THE VAPOR-LIQUID EQUILIBRIUM AND RELATED PROPERTIES OF ETHANOL, CHLOROFORM MIXTURES

by

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PART I

Introduction

Equilibrium pressure, temperature, vapor-liquid composition measurements for binary liquid systems are of value from two points of view. Measurements of this type give the experimental background for the consideration of the problem of the thermodynamics of binary systems. Also these dataare necessary in the design of fractionating apparatus for the separation of liquid mixtures into their components.

From the vapor pressure, temperature and vapor composition, values for the chemical potentials of each of the components in a mixture and the free energy change for the change in state of mixing the pure components can be derived. Values of the changes in entropy and heat content for this change in state can be calculated from the variation of the free energy change with temperature. Values of these thermodynamic functions must be known from experiment to verify the validity of the statistical development of the theory of binary liquid solutions.

The exact calculation of the chemical potentials can be made only if the deviations of the vapors from the ideal gas laws are known. The Gibbs-Duhem(1) equation relating the vapor and liquid composition offers a means for estimating these deviations.

The experimental problem of measuring the equilibrium pressure, temperature and compositions of the two phases has one outstanding difficulty; the determination of the vapor phase composition. Cunaeus(2) attempted a direct analysis of the vapor phase in the gaseous state in a purely static system by measuring the refractive index. The lack of precision of this method of analysis of a gas mixture accounted for the failure of this apparatus. Other methods previous and subsequent to this depended on condensing the vapor in sufficient quantity for analysis in the liquid state. In a distillation method such as was employed by Zawidski(3) vapor is constantly being removed from the system by distillation. At no time during the process is the system at equilibrium. In practical cases where the quantity of liquid is finite, this continuous removal of vapor at constant pressure causes continuous changes in the temperature and compositions of both the liquid and vapor phases. The accuracy of this simple distillation method depends on the ratio of the volumes of the condensed vapor and residual liquid, the rate of distillation and the nature of the heat source. The results of such a method can under the best experimental conditions be only approximate.

Later Rosanoff, Lamb and Breithut(4) suggested a means to avoid these difficulties which involved attaining equilibrium between the liquid phase and a vapor of constant composition supplied continuously from an external source. At equilibrium as much of the vapor can be condensed as desired without disturbing the equilibrium conditions.

Sameshima(5,6) introduced a continuous distillation method which is basically a flow process. In this method vapor is continuously condensed, but it is not removed from the system. After a portion of the distillate has been trapped the overflow feeds back into the liquid. If during the distillation process the temperature, the composition of the system and the volumes of the liquid and condensed vapor are constant, a steady state will be produced where the pressure and the composition of each phase will be invariant with time. An apparatus operating on this principle will be termed an equilibrium still.

In such a still equilibrium between the liquid and vapor phases must be produced at the point where the temperature and pressure are measured; that is both liquid and vapor must be continuously in contact with the thermometer. The successful operation of this apparatus requires that the composition of the condensed vapor and residual liquid be equal to those existing at the point where equilibrium is produced.

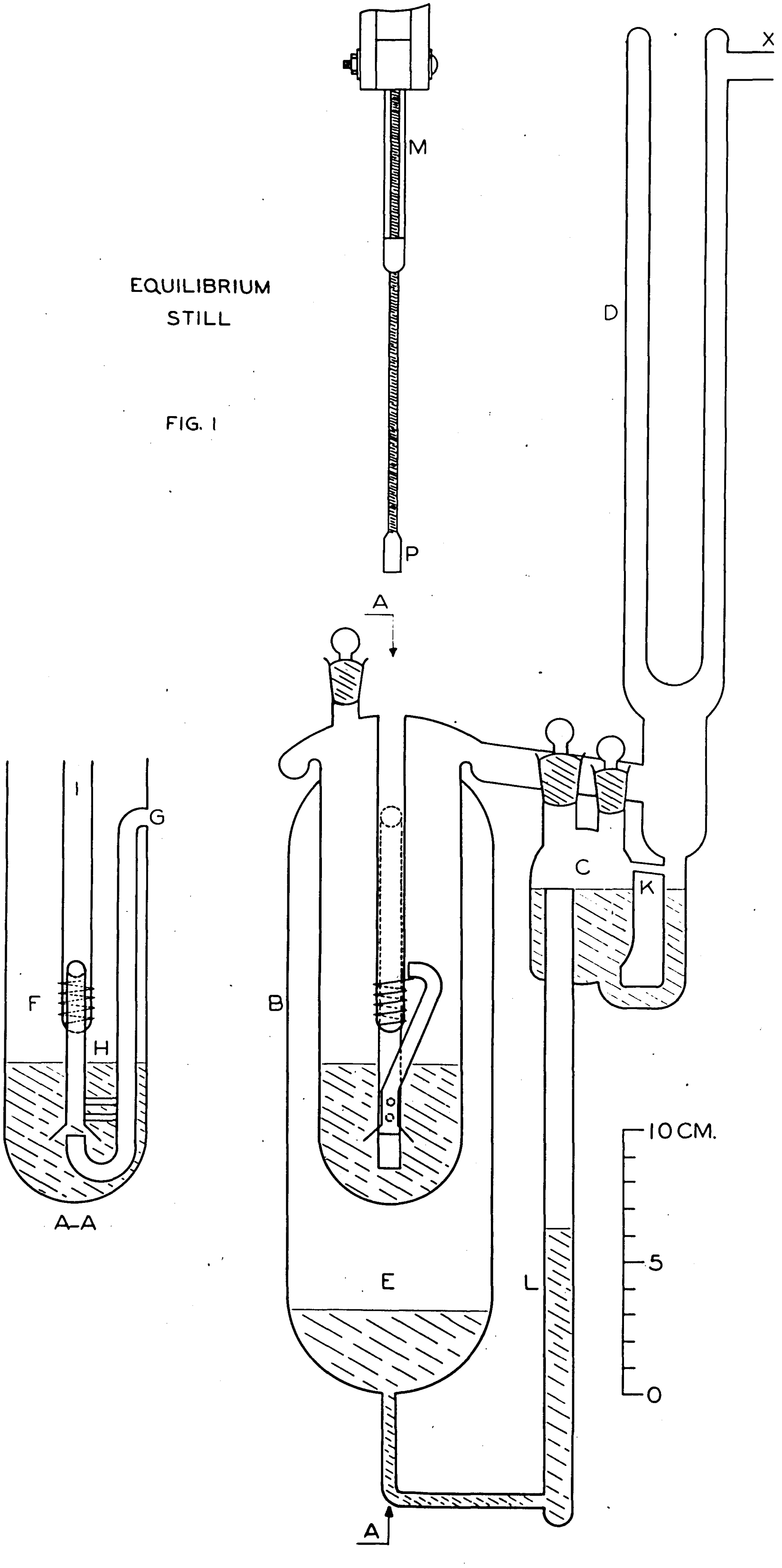
An apparatus based on the principle of the equilibrium still has been constructed to measure the liquid vapor equilibrium isotherms of binary mixtures of volatile, completely miscible liquids. Three equilibrium isotherms have been determined for the ethanol-chloroform system.

Apparatus

The apparatus consisted of three principal parts, the equilibrium still, a manometer system for pressure measurements and thermocouples for temperature measurements.

The equilibrium still was similar to the one described by Chilton[7]. Several improvements were added, and the apparatus arranged to operate over a pressure range of 100 m.m. of Hg. to 1 atm. rather than constantly at 1 atm. A scale drawing of the still is shown in figure (1). The still is blown in one piece and is entirely of pyrex glass. The three principal parts are the liquid boiler (B), the condenser (D) and the distillate trap (C). The liquid boiler is constructed of two concentric cylindrical vessels which form an outer liquid vessel (E) and an inner liquid vessel (F). Heat is applied at the bottom of the outer vessel by means of a shielded, circular gas burner.

It is desired that equilibrium take place around the lower portion of the thermometer well (I). A glass spiral is wound around the well to hold an appreciable volume of liquid in contact with it. A mixture of vapor and liquid is lifted from the inner liquid vessel (F) by the pumping device (H) and discharged over the spiral surrounding the thermometer well. The liquid in the inner vessel is heated by a jacket of vapor produced in the outer boiler. The vapor is conducted to the bottom of the inner vessel through tube (G) where as it escapes it bubbles through the liquid and



EQUILIBRIUM
STILL

FIG. 1

operates the pumping device. The outer boiler is maintained at a slightly higher pressure than the inner one depending on the level of the liquid in (F). Consequently the vapor produced in the outer boiler is slightly super heated. This vapor jacket prevents condensation on the inner walls of the inner vessel and protects the thermometer well from external influences. The vapor leaving the inner liquid boiler enters the condenser (D), and the distillate conducted to the bottom of the distillate trap (C). The overflow enters the bottom of the liquid boiler through tube (L).

When a steady state exists no condensation or vaporization occurs in the inner liquid vessel. Then, if the vapor after leaving the liquid in the inner liquid vessel does not change in composition until it is condensed, the compositions of the distillate and the liquid remaining in the inner vessel are equal to the equilibrium compositions.

To minimize fractionation effects resulting from reflux of the liquid the top of the inner boiler was provided with a flanged lip the lowest point of which emptied into the distillate trap. The distance between this flange and the ringseal joining the outer and inner liquid boilers was made as small as possible to reduce the exposed surface.

The relative heights of tube (G) and the distillate overflow tube (L) were adjusted so that it was possible to increase the pressure in the system quite rapidly without sucking over the contents of the inner liquid boiler through tube (G). The gas necessary to fill the outer liquid boiler entered entirely through the distillate over flow tube.

The tube (K) connecting the condenser outlet with the upper part of the distillate trap was for the purpose of equalizing the pressure over the surfaces of the condensate and to allow the passage of gas from the condenser into the liquid boiler. The tube was mounted on an angle slanting downwards toward the condenser outlet to prevent any distillate from entering the trap at this point.

The inner liquid vessel and the distillate trap were provided with tubular openings which were sealed by means of ground glass stoppers for removing samples of the liquid and distillate for analysis. A third tube also provided with a ground glass stopper was mounted directly above the distillate overflow tube to afford easy access to the outer liquid boiler. The grindings of these stoppers were carefully polished and the use of lubricant was not necessary.

The condenser (D) was constructed in a manner to furnish both inside and outside condensing surfaces. The outside surface was cooled by means of a surrounding ice jacket and the inside surface by means of water precooled to ice temperature. The tube (X) at the top of the condenser is a pressure connection leading through a liquid air trap to the manometer system. The condenser was mounted in a vertical position which allows the lighter gas filling the manometer system to float above the heavier condensing vapors and gives a sharp vapor gas interface. It is then certain that no gas is mixed with the vapor in the still. A sharp interface is also necessary for the existence of constant pressure in the system.

The condenser was designed to have as large a condensing surface as possible and yet have the volume per unit length small. This is desirable so that fluctuations in the level of the condensing vapor in the condenser caused by slight changes in rate of boiling etc. will not produce any appreciable pressure change in the manometer system. The relative volumes of the manometer system were such that a change of 2 m.m. in the vapor level produces a change of 1 part in 100,000 in the pressure of the system.

The thermocouples consisted of twenty copper-constantan junctions connected in series. Each junction head and each lead wire were individually insulated with four coats of bakelite enamel. The twenty insulated thermo junctions were bound together with silk thread and mounted in a rigid bakelite support. The hot and cold junctions extended downward parallel to each other a distance of 6 1/2 inches out of the bakelite support. The cold junction was surrounded by 8 mm. glass tubing filled to a depth of 4 1/2 inches with mineral oil which served as a conducting medium for heat transfer. The ice point temperature (0°C.) was used as a reference temperature in all thermocouple measurements.

The construction of the hot junction is shown in fig. (1). The junction leads are conducted away from the bakelite support through the glass tube (M) for a distance of 2 inches. The remaining 4 1/2 inches of lead wire and the junction heads (P) were tightly wound with silk thread and impregnated with bakelite enamel. The junction heads were given the added protection of a shield of two turns of silk tape also impregnated with bakelite enamel. The hot junction when inserted in the thermometer well extends to the bottom, and the clearance between the junction heads and the side walls is about 1/16 inches on each side. The thermometer well was filled to a depth of 3 3/4 inches with mineral oil. With the hot junction constructed in this manner the ratio of the heat conduction along the leads in a vertical direction to the conduction to the surface of the thermometer well in a horizontal direction was small enough to make the thermocouples relatively insensitive to depth of immersion at the operating depth.

