	100	100	98	13
2:30	94	100	99	97	16
3:00	94	98	100	98	15
3:30	95	100	100	98	15

Time Hours & Min.	Specific Gravity Of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bottom of Col.	% CCl_4 in Air Into Col.	Out of Column
0	0.946	0.938	36.2	33.4	4.4	7.0
0:30	.934	.924	31.9	28.3	3.9	6.6
1:00	.922	.915	27.6	25.2	3.9	6.5
1:30	.912	.908	24.1	22.8	3.8	5.5
2:00	.908	.904	22.8	21.5	4.0	5.3
2:30	.902	.900	20.9	20.3	3.7	4.7
3:00	.899	.899	20.5	20/0	4.4	4.9
3:30	.896	.897	19.1	19.4	4.2	

N.B. The per cent CCl_4 in the air out was run on the quarter hour.

RUN NUMBER 3-D

Time Hours & Min.	Temperature Bottom of Col. Oil	Air	Temperature Top of Column Oil	Air	Liquid Rate lbs/hr.
0	100 F	98 F	100 F	98 F	11
0:30	98	98	100	98	13
1:00	98	97	99	97	17
1:30	96	101	99	97	14
2:00	96	100	100	97	18
2:30	97	101	100	98	15
3:00	97	100	100	98	14
3:30	96	101	100	98	17
4:00	95	100	100	97	20
4:30	96	100	100	98	18
5:00	96	100	100	98	14
5:30	95	100	100	97	15

RUN NUMBER 3-D (Continued)

Time Hours & Min.	Specific Gravity of Oil Top	Bottom	%CCl_4 in Oil Top of Col.	Bottom of Col.	% CCl_4 in Air Into Col.	Out of Column
0	0.855	0.859	7.4	8.5	4.0	2.3
0:30	.860	.865	8.8	10.1	3.9	2.7
1:00	.867	.870	10.7	11.5	4.1	3.1
1:30	.871	.874	11.6	12.6	3.9	3.3
2:00	.874	.878	12.6	13.8	4.2	3.3
2:30	.877	.880	13.5	14.4	4.2	3.5
3:00	.879	.881	14.1	14.7	4.0	.38
3:30	.881	.882	14.7	14.9	4.2	3.7
4:00	.882	.883	14.9	15.3	3.9	3.8
4:30	.883	.883	14.9	15.3	3.9	3.9
5:00	.883	.885	15.4	15.9	4.1	3.9
5:30	.883	.883	15.4	15.3	3.8	

N.B. All analyses of the air out were run on the quarter hour.

RUN NUMBER 4-A

Time Hours &Min.	Temperature Bottom of Col. Oil	Air	Temperature Top of Col Oil	Air	Liquid Rate lbs./hr.
0	109 F	116 F	116 F	110 F	17.5
0;30	106	115	115	110	15.5
1:00	105	114	116	112	11.8
1:30	106	116	115	110	12.0
2:00	105	116	115	110	16.4
2:30	106	115	115	110	4.0
3:00	108	114	115	110	16.2
3:30	106	115	115	111	10.0
4:00	106	114	115	111	12.0

Time Hours & Min.	Specific Gravity Of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col.	% CCl_4 in Air Into Col.	Out of Column
0	)0.876	0.874	13.2	12.6	4.2	--
0:30	.873	.872	12.4	12.1	4.0	4.7
1:00	--	.870	--	11.6	4.3	4.9
1:30	.868	.867	11.0	10.7	4.3	4.2
2:00	.867	.865	10.7	10.2	3.7	4.2
2:30	.866	.870	10.4	11.5	4.7	4.3
3:00	.865	.868	10.1	10.9	4.5	--
3:30	.865	.868	10.1	10.9	4.0	
4:00	.865	.866	10.1	10.4	3.5	

N.B. All analyses of the air were run on the quarter hour.

RUN NUMBER 4-B

Time Hours & Min.	Temperature Bottom of Col. Oil	Air	Temperature Top of Column Oil	Air	Liquid Rate lbs./hr.
0	104 F	116 F	114 F	109 F	15
0:30	106	114	114	109	--
1:00	106	114	116	110	18
1:30	106	116	115	110	13.8
2:00	106	116	116	112	812
2:30	106	116	116	111	13.0
3:00	104	114	115	110	13.0
3:30	104	116	115	110	13.0
4:00	106	116	116	110	14.4

Time Hours & Min.	Specific Gravity of Oil Top	Bottom	% CCl_4 in Oil Top of Column	Bot. of Col	% CCl_4 in air Into Col.	Out of Column
0	0.861	0.865	9.1	10.2	4.1	3.5
0:30	.859	.866	8.5	8.8	4.1	
1:00	.861	.863	9.1	9.3	--	
1:30	.861	.862	9.1	9.3	4.1	3.6
2:00	.862	.865	9.3	10.2	4.0	--
2:30	.863	.864	9.6	9.8	4.0	3.7
3:00	.864	.866	9.9	10.4	4.0	3.6
3:30	.866	.867	10.4	10.7	4.0	3.8
4:00	.866	.868	10.4	11.0	4.1	

N.B. All analyses of the air were run on the quarter hour.

DATA FOR FIGURE NUMBER 6

Temp. $^{o}K.$	1/T	K_p	ln K_p
300	0.00333	853	6.7488
303	.00330	750	6.6201
311	.00322	575	6.3544
319	.00313	378	5.9349

SPECIFICATIONS OF "A" OIL

A.P.I. Gravity at 60°F.	36.8
Flash, o.c. °F.	250
Fire, o.c. °F.	285
S.U. Vis. at 100°F.	38"
Pour, °F.	10
A.S.T.M. Color	¼
A.S.T.M. Distillation:	
Initial Boiling Point, °F.	488
10% Recovery at, °F.	514
50% " " °F.	540
90% " " °F.	570
End Point, °F.	585