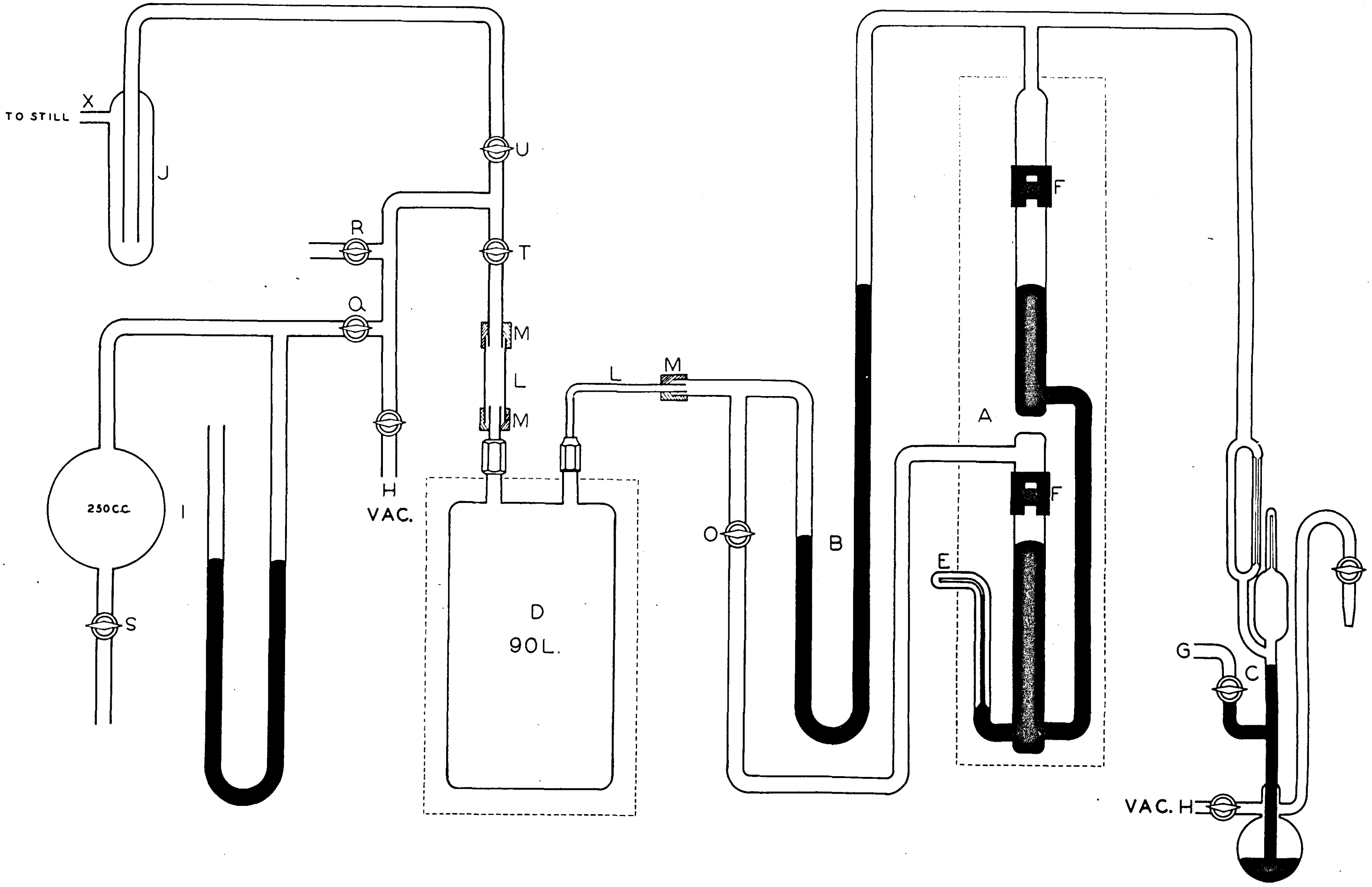
Electromotive measurements were made with a Leeds and Northrup type "K" Potentiometer. The potentiometer system was sensitive to a change of 1 microvolt. A temperature difference of 1°C. produced an E.M.F. of .8 millivolts. Hence a temperature difference of .001°C. could be detected. Assuming the E.M.F. of five Epply saturated cadmium cells remained constant, temperatures could be reproduced to .001°C. The absolute value of the temperature was uncertain to ± .01°C.

The thermocouples were calibrated by comparing with a 25 ohm platinum resistance thermometer over a range of 25°C.

to 100°C. The resistance thermometer had been recently calibrated by other workers in this laboratory.(8,9) As an independent check the thermocouples were calibrated in the equilibrium still by the vapor pressure curve of water over a range of 60°C. to 100°C. The relation between the vapor pressure and temperature for water of Smith, Keyes and Gerry(10) was used to calculate the temperature from the observed pressures. These two independent calibrations agreed to ± .01°C.

The manometer system is shown schematically in fig. 2. The system was filled with nitrogen when measurements were made on alcohol and chloroform vapors and helium for those on water vapor. Pressures were measured with a mercury manometer (A) in conjunction with a cathetometer and graduated scale. The scale was a two meter invar bar graduated in millimeters and was calibrated by the U.S. Bureau of Standards in Oct. 1934. The mercury column was thermostated by means of an air bath, and the mean temperature of mercury could be determined to ± .01°C. The observed mercury heights were reduced to pressures in m.m. of Hg. at 0°C. and standard gravity and corrected for capillary depression, static head and calibration and thermal expansion of the scale. The uncertainty in the absolute values of the pressure was ± .01 m.m. of Hg. at a pressure of 1 atm.

The manometer (B) is connected in parallel with the main manometer and is used for rough pressure measurements. The



MANOMETER SYSTEM

FIG. 2

barostat (D) consisted of a 90 liter thermostated volume for the purpose of minimizing pressure fluctuations caused by temperature changes in the leads and changes in vapor level in the still condenser. The connections labeled H in fig. 2 lead to a Hyvac oil pump. The pressure in the system was regulated through stopcocks (V) and (Q). By opening stopcock (Q) small quantities of gas could be admitted to the system by noting the pressure dropin a 250 cc. bulb by the manometer (I). In this manner the pressure could be controlled in the system to ±.01 m.m. of Hg. Tank nitrogen and helium were admitted to the 250 c.c. bulb through stopcock (S) after passing through drying tubes.

Materials

Ethanol: The source of ethanol was the commercial grade of absolute alcohol. The commercial product was purified by the method recommended by Castille and Henri(12). Harris(13) found that absolute alcohol from the same source(14) as used in this work after purification by the Castille and Henri method had a benzene content of less than .001% by weight and an aldehyde content of less than .02%. The vapor pressures of 55°C. of samples of three separate purifications were 279.820 m.m., 279.902 m.m., 279.815 m.m. Densities of the different purified samples indicated the presence of .05% to .1% of water. The pure alcohol was stored in 100 c.c. glass stoppered bottles.

Chloroform: Chloroform is unstable in the presence of air and oxidizes to form carbonyl chloride and hydrochloric acid. This decomposition is catalysed in the presence of light, but is stabilized by the presence of a small amount of ethanol. The principal impurity in the ordinary grade of purified chloroform is about 1% of ethanol which has been added for this purpose. This alcohol was removed during the purification process suggested by Timmerman and Martin(15). Approximately 1% by volume of ethanol was added to the purified chloroform and the mixture stored in the dark in 100 c.c. glass stoppered bottles. Pure chloroform was used only in the measurement of its vapor pressure curve and the densities of chloroform, ethanol mixtures. In these cases measurements were made as rapidly as possible after purification. It was found that the density of a sample of pure chloroform increased only .03% after standing in the light for a period of 1 month. Since the decomposition products of chloroform are volatile, they should gradually be eliminated during the process of vapor pressure measurements made by the distillation method. The vapor pressures at 55°C. of samples of the products of three different purifications were 617.772 m.m., 617.903 m.m., 617.837 m.m.

Manometer Mercury: The ordinary grade of redistilled mercury was purified further first by the electrolytic process and then by two successive distillations. The first distillation was carried out under a pressure of 20 m.m. of air, and the second under vacuum.

Density Measurements

Analyses of the liquid and distillate samples were made by means of density measurements. The densities of the mixtures were determined in glass pycnometers at 25°C.

Mixtures of chloroform and ethanol of known composition were made up by weight in glass weighing bottles and their densities determined. The results of these measurements are given in table I. The composition (Z) in mole fractions was expressed as the deviations Z - Z(calc.) from a quadratic function of the specific volumes.

$$Z(\text{calc}) = -3.43407 + 6.88931V - 2.67566V^2$$

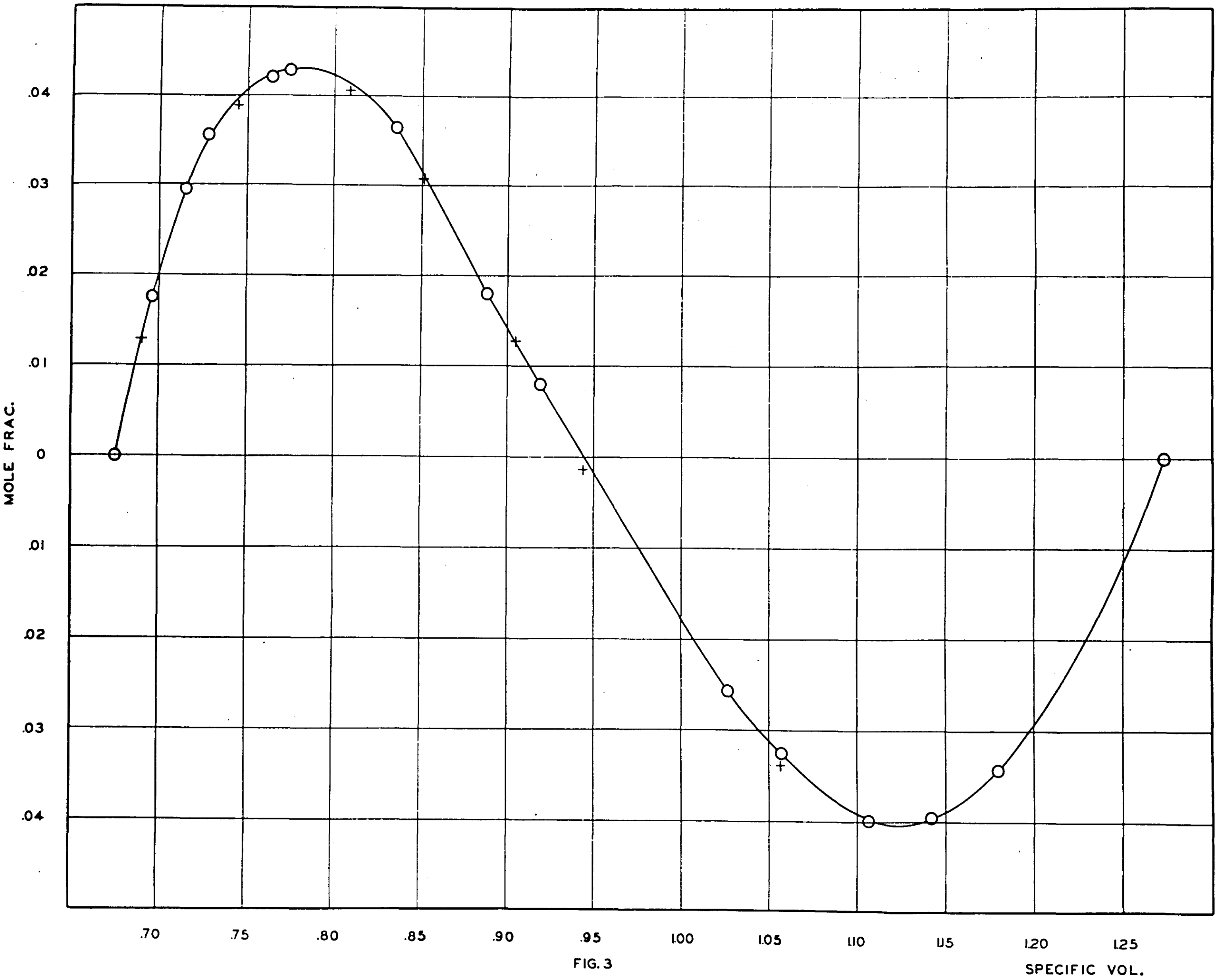
The deviations of the observed values of Z from the values calculated from this equation are plotted as ordinates in figure 3 against the specific volume as abscissae. The measured points are indicated by circles and fall on a smooth curve within .03 mol %. The points indicated by crosses in figure 4 are the deviations of the measurements of Hirobe(11) from the given equation. The density method is particularly applicable to the analysis of chloroform, ethanol mixtures because of the large spread between the densities of the pure components. Analyses were made by use of the deviation curve, and the maximum uncertainty in composition is .05 mole %.

Table I

Specific Volume of Ethanol, Chloroform Mixtures 25°C.

Weight Frac. Ethanol	Mole Frac. Ethanol (Z)	Density	Specific Volume	D(Z obs.-Z calc.)
0	0	1.47955	.67588	.00000
.03371	.08293	1.43640	.69619	.01759
.06581	.15443	1.39796	.71533	.02950
.08652	.19713	1.37477	.72739	.03566
.14834	.31108	1.30804	.76450	.04208
.16509	.33889	1.29163	.77422	.04297
.27136	.49122	1.19656	.83573	.03649
.35914	.59230	1.12584	.88823	.01806
.41301	.64589	1.08789	.91921	.00803
.59394	.79131	.97374	1.02697	-.02780
.64787	.82668	.94561	1.05752	-.03251
.72669	.87330	.90360	1.10668	-.03990
.78558	.90474	.87544	1.14228	-.03950
.84801	.93525	.84774	1.17961	-.03425
1	1	.78562	1.27288	-.00002

$$Z(\text{calc.}) = -3.43407 + 6.88931V - 2.67566V^2$$



MOLE FRAC.
.04
.03
.02
.01
0
.01
.02
.03
.04
.70
.75
.80
.85
.90
.95
1.00
1.05
1.10
1.15
1.20
1.25
SPECIFIC VOL.

FIG. 3

Experimental

A mixture of chloroform and ethyl alcohol in the proper proportions to give approximately the desired final equilibrium compositions was introduced into the still. The total volume of liquid mixture required was about 157 c.c. of which 85 c.c. was placed in the inner boiler, 45 c.c. in the outer boiler and 27 c.c. in the distillate trap. The volumes in the inner and outer liquid boilers changed somewhat during the operation of the still. The pressure was reduced through stopcocks (U) and (V) until the liquid in the still just started to boil. Stopcock (V) was then closed, and gas from the manometer system, in which the pressure had been adjusted to approximately the desired value, was slowly admitted to the still by partially opening stopcock (T). When the pressure in the still and the manometer system became equal, stopcock (T) was fully opened; and heat was applied at the bottom of the liquid boiler. The liquid was allowed to boil vigorously for a time to allow the vapors to flush out other gases. The heat was then reduced to the point where uniform boiling occurred.

The potentiometer system was adjusted to the E.M.F. corresponding to the required temperature; and throughout the time a steady state condition was being attained, the temperature was maintained as constant as possible by regulation of the pressure. The criterion for a steady state was the existence of constant pressure and constant temperature over an interval of at least 5 minutes. The time necessary to attain a state very near to the equilibrium or steady state was usually about 20 minutes after boiling first occurred. The actual equilibrium point is then reached only after very careful pressure adjustment. The total time required to reach the steady state condition was from a minimum of 45 minutes to a maximum of 2 1/2 hours depending on the initial compositions and the region of temperature and pressure.

At the equilibrium point a temperature drift towards higher temperature occurred. The value of this drift reached a maximum in the middle of the concentration range of .003°C. per minute and decreased to a minimum value of less than .001°C. per minute in the vicinity of each of the pure components and the constant boiling mixture. Since at the condensing temperature (0°C.) the vapor pressure of chloroform is 5 times that of ethanol, this drift was attributed to unequal rates of escape of the vapors of chloroform and ethanol through the condenser. It was estimated by the volume of liquid condensed in the liquid air trap that loss of material through the condenser had a maximum value of .5 c.c. per hour and was usually much smaller than this.

When a steady state was reached the manometer system was shut off by closing stopcock (T). The heater was extinguished, and nitrogen gas was admitted to the still as rapidly as possible through stopcocks (U) and Q) until the internal pressure indicated by manometer (I) attained a valuc slightly in excess of 1 atm. The pressure was then measured on the main manometer by determining the heights and levels of the menisci and the temperature of the mercury and invar scale. Samples of the liquid and distillate were removed for analysis from the inner boiler and distillate trap by means of ice jacketed pipettes. Since the operating pressures in the work on mixtures were less than 655 m.m. of Hg. the rapid increase in pressure in the still to 1 atm arrested distillation immediately.

The still was also used to determine the vapor pressure, temperature curves for pure chloroform and ethanol. The procedure was similar to that described for mixtures except the pressure was read while the still was actually in operation without closing off the manometer system. The pressure drift in the system with time was very small and could not be detected over the time necessary for a pressure measurement. Pressure fluctuations about a mean value caused by changes in the vapor level in the condenser were small and in low pressure ranges where irregular boiling occurred in the still reached a maximum value of .02 m.m. of Hg.

Results and Calculations

The measured values of the vapor pressures of pure ethanol and chloroform at several temperatures are given in Table II. The pressures given are average values for several observations. The vapor pressures for both substances are somewhat lower than the published values (Int. Crit. Tables, Vol. III). For ethanol the difference between the observed values and published values ranges from -0.4 m.m. to -1.4 m.m. except at 75°C. where the difference is +0.4 m.m. For chloroform the differences are much greater and rangesfrom -4.8 m.m. to -9.5 m.m. Since ethanol and chloroform form azeotropic mixtures of maximum vapor pressure with the substances most likely to be present as impurities, low values of the vapor pressure would be expected to be the most probable.

Three vapor-liquid equilibrium isotherms were measured for mixtures of the two pure components at 35°C., 45°C., and 55°C.

Table II

Vapor Pressures of Chloroform and Ethanol

t°C.	$P_{m.m.}$(Ethanol)	$P_{m.m.}$(Chloroform)
35	102.78	295.11
40	134.09	360.28
45	172.76	433.54
50	221.18	519.18
55	279.86	617.84
60	351.32	730.14
65	438.36	
70	542.09	
75	666.49	

The experimental results at these three temperatures appear in Tables, III, IV and V. In the following discussion the terms will be defined as follows:

P = total vapor pressure in m.m. of Hg.
x = mole fraction of ethanol in the liquid.
y = " " " " " " vapor.
μ_1^E = excess chemical potential of ethanol.
μ_2^E = " " " " chloroform.

F_x^E = excess free energy per average mole.
S_x^E = " entropy " " "
H_x^E = " heat content" " "

A subscript (1) applied to any symbol refers to ethanol and a subscript (2) to chloroform. When the two pure liquid components are mixed the quantities, μ, F, H, S undergo corresponding changes. The changes in μ_1 and μ_2 on mixing are

$$\mu_1^M = RT \ln a_1$$
$$\mu_2^M = RT \ln a_2$$

where a_1 and a_2 are the activities. The symbols μ_1^E and μ_2^E represent the changes in chemical potential of each component for this change in state in excess of the changes that would have taken place if the solution had been ideal and are defined as follows.

$$\mu_1^M = RT \ln x_1 + \mu_1^E$$

$$\mu_2^M = RT \ln (1-x) + \mu_2^E$$

The values of μ_1^E and μ_2^E are hence equal to the RT times logarithm of the quantity generally known as the activity coefficient.

The symbols F_x^E, H_x^E and S_x^E represent the excess free energy, heat content and entropy changes when the mixture contains a total of 1 mole.

$$F_x^M = x\mu_1^M + (1-x)\,\mu_2^M$$
$$F_x^E = x\mu_1^E + (1-x)\,\mu_2^E$$

For ideal solutions the heat of mixing is 0. Therefore for any solution

$$H_x^M = H_x^E$$

Likewise:

$$S_x^M = -xR \ln x - (1-x)\,R \ln (1-x) + S_x^E$$

In the first three columns of Tables III, IV and V are given the experimental values of P, x and y for the three temperatures.

Table III

35°C. Isotherm

Mole frac. C_2H_5OH

x	y	$P_{m.m.}$	P y	P (1-y)	$\Delta \log_{10}P$
0	0	295.11	0	295.106	0
.0384	.0586	303.91	17.81	286.10	.039614
.0400	.0597	303.69	18.13	285.56	.039797
.0414	.0615	304.17	18.69	285.48	.041287
.0440	.0637	304.87	19.42	285.45	.043302
.0685	.0839	306.05	25.68	280.37	.054241
.1517	.1217	306.25	37.27	268.98	.071841
.1577	.1248	305.12	38.08	267.04	.071666
.1735	.1302	305.39	39.76	265.63	.074522
.2254	.1446	303.05	43.82	259.23	.077778
.3217	.1673	296.93	49.68	247.25	.079263
.3815	.1819	291.95	53.10	238.85	.078664
.5154	.2188	274.46	60.05	214.41	.068734
.5173	.2203	274.04	60.37	213.67	.068747
.5616	.2354	267.65	63.00	204.65	.065426
.6078	.2588	255.28	66.07	189.21	.05594
.6155	.2630	253.39	66.64	186.75	.054292
.6773	.2991	236.50	70.74	165.76	.040868
.6986	.3130	229.24	71.75	157.49	.033700
.7127	.3253	225.06	73.21	151.85	.031330
.7639	.3793	205.68	78.01	127.67	.016962
.8270	.4696	177.60	83.40	94.20	-.005405
.8891	.6115	148.26	90.66	57.60	-.018819
.9406	.7657	125.82	96.34	29.48	-.019471
.9458	.7846	123.54	96.93	26.61	-.018741
.9703	.8790	113.61	99.86	13.75	-.011915
.9759	.9009	111.31	100.28	11.03	-.010739
.9938	.9746	104.87	102.21	2.66	-.002880
1	1	102.78	102.78	0	0

Table IV

45°C. Isotherm

Mole frac. C_2H_5OH					
x	y	$P_{m.m.}$	P y	P (1-y)	$\Delta\ \log_{10}P$
0	0	433.54	0	433.54	0
.0134	.0273	439.89	12.01	427.88	.017231
.0242	.0421	443.07	18.64	424.43	.026252
.0323	.0546	445.38	24.32	421.06	.033518
.0443	.0681	448.49	30.52	417.97	.041931
.0837	.1026	453.76	46.56	407.21	.060797
.0875	.1054	454.02	47.85	406.17	.062167
.0900	.1067	454.54	48.45	406.09	.063177
.1148	.1217	455.79	55.47	400.32	.070364
.1794	.1484	455.56	67.61	387.98	.080818
.2852	.1809	448.17	81.07	367.10	.086702
.3717	.2046	438.89	89.80	349.09	.087079
.4595	.2297	425.28	97.69	327.59	.083435
.4860	.2397	420.63	100.83	319.80	.082650
.5561	.2660	403.91	107.44	296.47	.075548
.5985	.2857	391.51	111.85	279.66	.069875
.6702	.3286	365.07	119.96	245.11	.056645
.6884	.3443	355.66	122.45	233.21	.051579
.7431	.3940	329.62	129.87	199.75	.038415
.7989	.4605	299.63	137.98	161.65	.023566
.8003	.4634	298.08	138.13	159.95	.022472
.8740	.6026	249.92	150.60	99.32	.001555
.9288	.7533	214.44	161.54	52.90	-.004720
.9524	.8283	199.62	165.34	34.27	-.005863
.9811	.9284	182.63	169.55	13.08	-.004509
.9843	.9400	180.96	170.10	10.86	-.003846
1	1	172.76	172.76	0	0

Table V

55° Isotherm

Mole frac. C_2H_5OH

x	y	P m.m.	P y	P(1-y)	Δ $\log_{10}$ P
0	0	617.84	0	617.84	0
.0348	.0592	626.79	37.71	599.08	.033488
.0570	.0850	644.24	54.79	589.46	.047420
.0963	.1202	650.38	78.18	572.20	.063634
.1610	.1583	653.11	103.39	549.72	.078557
.2236	.1819	650.96	118.41	532.55	.085242
.2731	.1990	646.79	128.71	518.08	.088330
.3149	.2143	641.49	137.47	504.02	.090023
.3789	.2361	632.14	149.25	482.89	.091139
.4270	.2473	623.67	154.23	469.44	.089133
.5206	.2839	599.03	170.06	428.97	.084217
.6035	.3240	569.02	184.36	384.66	.075687
.6096	.3280	566.74	185.89	380.85	.075315
.6233	.3359	560.25	188.19	372.06	.073033
.6555	.3581	545.72	195.42	350.30	.069255
.6588	.3593	543.53	195.29	348.24	.067919
.7194	.4058	508.78	206.46	302.32	.055225
.7799	.4729	469.41	221.98	247.43	.043323
.8131	.5205	441.04	229.56	211.48	.032614
.8521	.5965	407.90	243.31	164.59	.024832
.8971	.6877	367.01	252.40	114.62	.010328
.9198	.7467	346.89	259.02	87.87	.006121
.9288	.7698	339.89	261.65	78.24	.005224
.9669	.8838	306.38	270.78	35.60	-.000652
1	1	279.86	279.86	0	0

The vapor pressure P is plotted against x and y in figure (4). The P-x points are indicated by circles and the p-y points by flagged circles. The lowest curve is the 35°C. isotherm and the highest curve the 55°C. isotherm. This data shows that mixtures of chloroform and ethanol form an azeotropic system of maximum vapor pressure at the three temperatures, 35°C., 45°C., 55°C. The composition of the constant boiling mixture shifts with increasing temperature toward higher ethanol content. The compositions of the mixtures of maximum vapor pressure at 35°C., 45°C., and 55°C.

Table V

55° Isotherm

Mole frac. C_2H_5OH

x	y	$P_{m.m.}$	P y	P(1-y)	$\Delta \log_{10} P$
0	0	617.84	0	617.84	0
.0348	.0592	626.79	37.71	599.08	.033488
.0570	.0850	644.24	54.79	589.46	.047420
.0963	.1202	650.38	78.18	572.20	.063634
.1610	.1583	653.11	103.39	549.72	.078557
.2236	.1819	650.96	118.41	532.55	.085242
.2731	.1990	646.79	128.71	518.08	.088330
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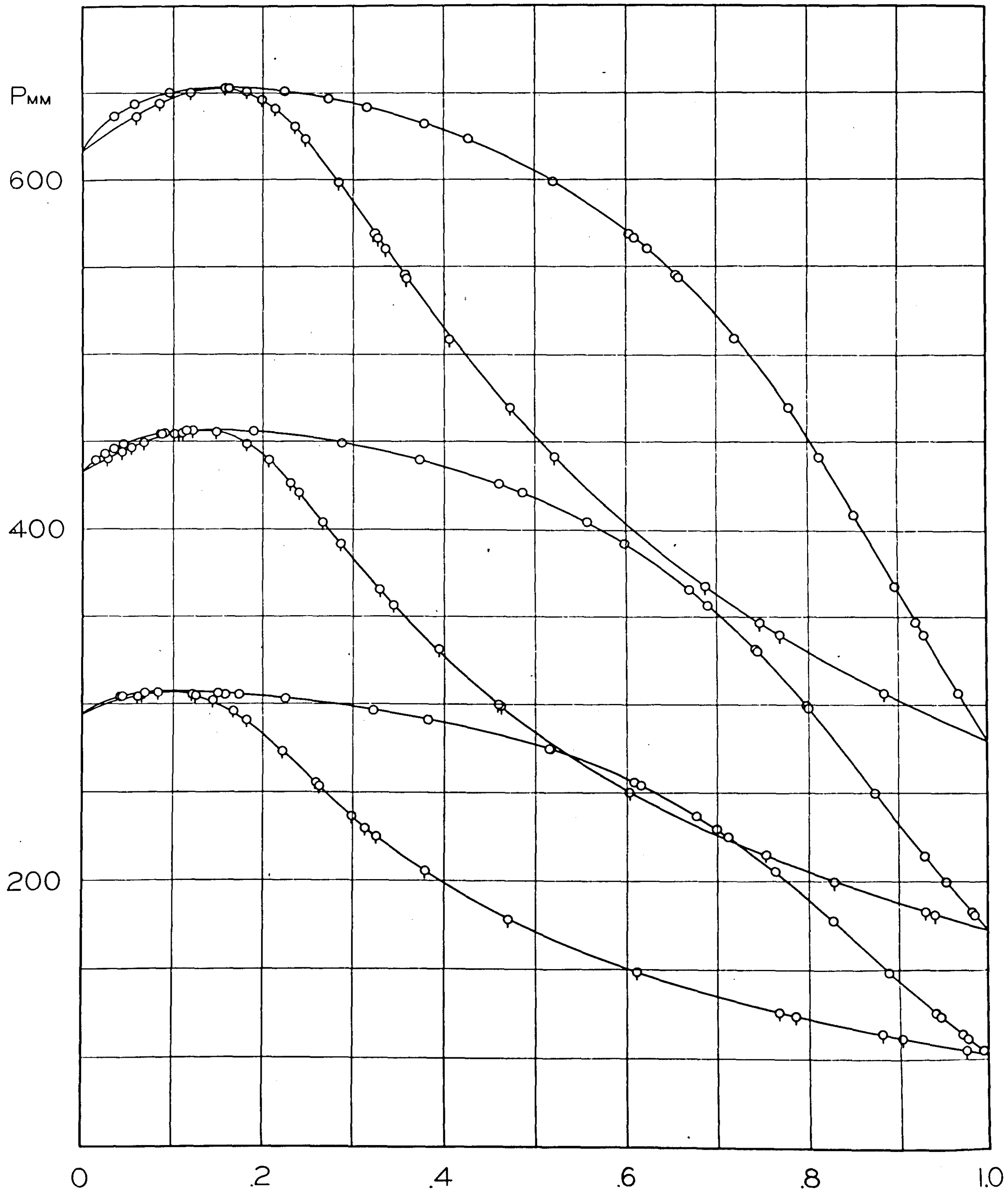


FIG. 4

are x = .105, x = .130, x = .155. In the third and fourth columns of Tables III, IV and V are given values of Py and P (1-y) which are by definition the partial pressures of ethanol and chloroform. The values of P, P y and P (1-y) at 45°C. are plotted against x in figure (5). The P y curve crosses the Raoult law line. This crossing is more pronounced at 35°C. and becomes less noticeable at 55°C.