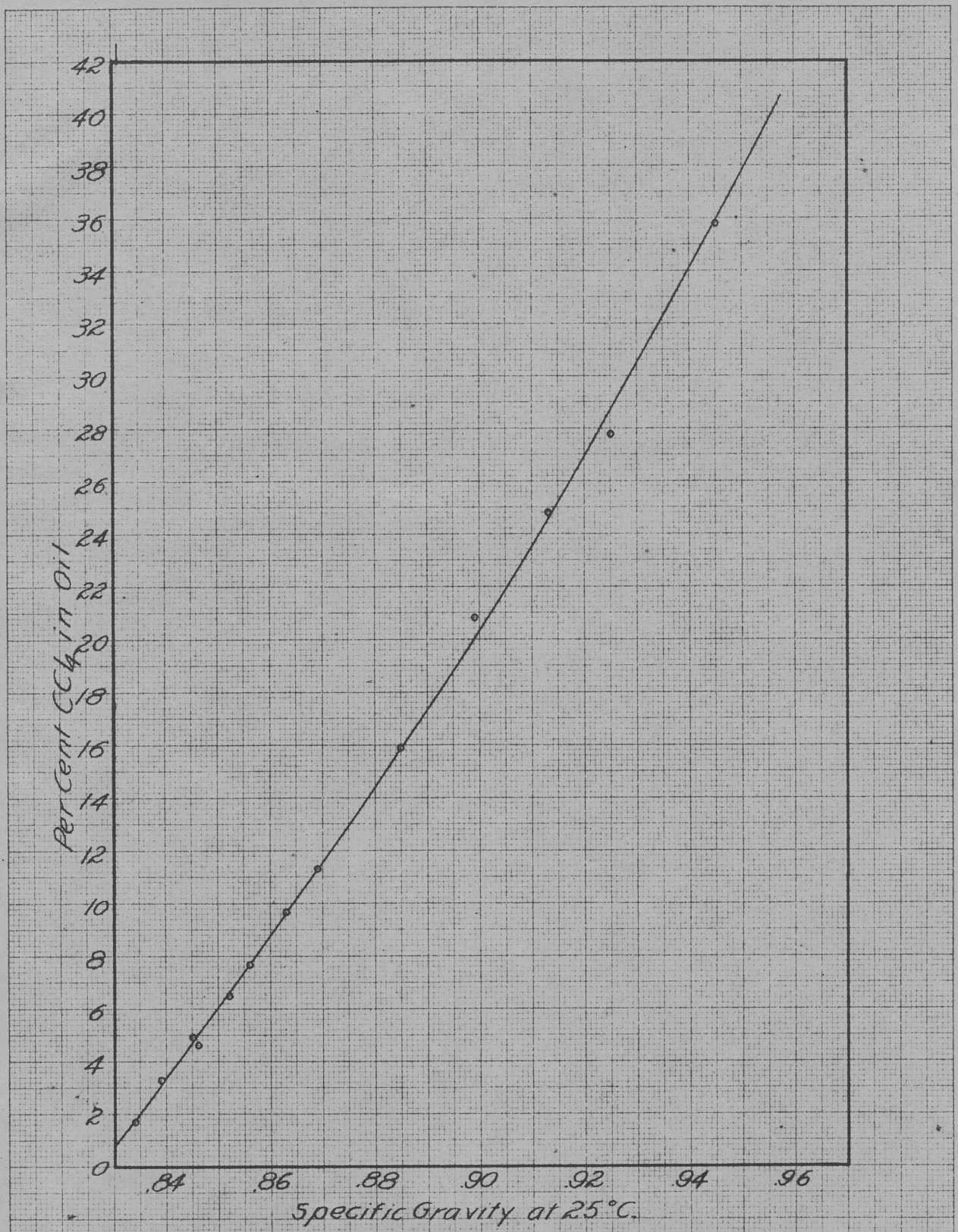

FIG. 5 GRAVITY CALIBRATION OF OIL-CCl_4 SOLUTIONS

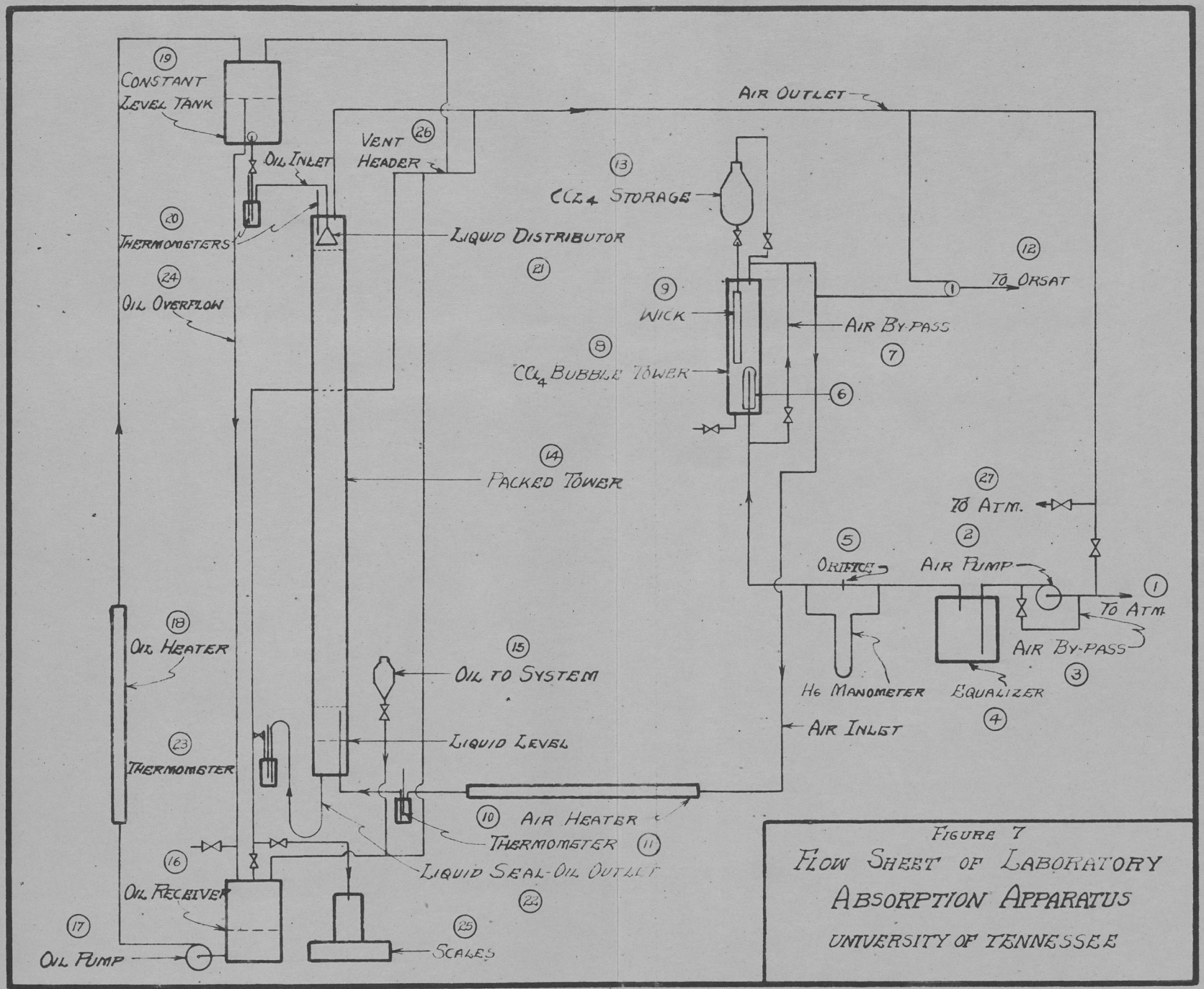

FIGURE 7

FLOW SHEET OF LABORATORY ABSORPTION APPARATUS

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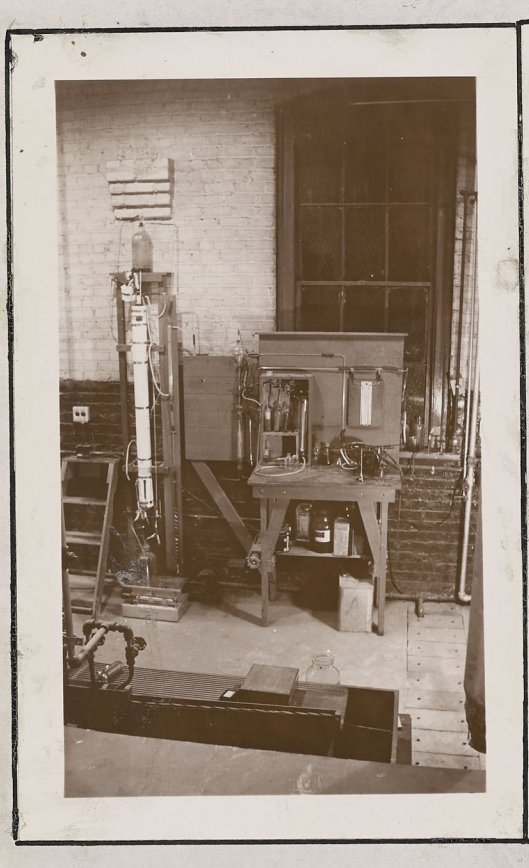