The values of the chemical potentials can be calculated from the total vapor pressure and the vapor composition if the vapors are assumed to obey the perfect gas laws. If for real vapors the deviations from the gas laws are known then the exact calculation can be made. If the equation of state for mixtures of the vapors of a two component system is expressed as

$$\frac{V}{N} = \frac{RT}{P} + \beta_1 y_1^2 + \beta_2 y_2^2 + 2\,\beta_{12}\, y_1 y_2$$

or if $\delta = 2\beta_{12} - \beta_1 - \beta_2$

$$\frac{V}{N} = \frac{RT}{P} + \beta_1 y_1 + \beta_2 y_2 + \delta\, y_1 y_2$$

where δ is the deviation of the volume of the mixture from aditivity, then the changes in chemical potential on mixing in the liquid (μ^M) for each component at constant pressure equal to final vapor pressure above the mixture are

$$\mu_1^M = RT \ln \frac{Py}{P_1} + (\beta_1 - V_1)(P - P_1) + \delta P\,(1-y)^2$$

$$\mu_2^M = RT \ln \frac{P(1-y)}{P_2} + (\beta_2 - V_2)(P - P_2) + \delta\, P y^2$$

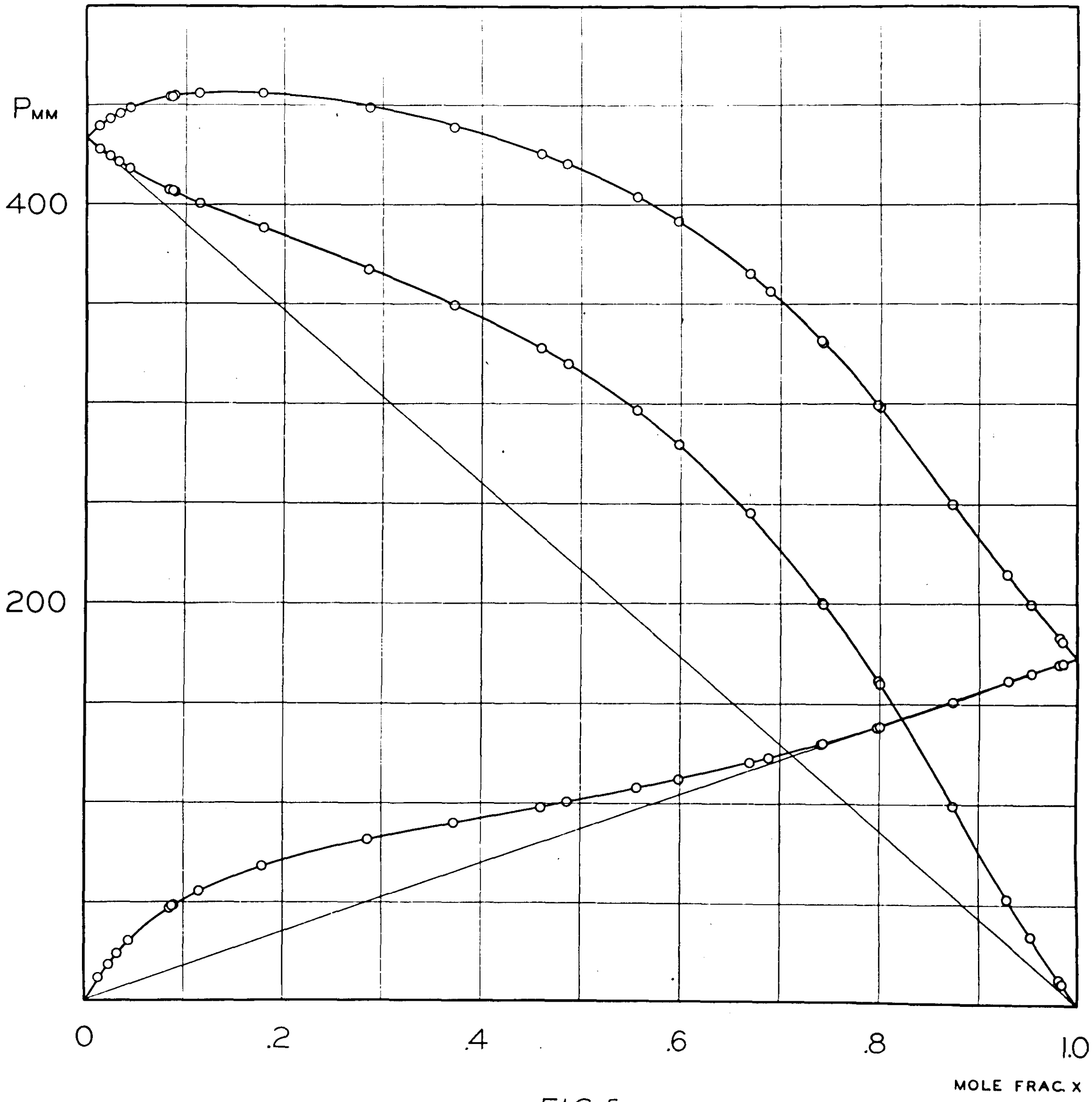


FIG. 5

where P_1 and P_2 are the vapor pressures of the pure components at temperature T and V_1 and V_2 are the molal volumes of the pure liquids.

The Gibbs-Duhem equation, relating the value of the chemical potential of one component to that of the other, offers a means of estimating these deviations of the vapor mixtures from the perfect gas laws by the use of vapor-liquid equilibrium measurements. Since the values of these deviations are small, equilibrium data of a comparatively high degree of accuracy are required to carry out this calculation successfully. The Gibbs-Duhem equation for a binary system is

$$x\, d\mu_1 + (1-x)\, d\mu_2 = 0$$

By differentiating the expressions for μ_1^M and μ_2^M at constant T and considering P and y variables and substituting, the above equation takes the following form

$$y\,(1-y)\,\frac{d\ln P}{dy} = -(x-y)\,\frac{1-2\delta\,(P/RT)\,y\,(1-y)}{1+P/RT\left\{x\,(\beta_1-V_1)+(1-x)(\beta_2-V_2)+\delta\left[x(1-y)^2+(1-x)y^2\right]\right\}}$$

For simplicity let the second factor on the right hand side of the expression equal R and let the equation be written

$$y\,(1-y)\,\frac{d\ln P}{dy} = -R\,(x-y)$$

The quantities $(x-y)$ and $y(1-y)\,\dfrac{d\ln P}{dy}$ can be derived from the experimental data. If the data represents equilibrium accurately, the difference in the values of these two quantities is caused entirely by the deviations of the vapors from the perfect gas laws. By determining R at different values of y so that the above equation is satisfied, values of β_1, β_2 and S can be estimated.

In order to carry out this calculation it is necessary to obtain values of $\frac{d \ln P}{dy}$. These slopes were obtained by numerical differentiation using the Rutledge (16) method for five points. The method assumes that essentially the desired slope is given by the slope of a biquadratic passed through five evenly spaced, adjacent points including the point at which the sloped desired. The symetrical case where the point in question is the third of the five adjacent points was used in this work.

The differentiation was not carried out directly on the log P-y curve but on the Δ log P-y relation. Δ log P represents the deviations of the observed values of log P from those calculated assuming log P as a linear function of y.

$$\Delta \log P\ (35°C) = \log P_{obs.} - (2.469978 - .458091y)$$

$$\Delta \log P\ (45°C) = \log P_{obs.} - (2.637026 - .399573y)$$

$$\Delta \log P\ (55°C) = \log P_{obs.} - (2.790874 - .343927y)$$

The values of Δ log P for the experimental points at these three temperatures appear in the last columns of Tables III, IV and V. Figure (6) shows the curves obtained by plotting

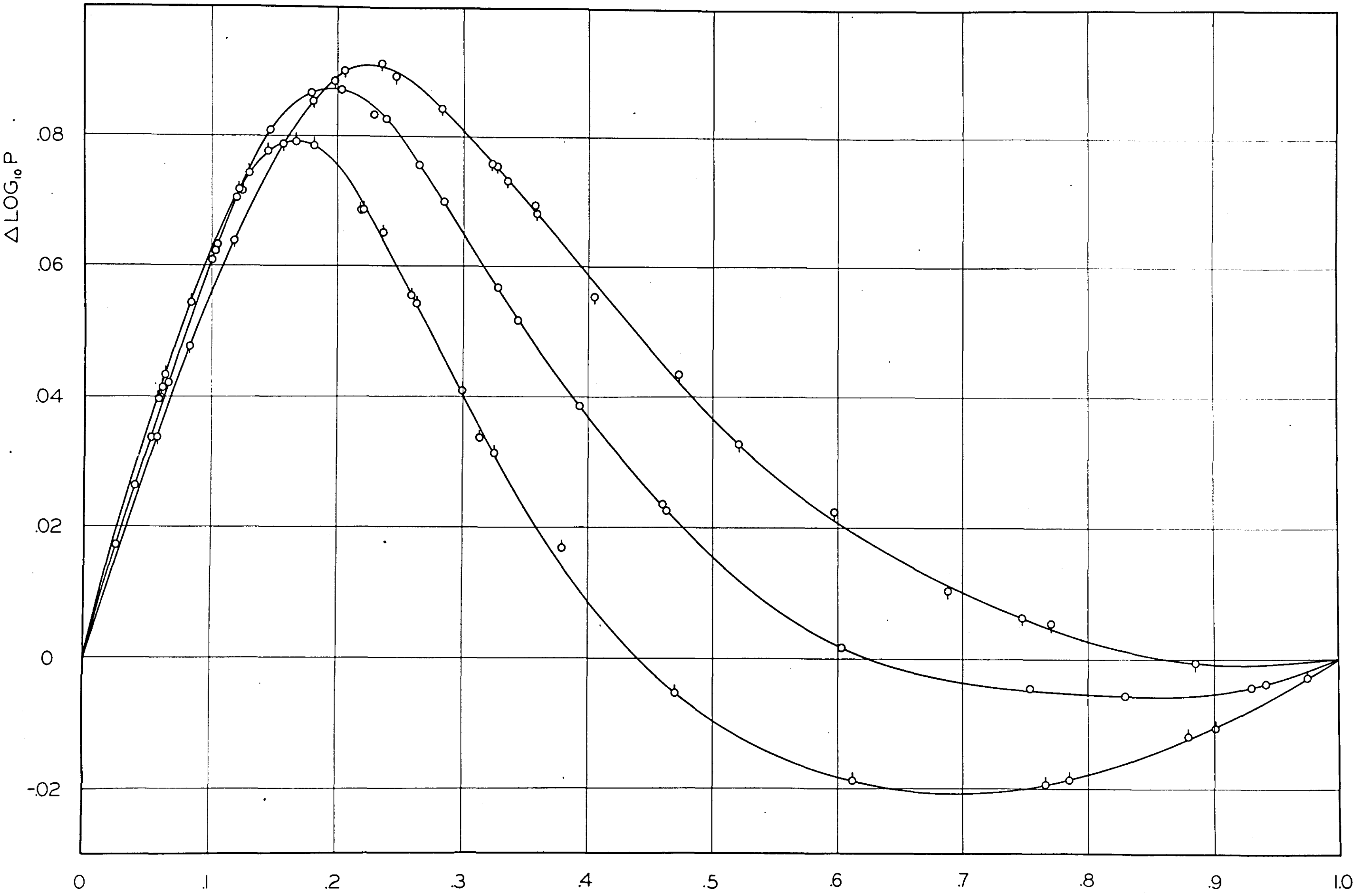


FIG. 6

these values against y. The 35°C. curve is indicated by circles with flags pointing upwards, the 45°C. curve by circles and the 55°C. curve by circles with flags pointing downwards. These points fall on a smooth curve with a few exceptions to corresponding pressure errors of 0.1 m.m. of Hg, assuming the values of y to be exact. The values of $\Delta \log P$ were smoothed in the third difference for rounded values of y at 1 mole % intervals. The numerical differentiation was carried out and by adding the slope of the straight line values of $\frac{d \ln P}{dy}$ obtained at y intervals of every 2 mole %. The accuracy of determining these slopes by this method depends on how rapidly the slope is changing at the point in question. It was found for the curves in figure(6) for which the differentiation was carried out that the calculated values of the slopes had a maximum uncertainty of about 0.1% for any given set of smoothed data. The smoothed values of $\Delta \log_{10} P$ and $-y\,(1-y)\,\frac{d \ln P}{dy}$ for 35°C., 45°C. and 55°C. appear at 4 mole % intervals of y in the second and third columns of Tables, VI, VII and VIII.

The solid lines in figure (7) represent $-y\,(1-y)\,\frac{d \ln P}{dy}$ calculated from the slopes as abscissae plotted against y as ordinates at 35°C., 45°C. and 55°C. The scale of the 45°C. curve is as indicated, and the ordinate scale for the other two temperatures displaced .05 units. The crosses in figure (7) represent the experimental values of (x-y).

The irregularities in the calculated curves apparently are caused for the most part by error in the experimental points. By referring to the Δ log P curves in figure (6), it can be seen that there is a certain degree of uncertainty as to their position. It was necessary in drawing the curves to miss points even though the corresponding errors in the pressures were not greater than 0.1 m.m. The recalculation of $\frac{d \ln P}{dy}$ was carried out by differentiating the ΔP-y curve and obtaining $\frac{dP}{dy} \times \frac{1}{P}$. The values of $y(1-y)\frac{d \ln P}{dy}$ calculated on this basis differed from those calculated on the original basis by about .5 mole % in the irregular parts of the curve. The agreement was much better than this on the regular portions. Since the maximum difference between the calculated curve and the experimental values of (x-y) are about 2.4 mole % and since the uncertainty of the position of the calculated curve is relatively large, the values of β_1, β_2 and S cannot be independently determined with any degree of accuracy from the values of R derived from the equilibrium data alone. It is, therefore, convenient to obtain an idea of the values of β_1 and β_2 from another source.

Table VI

35°C.
Smoothed values for Rounded Y

			S=0	S= -1300
mole fraction Y	$\Delta \log_{10} P_{m.m.}$	$-2.3y(1-y)\frac{d \log P}{dy}$	$\frac{1}{R_o}$	$\frac{1}{R}$
.00	.00000			
.04	.02748	-.0189		
.08	.05238	-.0154	.97110	.97569
.12	.07098	.0291	.96901	.97628
.16	.07914	.1279	.96872	.97778
.20	.07562	.2533	.96842	.97989
.24	.06270	.3472	.96944	.98182
.28	.04762	.3882	.97107	.98352
.32	.03280	.4083	.97306	.98498
.36	.01970	.4016	.97491	.98620
.40	.00880	.3890	.97668	.98723
.44	-.00004	.3711	.97839	.98813
.48	-.00692	.3495	.98002	.98890
.52	-.01206	.3253	.98152	.98959
.56	-.01576	.3043	.98282	.99019
.60	-.01830	.2819	.98402	.99071
.64	-.01996	.2595	.98517	.99118
.68	-.02078	.2340	.98654	.99162
.72	-.02076	.2071	.98733	.99201
.76	-.01976	.1769	.98838	.99231
.80	-.01786	.1481	.98937	.99260
.84	-.01530	.1197	.99030	.99291
.88	-.01226	.0914	.99122	.99320
.92	-.00872	.0615	.99212	.99347
.96	-.00464	.0308	.99300	.99371
1.00	.00000			

Table VII

45°C.

Smooth Values for Rounded Y

			$\delta=0$	$\delta=-650$
Y	$\Delta \log_{10} P_{m.m.}$	$-2.3\, y(1-y)\frac{d \log P}{dy}$	$\frac{1}{R_o}$	$\frac{1}{R}$
.00	.00000			
.04	.02490	-.0187	.96802	.96945
.08	.04858	-.0275	.96593	.96903
.12	.06958	-.0183	.96452	.96926
.16	.08366	.0602	.96398	.97030
.20	.08722	.1545	.96432	.97211
.24	.08258	.2581	.96541	.97443
.28	.07142	.3285	.96729	.97661
.32	.05916	.3533	.96937	.97854
.36	.04744	.3583	.97142	.98018
.40	.03698	.3580	.97337	.98157
.44	.02564	.3521	.97513	.98280
.48	.01928	.3435	.97680	.98391
.52	.01188	.3270	.97837	.98488
.56	.00602	.2976	.97981	.98570
.60	.00178	.2694	.98114	.98643
.64	-.00110	.2427	.98234	.98710
.68	-.00298	.2194	.98347	.98769
.72	-.00410	.1963	.98453	.98820
.76	-.00486	.1754	.98559	.98871
.80	-.00548	.1524	.98662	.98918
.84	-.00586	.1243	.98761	.98960
.88	-.00568	.0949	.98853	.99001
.92	-.00476	.0618	.98942	.99042
.96	-.00286	.0456		
1.00	.00000			

Table VIII

55°C.

Smoothed Values for Rounded Y

			S=0	S=-325
Y	$\Delta \log_{10} P_{m.m.}$	$-2.3\ y(1-y)\ \frac{d \log P}{dy}$	$\frac{1}{R_o}$	$\frac{1}{R}$
.00	.00000			
.04	.02274	-.0202		
.08	.04492	-.0286	.95965	.96151
.12	.06380	-.0232	.95840	.96145
.16	.07904	.0093	.95800	.96219
.20	.08874	.0688	.95843	.96320
.24	.09050	.1699	.95970	.96581
.28	.08496	.2474	.96160	.96825
.32	.07686	.2813	.96379	.97057
.36	.06792	.3040	.96600	.97213
.40	.05862	.3194	.96815	.97449
.44	.04928	.3528	.97017	.97609
.48	.04046	.3190	.97200	.97747
.52	.03258	.3010	.97361	.97868
.56	.02602	.2796	.97510	.97974
.60	.02052	.2603	.97652	.98070
.64	.01584	.2400	.97795	.98158
.68	.01174	.2204	.97930	.98242
.72	.00814	.1986	.98056	.98325
.76	.00502	.1748	.98169	.98402
.80	.00242	.1477	.98273	.98471
.84	.00052	.1185	.98372	.98534
.88	- .00060	.0880	.98471	.98591
.92	- .00100	.0582		
.96	- .00074	.0293		
1.00	.00000			

The theory of corresponding states offers a means for the calculation of the β values of one substance from those of another which have been experimentally measured. The theory of corresponding states assumes that P/P_c and V/V_c are the same function of T/T_c for all substances. For a van der Waal's gas at the limit of zero pressure the relation is

$$(V - \frac{RT}{P})\frac{P_c}{RT_c} = 1/8 - 27/64\ T_c/T$$

Experimental measurements show that the measured values of $(V - \frac{RT}{P})\frac{P_c}{RT_c}$ for different substances at the same values of the reduced temperature, while differing widely from the value for a van der Waal's gas, agree quite well among themselves. Cope, Lewis and Weber(33) have shown this to be true for several gaseous hydrocarbons. This work was extended to higher values of the reduced temperatures and pressures and generalized to include all gases by Newton(33) and Newton and Dodge(34). Most of the experimental work has been carried out over a range of the reduced temperature near 1 or higher. Water vapor is the only substance on which measurements have been made over a range corresponding to the region of interest in this work. These measurements were reported by Keyes, Smith and Gerry(35) and cover a wide range of temperature. In the range where these measurements for water vapor overlap with those for other substances the values of $(V - \frac{RT}{P})\frac{P_c}{RT_c}$ agree quite well. As an approximate method of calculation, the β values for ethanol and chloroform are derived on the basis of corresponding states from those measured for water at the same values of the reduced temperature.

If the equations of state of the vapors of water, ethanol and chloroform are of the form

$$P = \frac{RT}{V-\beta} \text{ or } \beta = V - \frac{RT}{P}$$

then on the basis of corresponding states

$$\beta_1 \left(\frac{P_c}{T_c}\right)_1 = \beta_2 \left(\frac{P_c}{T_c}\right)_2 =$$

$$\beta_1 \left(\frac{P_c}{T_c}\right)_1 = \beta_2 \left(\frac{P_c}{T_c}\right)_2 = \beta_{H_2O} \left(\frac{P_c}{T_c}\right)_{H_2O}$$

$$\text{at } \left(\frac{T}{T_c}\right)_1 = \left(\frac{T}{T_c}\right)_2 = \left(\frac{T}{T_c}\right)_{H_2O}$$

The value of β_{H_2O} was taken equal to the values B_o calculated from the equation given by Keyes, Smith and Gerry(35).

The results of this calculation appear below:

t°C.	T_c/T	t°C. (H_2O)	B_o $\frac{cm^3}{mole}$ (H_2O)	β_1 $\frac{cm^3}{mol}$
	Ethanol			
35	1.6753	113.20	-394.7	-1088
45	1.6226	125.75	-350.4	- 966
55	1.5732	138.27	-313.7	- 865
	Chloroform			β_2
35	1.7301	100.96	-447.2	- 1464
45	1.6758	113.09	-395.3	- 1293
55	1.7301	125.23	-352.0	- 1152

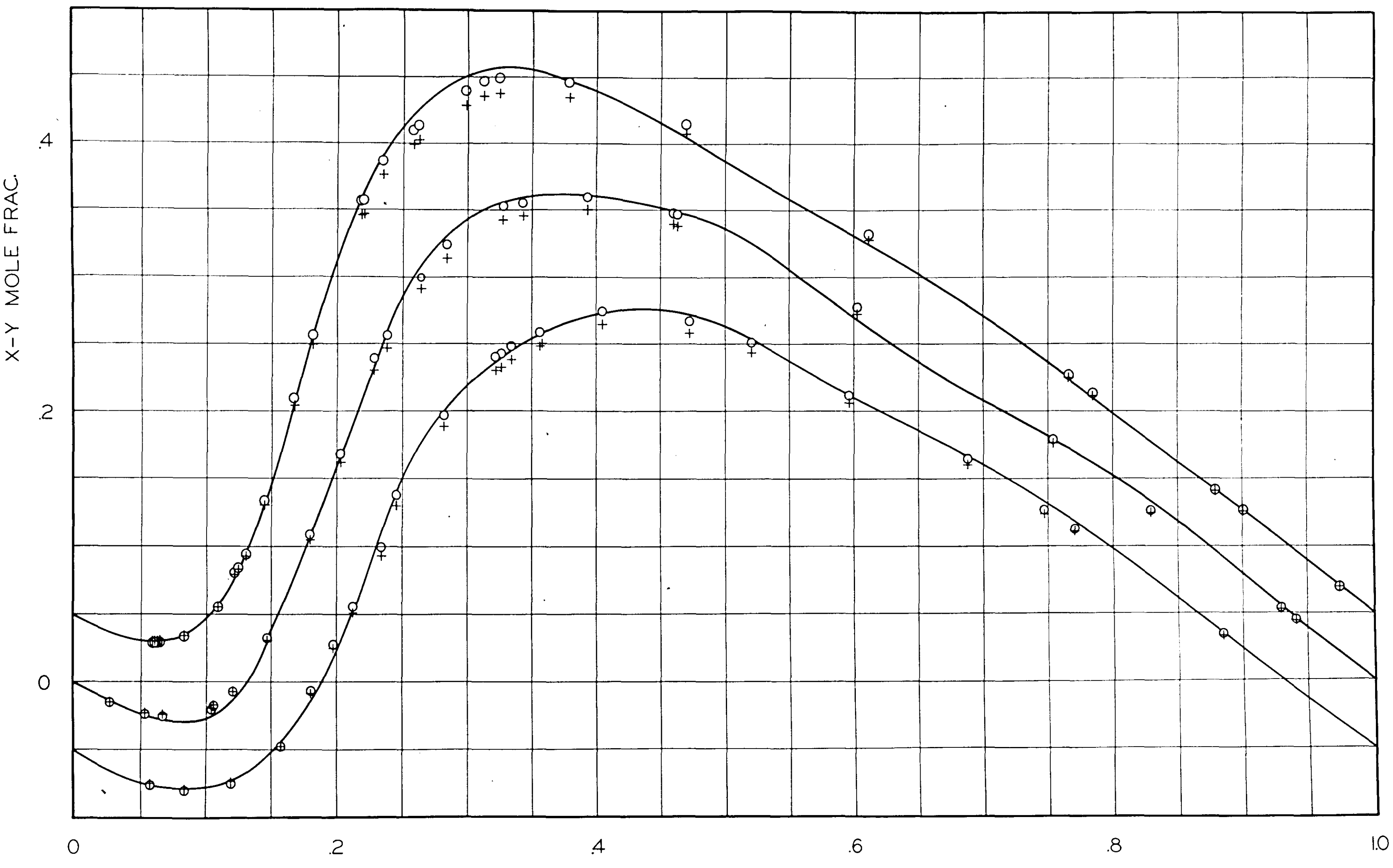


FIG. 7

	T_c°K	P_c atm.
Water	647.27	218.167
Ethanol	516.3	63.1
Chloroform	533.2	54.9

The values of R_o (x-y) were calculated assuming the above values of β_1 and β_2 where R_o is the value of R for δ=0. It was found that better agreement between the calculated curve and R (x-y) was obtained using these same values of β if the δ values of $-1300 \frac{cm^3}{mol}$, $-650 \frac{cm^3}{mol}$ and $-325 \frac{cm^3}{mol}$ were assumed at 35°C., 45°C., and 55°C. The values of R (x-y) calculated using these values of δ are represented by the circles in Figure (7). It is evident the corrections are of the right order to give agreement between R (x-y) and the calculated curve. The correction, while it is only approximate, is nevertheless, quite significant.

The relatively large values of δ which were assumed would require that the interaction between a molecule of chloroform and one of alcohol be considerably larger than between two molecules of chloroform or two molecules of alcohol. Since ethanol and chloroform both have sizeable dipole moments, this large interaction may be explained by assuming a result of the structure of the molecules the dipoles of the two unlike molecules can approach closer in a parallel position than the two like molecules. If this were true δ would also be expected to decrease rapidly with increasing temperature.

In the last two columns of Tables VI, VII, and VIII are given smoothed values of $\frac{1}{R_0}$ and $\frac{1}{R}$ for the three temperatures where R_0 is calculated for $\delta=0$ and R is calculated for $\delta = -1300 \frac{cm^3}{mol}$ at 35°C., $\delta=-650 \frac{cm^3}{mol}$ at 45°C., and $\delta = -325 \frac{cm^3}{mol}$ at 55°C. These values of δ together with the β values derived from B_0 of water on the basis of corresponding states will be used in the subsequent calculations.

The values of μ_1^E and μ_2^E in International Joules calculated for smoothed values of P and y at round x appear in Tables IX, X and XI at 35°C., 45°C., and 55°C., and are plotted for these temperatures in figure (8) {μ_1^E)and figure (9) {μ_2^E). The 35°C. curve is indicated by circles, the 45°C. by triangles and the 55°C. by flagged circles. The ordinates for each temperature are displaced 500 joules. The values of μ_1^E become negative and the curve passes through a minimum becoming less pronounced with increasing temperature. The μ_2^E goes through a corresponding maximum.