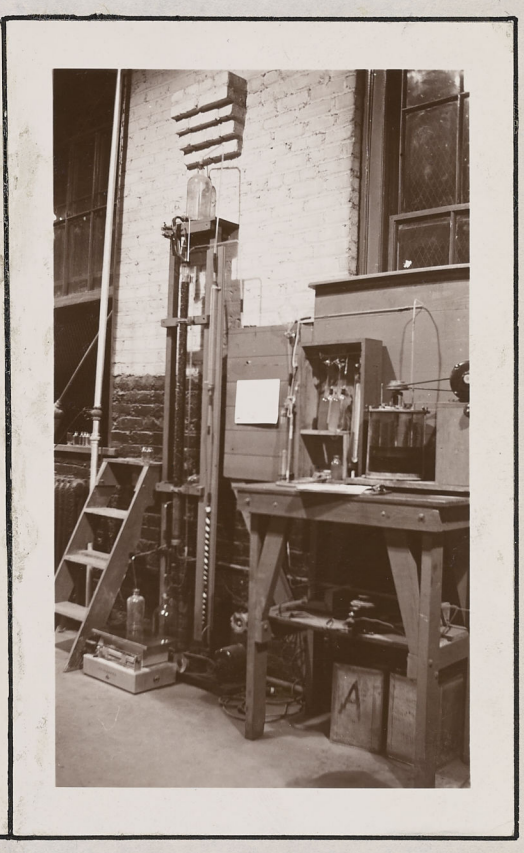

Figure 8. Pictures of Apparatus

APPROVAL

The forgoing 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 is submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinion expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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