The Free Energy excess per average mole was calculated from μ_1^E and μ_2^E. The values for the three temperatures are given in the last columns of Tables IX, X and XI and are plotted against x in figure (10). The corrections included in F_x^E introduced by the (β-V) term are represented by corr$_1$ and that introduced by the δ term by corr$_2$.

$$-\mathrm{Corr}_1=(\beta_1-V_1)(P-P_1)\,x + (\beta_2-V_2)(P-P_2)(1-x)$$

$$-\mathrm{Corr}_2=\delta P\,(1-y)^2 x + \delta\,P\,y^2\,(1-x)$$

The values of corr$_1$ and corr$_2$ are given in Tables XII and XIII.

Table IX

35°C. Isotherm

Smoothed Values at Rounded x

Mole frac. C_2H_5OH

x	y	$P_{m.m.}$	μ_1^E joules	μ_2^E joules	F_x^E joules
0	.0000	295.11		0	0
.01	.0196	298.29	4369.9	1.8	45.4
.02	.0356	300.74	4144.2	6.0	88.8
.05	.0696	304.89	3555.9	27.9	204.3
.10	.1024	306.84	2788.0	90.0	359.8
.20	.1382	304.22	1762.3	265.6	565 .0
.30	.1622	298.53	1090.1	487.8	668.5
.40	.1864	290.20	640.9	736.4	698.2
.50	.2142	276.98	311.7	997.2	654.5
.60	.2554	257.17	113.0	1244.6	565.6
.70	.3156	228.88	- 28.0	1472.4	422.2
.80	.4246	190.19	- 70.5	1599.1	263.4
.90	.6412	143.23	- 27.8	1442.1	119.2
.95	.8000	121.58	- 13.7	1301.6	52.1
.98	.9168	109.83	- 2.0	1143.6	20.9
.99	.9586	106.20	.7	1046.2	11.2
1.00	1.0000	102.78	0		0

Table X

45°C. Isotherm

Smoothed Values for Rounded x

Mole frac. C_2H_5OH

x	y	$P_{m.m.}$	μ_1^E joules	μ_2^E joules	F_x^E joules
0	.0000	433.54		0	0
.01	.0206	438.59	4297.7	1.3	44.2
.02	.0374	442.16	4051.2	3.1	84.1
.05	.0746	449.38	3514.6	22.4	197.0
.10	.1132	455.06	2819.2	84.6	358.0
.20	.1552	454.53	1821.4	264.3	575.7
.30	.1850	446.75	1170.9	477.8	685.8
.40	.2126	435.19	712.6	727.1	721.3
.50	.2440	417.71	383.3	995.9	689.6
.60	.2862	391.04	155.4	1262.8	598.4
.70	.3530	351.18	28.5	1486.9	466.0
.80	.4640	298.18	- 21.7	1636.7	309.9
.90	.6688	232.58	- 9.2	1548.4	146.5
.95	.8202	200.81	4.9	1380.4	73.7
.98	.9242	183.38	1.3	1280.8	26.9
.99	.9610	177.95	- 1.1	1274.3	11.7
1.00	1.0000	172.76	0		0

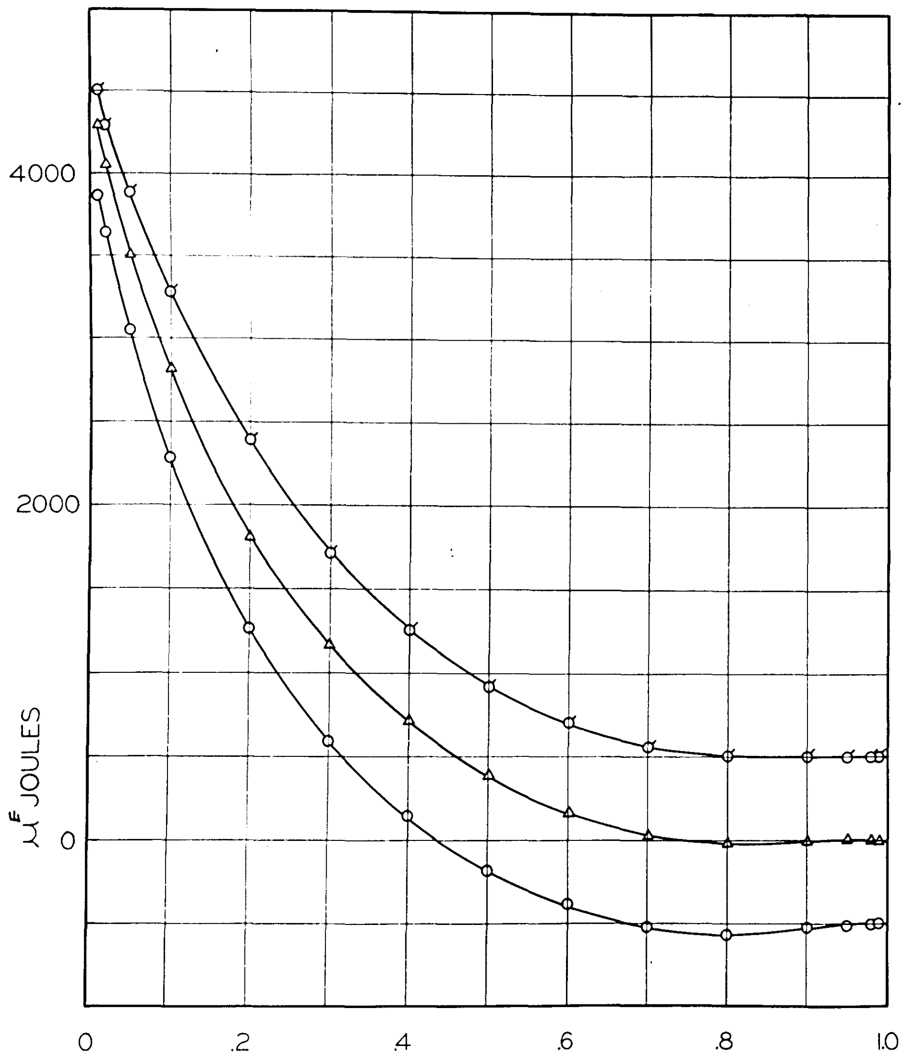
Table XI

55°C. Isotherm

Smoothed Values for Rounded x

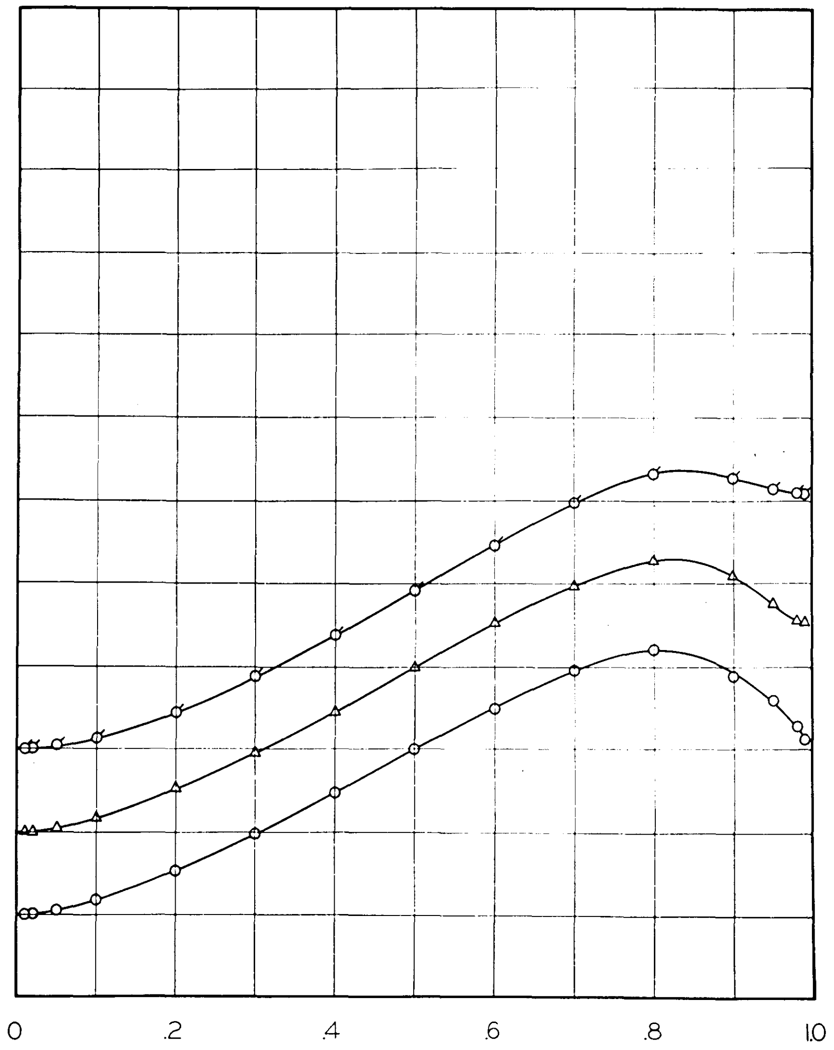
Mole frac. C_2H_5OH

x	y	$P_{m.m.}$	μ_1^E Joules	μ_2^E Joules	F_x^E Joules
0	.0000	617.84		0	0
.01	.0200	624.02	4008.5	-1.6	38.5
.02	.0366	629.94	3791.3	4.3	80.1
.05	.0774	642.22	3390.3	21.3	189.8
.10	.1226	650.84	2790.2	66.7	339.1
.20	.1736	652.23	1898.9	220.9	556.5
.30	.2086	643.65	1218.4	440.9	674.2
.40	.2402	628.77	758.2	688.7	716.5
.50	.2748	605.23	417.3	958.2	687.8
.60	.3226	570.62	203.4	1225.4	612.2
.70	.3892	521.14	56.6	1487.8	486.0
.80	.5012	452.00	5.9	1662.8	337.3
.90	.6946	364.32	.9	1639.1	164.8
.95	.8306	320.64	- .8	1571.4	77.8
.98	.9274	295.85	-1.0	1549.7	30.1
.99	.9628	287.85	- .2	1542.9	15.2
1.00	1.0000	279.86	0		0



4000
2000
0
μ^E JOULES
0
.2
.4
.6
.8
1.0
X-MOLE FRAC.

FIG. 8



0
.2
.4
.6
.8
1.0
X-MOLE FRAC.

FIG. 9

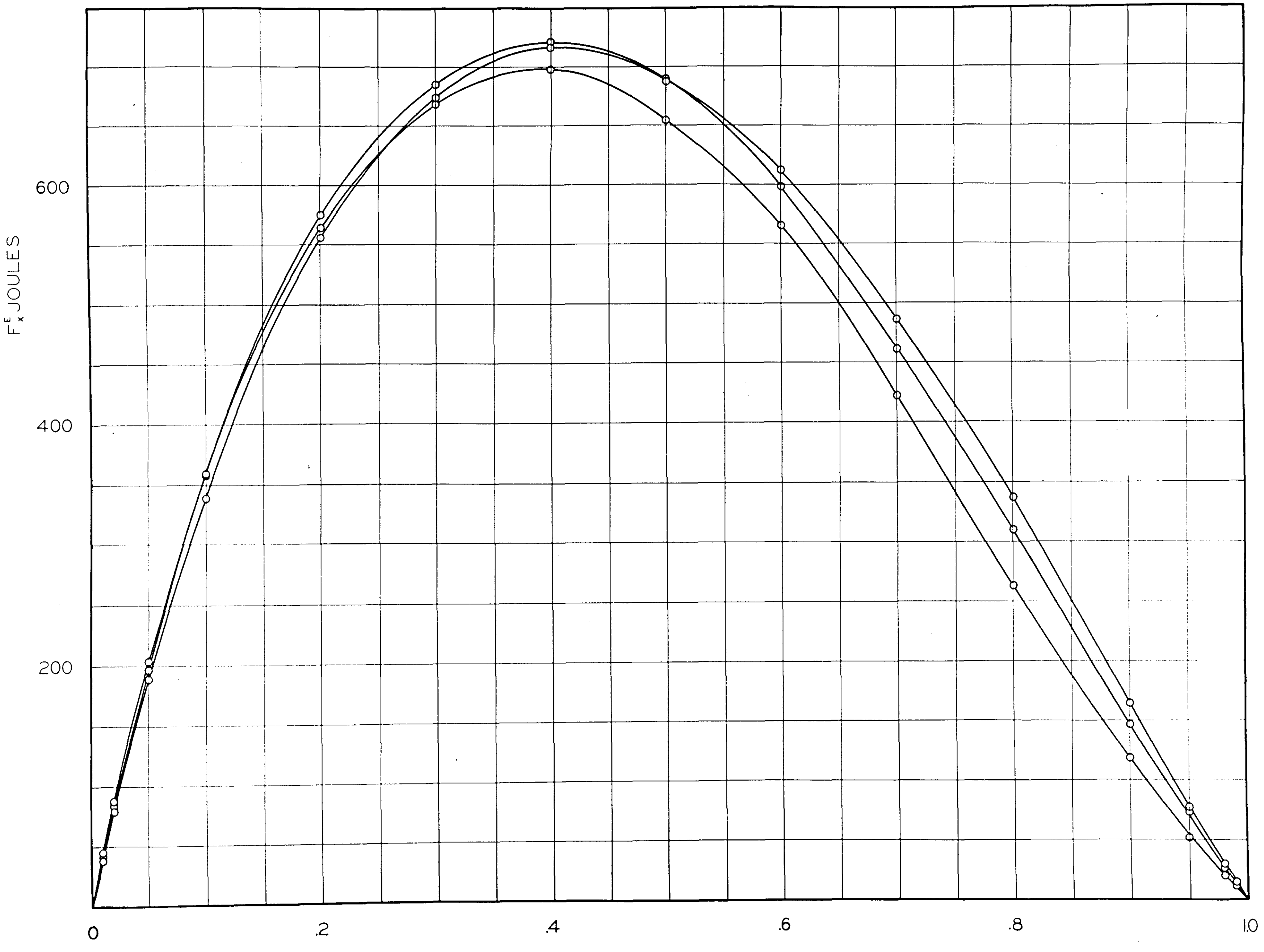


FIG.10

Table XII

	35°C.			55°C.		
x	F_x^E joules	corr.(1)	corr. (2)	F_x^E joules	corr(1)	corr(2)
0	0			0		
.01	45.4	1.0	0.5	38.5	1.4	0.3
.02	88.8	1.7	1.0	80.1	2.8	0.5
.05	204.3	3.5	2.5	189.8	6.1	1.6
.10	359.8	5.3	4.8	339.1	9.5	2.6
.20	565.0	7.7	8.6	556.5	13.8	4.5
.30	668.5	9.5	11.8	674.2	16.5	6.1
.40	698.2	10.9	14.4	716.5	18.4	7.2
.50	654.5	11.5	15.9	687.8	19.1	7.9
.60	565.6	11.1	15.9	612.2	18.5	7.8
.70	422.2	9.5	14.0	486.0	16.1	6.9
.80	263.4	6.4	9.6	337.3	13.6	4.9
.90	119.2	2.5	3.9	164.8	5.2	2.1
.95	52.1	1.0	1.5	77.8	2.3	0.9
.98	20.9	0.3	0.5	30.1	0.9	0.2
.99	11.2	0.1	0.2	15.2	0.4	0.1
1.00	0			0		

The values of S_x^E and H_x^E can be calculated by means of the second law equation from the change in F_x^E with temperature.

$$\left(\frac{d\ F_x^E}{d\ T}\right)_{x,P} = -S_x^E$$

The values of $\left(\frac{d\ F_x^E}{d\ T}\right)_x$ along the saturation curve at 45°C. can be calculated from the tabulated values of F_x^E at 55°C. and 35°C.

$$\left(\frac{d\ F_x^E}{d\ T}\right)_{x\ sat.} = {\frac{F_x^E\ (55°C.) - F_x^E\ (35°C)}{20}}_x$$

$$\left(\frac{d\ F_x^E}{d\ T}\right)_{xP} = \left(\frac{dF_x^E}{dT}\right)_{x\ sat.} - V_x^M \left(\frac{d\ P}{d\ T}\right)_{x\ sat.}$$

The second term which depends on the deviation of the volumes of the liquids from additivity(V_x^M) is for this system always less than 0.1 of a joule and can be neglected. Then

$$-S_x^E\ (45°C.) = \frac{F_x^E\ (55°C.)-F_x^E(35°C)}{20}$$

The values of TS_x^E (45°C.) are given in the third column of Table XIII. By combining TS_x^E (45°C.) and F_x^E (45°C.) values of ΔH_x^E (45°C.) were calculated and are given in the second column of Table XIII. In figure (11) F_x^E (45°C.), H_x^E (45°C.) and $-TS_x^E$ (45°C.) are plotted against x. The H_x^E curve is indicated by flagged circles, F_x^E by circles and $-TS_x^E$ by triangles.

The values of H_x^E have been measured calorimetrically for chloroform-ethanol mixtures at 25°C. by Hirobe(11). The results were later correlated by Coleman and Germann(17) by the equation

$$H_x^E = x_1 x_2\ (-6.30+11.3\ x_1)\ \text{kilo joules}$$

where x_1 is the mole fraction of chloroform. The values of H_x^E (25°C.) calculated from this equation are in agreement with the measured values at 45°C. The calculated values H_x^E (25°) appear in the last column of Table XIII and can be seen to be on the whole more negative than H_x^E (45°C.) calculated from the equilibrium data.

Table XIII

x	45°C. H_x^E joules	45°C. TS_x^E joules	45°C. F_x^E joules	corr.(1)	corr.(2)	25°C. H^x_E (17) joules
0	0	0	0			
.01	154	110	44.2	1.3	1.4	
.02	223	139	84.1	4.2	.8	
.05	428	231	197.0	4.7	1.9	211
.10	688	330	358.0	7.4	3.6	348
.20	710	134	575.7	10.8	64	438
.30	595	- 91	685.8	13.0	8.6	338
.40	430	- 291	721.3	14.6	10.4	115
.50	160	- 530	689.6	15.3	11.4	-163
.60	- 143	- 741	598.4	15.2	11.6	-427
.70	- 549	-1015	466.0	12.6	10.1	-611
.80	- 865	-1175	309.9	8.8	7.1	-646
.90	- 578	- 743	146.5	3.7	2.9	-465
.95	- 336	- 409	73.7	1.9	1.1	-272
.98	- 119	- 146	26.9	0.5	0.4	
.99	- 53	- 65	11.7	0.2	0.2	
1.00	0	0	0			

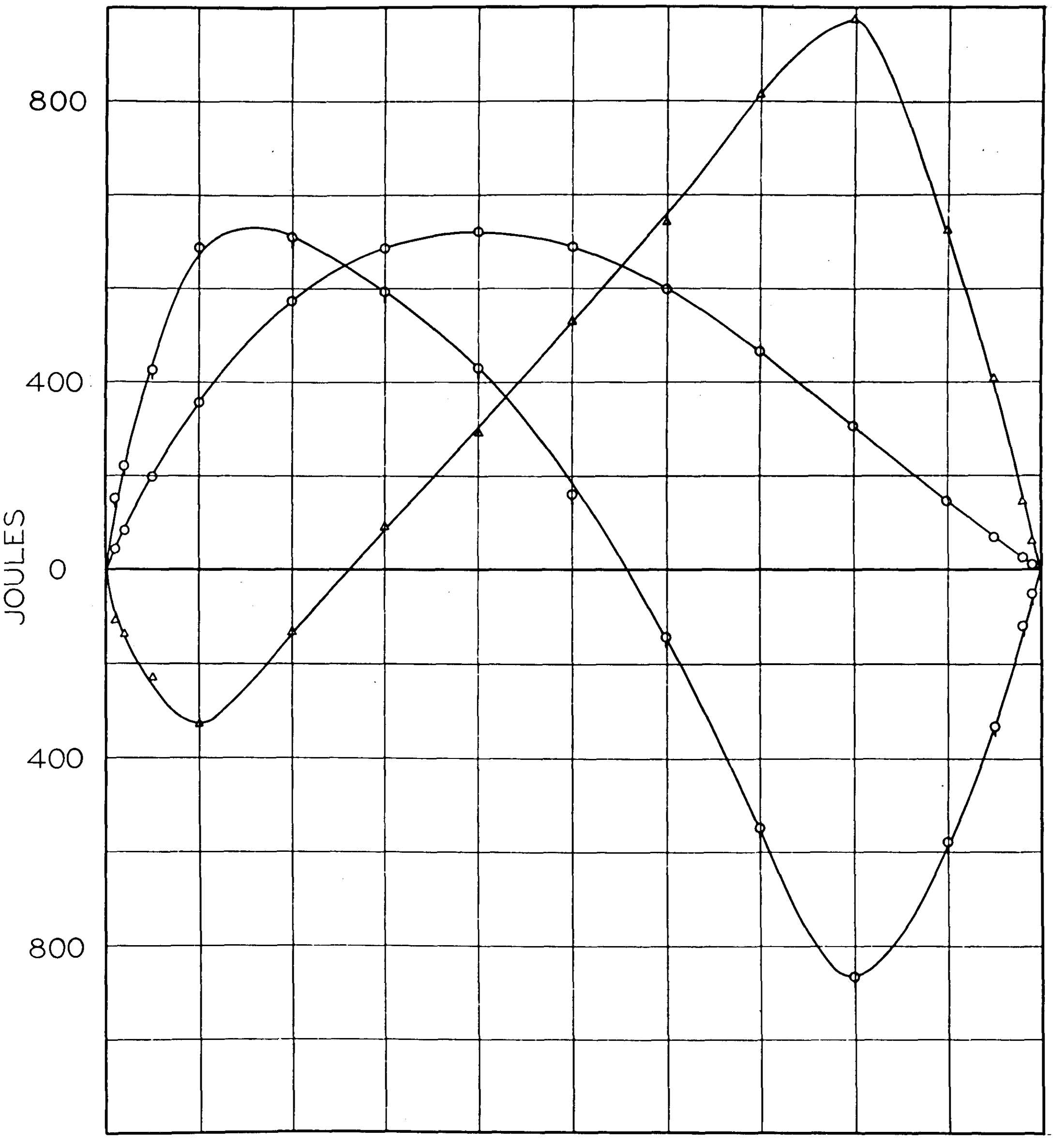


FIG.11

Discussion

In regard to the experimental measurements it should be emphasized that the accuracy of the results are probably limited, not by the actual precision of the measurements, but by departure of the measured conditions from the true equilibrium state. Of the four measured quantities, the two compositions, the temperature and the pressure, the determination of the compositions is the least precise. There are no definite criteria to judge with certainty the degree of approach of experimental conditions to the true equilibrium state. The application of the Gibbs-Duhem equation which has been discussed previously is an indication of the existence of equilibrium but not an absolute criterion. The deviations of experimental measurements from this equation larger than those corresponding to error of the measuring instruments can be attributed not only to the failure of the measurements to represent equilibrium accurately, but also to an inaccurate knowledge of the deviations of the vapors from the perfect gas laws. The impossibility of separating these two effects probably accounts for most of the difficulty encountered in the independent calculation of the deviations of mixtures of chloroform and ethanol vapors from the gas laws by the use of equilibrium data alone. However, the departure of the reported experimental results for chloroform, ethanol mixtures from equilibrium must be small as indicated by the agreement obtained by the application of the Gibbs-Duhem Equation as shown in figure (7). The fact that this system gives such large separations between the liquid and vapor compositions, which reach a maximum value of 40 mole %, places rather severe demands on the experimental method. The equilibrium state could probably be approached more closely for systems where this separation is not as great.

Mixtures of chloroform and ethanol form solutions which give large deviations from ideality. For ideal solutions the excess entropy, heat and free energy of mixing are zero by definition, but for this system the excess free energy assumes large positive values while the excess heat and entropy assume both positive and negative values.

For two components to form an ideal solution the interaction between any molecule in the solution and the surrounding medium must be independent of the composition and equal to that in the pure components. Molecular interaction between non-electrolytes can be attributed to physical forces which are the resultant of the following components, London dispersion forces, interaction between two permanent dipoles and interaction between a permanent dipole and an induced dipole. In addition to these forces of physical nature there is the possibility of chemical action between the two components to form compounds causing abnormal behavior as a result of what is commonly known as association.

Both chloroform and ethanol are polar liquids with dipole mo~~ve~~ments of 1.05 x 10^{-18} and 1.70 x 10^{-18} e.s.u. respectively. Experimental evidence indicates that ethanol is presumably associated in the pure state while chloroform is not to any appreciable degree. However, since chloroform has a sizeable dipole moment, the distribution in the pure liquid must depend on orientation and be far from random. Solutions of these two polar components would be expected to show large deviations from ideality, and also the deviations should vary with temperature. The more specific properties of the deviations cannot, however, be accounted for by assuming dipole-dipole interaction is the predominant effect.

The heats of mixing of chloroform with ethyl ether, acetaldehyde, acetone, ethyl acetate, methyl, n-propyl, isobutyl and isoamyl alcohols have been measured at 25°C. by Hirobe(11). The measured heats of mixing of chloroform with ethyl ether, acetone, acetaldehyde and ethyl acetate do not change sign but are negative throughout the composition range. The dipole moments of these four substances are about the same as the moment of ethanol; and consequently if the predominate effect in the interaction were dipole-dipole attraction, the mixtures of chloroform with ethanol and the above mentioned substances should behave in at least approximately the same manner. Since this is not true, it can be concluded that for mixtures of chloroform and ethanol other effects are important in addition to dipole-dipole attraction and that the explanation of their behavior must be more complicated.

The measured heats of mixing of chloroform with methyl, n-propyl, isobutyl and isoamyl alcohols agree qualitatively with those for chloroform and ethanol in that the values are positive in the high chloroform concentration range and negative in the high ethanol range. Since in the high chloroform range for ethanol, chloroform mixtures the excess entropy is also positive, there is an indication on the basis of the concept of entropy that the distribution in the mixture is more random than in the pure components. This effect can be thought of as resulting from an effect analogous to dissociative forces. Likewise in the high ethanol range where the excess entropy assumes relatively large negative values, large ineractions analogous to associative forces could be assumed to exist causing the distribution in the mixture to become less random. However, any assumption as to the exact nature of the interactions of chloroform and ethanol would on the basis of the existing theories be purely hypothesis.

Summary

The vapor-liquid equilibrium isotherms were measured for chloroform,ethanol mixtures at 35°C., 45°C., and 55°C. by the equilibrium distillation method.

The mixtures were found to form azeotropic systems of maximum vapor pressure at all three temperatures. The composition of the mixtures of maximum vapor pressure shifted with increasing temperature toward higher ethanol content.

The Gibbs-Duhem equation was applied to the results as a means of estimating the deviations of the vapor mixtures from the perfect gas laws.

The excess chemical potentials of mixing for each of the components in mixtures of several different compositions were calculated. This quantity for ethanol became negative and passed through a minimum in mixtures of high ethanol content. For chloroform this quantity passed through a corresponding maximum and was positive at all compositions. The maximum and minimum became more pronounced with decreasing temperature.

The excess free energies of mixing were calculated for the series of compositions at each of the three temperatures and were found to vary considerably with temperature.

The excess entropies and heats of mixing at 45°C. were calculated from the variation of the excess free energy with

temperature. The calculated heats of mixing at 45°C. were in qualitative agreement with values measured calorimetrically at 25° by Hirobe.

PART II

APPENDIX

Description of Previous Stills

The following discussion is a brief review of the contributions of various workers to the development of the distillation method of measuring vapor, liquid equilibrium.

DuClaux (1878). DuClaux(18) was interested in studying the equilibrium vapor, liquid compositions of binary mixtures from the viewpoint of separating by distillation mixtures of water and several different alcohols. The measurements were carried out at constant pressure (1 atm.) and no attempt was made to measure the equilibrium temperature. A simple distillation apparatus was used consisting of a liquid boiler, condenser, and distillate receiver. A 1010 c.c. volume of a liquid mixture of known composition and weight was introduced into the boiler and 11 separate portions of 10 c.c. each were distilled over. Each sample was analysed and weighed. The composition of the residual liquid at the end of each separate distillation could then be calculated. The equilibrium vapor composition was taken as the value given by the analysis of the different portions of the distillate. The corresponding equilibrium liquid composition was taken as the average of the initial and final compositions over each distillation interval. The values of the compositions obtained from this simple distillation method can at best be only approximately equal to the true equilibrium values.

Zawidski (1900). The method employed by Zawidski (3) was a dynamic one and was similar in principle to that of DuClaux. In addition to determining the equilibrium vapor and liquid compositions, the equilibrium temperature and pressure were measured. The ratio of the volumes of the condensed vapor sample and the residual liquid was small and the compositions of each were assumed to remain essentially constant during the distillation. Temperatures were measured with a precision ± .01°C. by means of a mercury thermometer immersed directly in the liquid. Pressures were measured with a mercury manometer with a precision of ± ,3 m.m. of Hg.

The liquid boiler was surrounded by a thermostat maintained at 1°C. above the desired boiling temperature. Additional heat was supplied by an internal electric resistance heater of platinum wire which also aided boiling by preventing super heating. The volume of the liquid in the boiler ranged from 100 c.c. to 120 c.c., and volume of the condensed distillate sample was about 1 c.c. The condenser was maintained at 0°C. by an ice jacket. The tube conducting the vapors from the boiler to the condenser was heated externally to prevent reflux. The pressure system was stabilized by a 20 liter barostat.

Compositions were determined by refractive indices, and the values had an uncertainty of ± .5 mole %. During the distillation, the compositions of the liquid and vapor vary continuously. The error introduced by this effect depends on the relative volumes of the liquid and distillate. Zawidski observed temperature drifts during the course of a distillation as large as .08°C.

Zawidski in his discussion of his apparatus stated that some distillation occurred so rapidly equilibrium between the vapor and liquid probably was not established. Any dynamic method where vaporization or condensation occurs at the point where equilibrium is desired is subject to this criticism.

Rosanoff, Lamb and Breithut (1909). It was proposed to obtain equilibrium between the vapor and liquid by bubbling a vapor of known composition continuously produced from an external source through a liquid mixture until the equilibrium state was attained. Then at the equilibrium point since no interchange is occurring between the liquid and vapor as much of the vapor can be condensed as desired. Rosanoff, Lamb and Breithut(4) were chiefly interested in investigating the applicability of the procedure and in experimenting with sources of vapor of constant composition.

Later Rosanoff and Easley(19) applied this method to several binary systems. Temperatures were measured with a mercury thermometer immersed in the liquid with a precision of ± .01°C. Pressures were measured by a mercury manometer stabilized by a 100 liter barostat with a precision of

± .1 m.m. of Hg. Compositions were measured by the refractive index method with about the same accurracy as those of Zawidski. The distillate receiver was designed to collect three separate samples of the vapor in order to verify the constancy of its composition. The production of vapor of constant composition proved to be experimentally a rather difficult problem. The measurements were carried out at constant pressure (1 atm.). It would be experimentally difficult to obtain isothermal data by adjusting the pressure with this apparatus.

Rosanoff, Bacon and White (1914). The method suggested by these workers(20) was a variation of the older dynamic method of Zawidski. The apparatus was essentially the same, and the difference came in the experimental procedure. Instead of distilling over only one small vapor sample, several successive were collected until as high as 80% or 90% of the original liquid had been distilled. The composition of each sample was plotted against the total weight distilled. By extrapolation to the composition axis the composition of the vapor that was in equilibrium with the original liquid could be determined. The advantages of this apparatus were its ease of manipulation and the rapidity of obtaining measurements. Here again, isopiestic data was obtained.

Sameshima (1918). Sameshima(5) introduced an apparatus for the measurement of vapor, liquid equilibrium which has been termed an equilibrium still. Essentially the method is a dynamic distillation one, but instead of the distillate being continuously removed from the system a portion of it is trapped and the overflow returned to the liquid. In this method, as in the simple distillation method, the question whether the vapor and liquid are in contact sufficiently long for the establishment of equilibrium when distillation takes place is doubtful. The liquid boiler of the still was surrounded by a thermostat and boiling produced by an internal resistance heater. Reflux was prevented by heating the tube leading to the condenser with an electric resistance coil. The condenser was mounted vertically and was maintained at 0°C. The apparatus was used to determine isothermal data for several binary systems. Pressures were measured with a precision of ± .1 m.m. of Hg. and regulated with the aid of a barostat. Temperatures were measured to ± .01°C. by a mercury thermometer immersed in the liquid. Compositions were measured by the density method.

Othmer (1925). The Othmer(21) still was an equilibrium still designed to measure equilibrium vapor, liquid compositions at 1 atm. pressure for use in the design of fractionating columns. The apparatus was similar in principle to that of Sameshima, but no provision was made for regulation of the pressure and no particular precautions taken to prevent reflux. The chief difference in these two stills was the method of heating and the position of the thermometer. In the Othmer still the liquid boiler was not surrounded by a thermostat, but heated directly by a gas flame. The thermometer instead of being immersed in the liquid was suspended in the vapor. Several variations and improvements of the Othmer still have been used for the determination of liquid, vapor composition curves of many systems for fractionating column design.

Smyth and Engel (1929). The equilibrium still of Smyth and Engel(22) was very similar to the one used by Sameshima. The condenser was maintained at solid CO_2 temperature (-80°C.), and a device for automatic pressure control was devised. The precision of the temperature, pressure and composition measurements were essentially the same.

Hovorka and Dreisbach (1934). The method of measuring vapor, liquid equilibrium introduced by these workers(23) was a combination of a static and dynamic method. The equilibrium temperatures and pressures were measured under essentially static conditions while the determination of the vapor, liquid compositions depended on a distillation process. The apparatus consisted of a liquid vessel communicating with a mercury manometer and connecting by means of a side arm to six vapor sampling tubes in which portions of the distillate could be collected.

After the liquid mixture had been introduced into the liquid vessel the apparatus was evacuated and sealed off.

The whole assembly was placed in a thermostat and the equilibrium pressure measured. One of the side arms was then cooled and about 1/6 of the mixture slowly distilled over. This side arm was then sealed off and the pressure read again. This procedure was repeated until all of the liquid had been distilled in six portions into the six sampling tubes. From the weights and compositions of the six samples of distillate equilibrium liquid and vapor compositions can be calculated. The method used was a variation of that of Rosanoff, Bacon and White(20). The total weight distilled at the end of each distillation period was plotted against the composition of the corresponding distillate sample, but instead of extrapolating the curve to the composition axis, calculations were made by utilizing the slope of the curve.

The compositions of the distillate samples were determined by refractive indices.

Supplementary References

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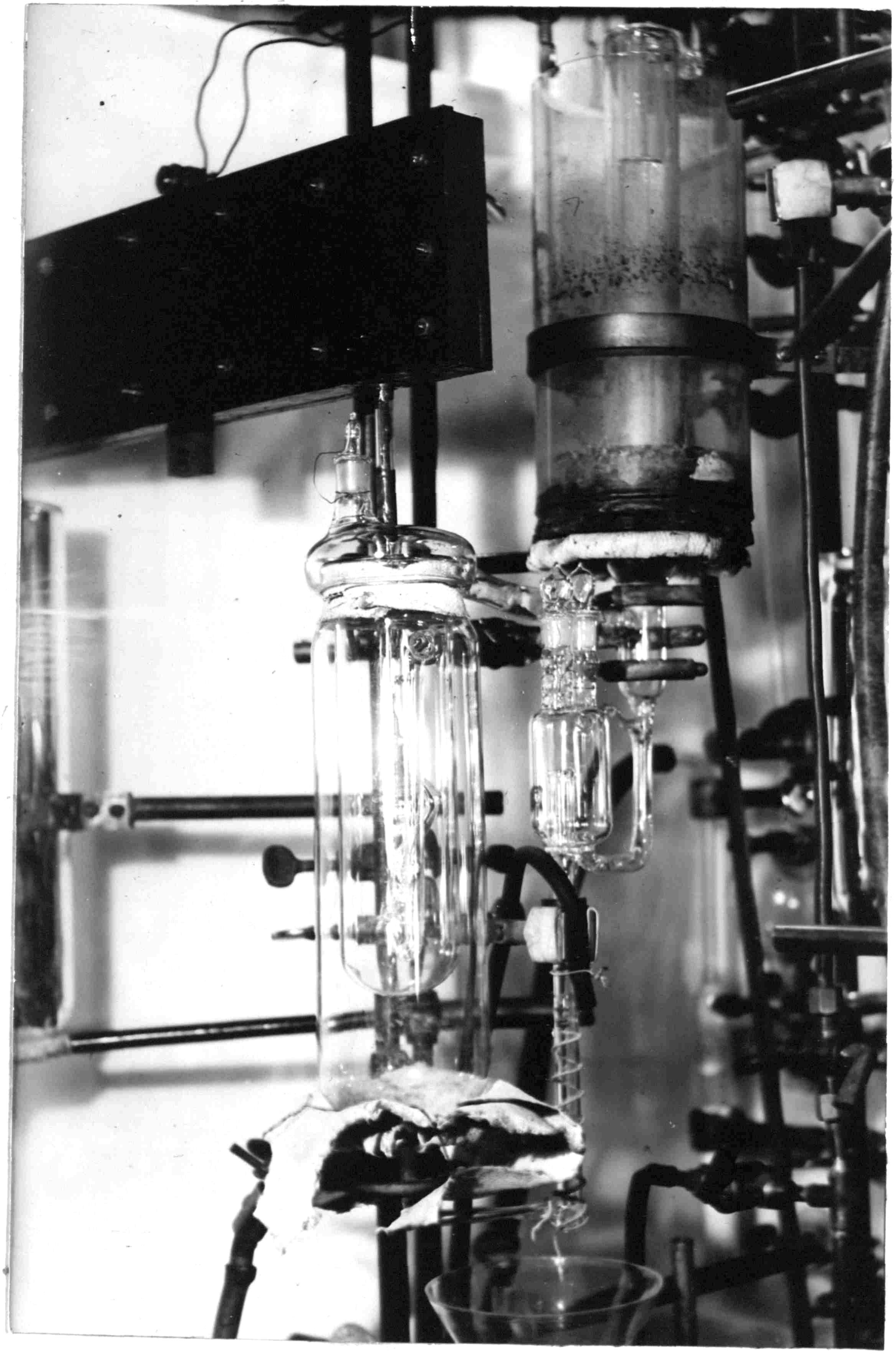


Equilibrium Still and Thermocouple.

Plate I

Operating Details of the Equilibrium Still

A photograph of the equilibrium still is shown in Plate I. When in operation the outer liquid boiler was protected from air currents by a shield of asbestos paper completely surrounding the outside of the still. A small square window was provided in order to observe the liquid level in the inner liquid boiler and the operation of the vapor pump. The exposed surface between the ringseal and the flange on top of the inner boiler was protected by a layer of asbestos tape to prevent condensation. An asbestos shield also surrounded the bottom of the outer liquid boiler to prevent the flame of the gas burner from coming directly in contact with the still.

The cooling water for the inner surface of the condenser was conducted through a glass tube to the bottom of the inner jacket, and allowed to overflow into the outer ice jacket. The water was precooled by running through cracked ice contained in a large glass funnel.

In low pressure ranges it was necessary to cool the vapor overflow tube to prevent the liquid in the outer boiler from boiling back into the distillate trap. This was accomplished by allowing tap water to flow over a spiral of silk covered copper wire surrounding the over flow tube. The water dropping from the bottom of the spiral was caught by a small funnel the outlet of which was connected to the drain.

During the distillation process there was a tendency for the level of the liquid in the inner liquid boiler to change. The direction of this change depended on the density and the initial compositions of the liquid; and whether in order to attain a steady state, the pressure in the still was being increased or decreased. In filling the still an attempt was made to adjust the volumes in the outer and inner boilers judging from the initial conditions so that when the steady state was reached the volumes would be equal to those prescribed in the previous discussion of the apparatus. When a steady state was reached there was no further tendency for the liquid to boil out or condense in the inner boiler.

The desirability of making up the initial compositions of the mixtures used to fill the still to roughly equal the estimated values of the equilibrium composition was investigated. In cases where this procedure was used the total time necessary to attain a steady state was but little shorter than when the initial compositions were entirely accidental. This is true chiefly because the time required to approach equilibrium closely is relatively short. The larger fraction of the total time is devoted to fine pressure adjustment. Such a procedure was, therefore, not worthwhile, and usually the liquid mixtures used to fill different parts of the still were of equal composition.

The ground glass stoppers closing the openings of the distillate trap and inner liquid boiler were carefully ground with several different grades of emery and carborundum. The final grinding was made with 60 minute carborundum flour. No lubricant was used, and the dry joints were sufficiently tight to make the rate of increase in pressure in the system caused by leaking very small. When the internal pressure in the system was less than 1 m.m., the pressure increased at a rate of .007 m.m. per minute. This rate would be expected to be much less under actual operating conditions where pressures were as great as 650 m.m. and never less than 100 m.m. This proved to be the case, and the effect became negligible under experimental conditions.

Two other stills were tried before building the one used in this work. The first was a development of Swietoslawski Ebullioscope (24). This apparatus has been successfully applied for measurement of vapor pressures of binary mixtures of one volatile component. Its application to systems of two volatile components where the vapor phase composition was desired proved to be unsatisfactory. The inherent design of the apparatus necessitated the placing of the distillate trap in a hydrodynamically unfavorable position. The pressure head necessary to lift the liquid to the thermometer well was less than the head required to force the contents of the liquid boiler back into the distillate trap. As a result the operating conditions were critical; and if any bumping in the liquid boiler occurred, the still had a tendency to run backwards. Other objections to this still were the unfavorable dimensions of the thermometer well and the extent of the exposed surface where reflux could take place.

The second still tried was nearly the same as the one finally used. The only difference between the two was that the relative heights of the distillate overflow tube and the tube conducting vapor from the outer to inner boilers in the second still rendered this apparatus more critical to increasing the pressure without sucking over contents of the inner boiler. This still would have probably worked with careful handling, but the vapor pump in the inner boiler was broken. An entirely new liquid boiler was built, and the dimensions changed slightly to eliminate the above difficulty.

The most obvious way of improving the present still would be to reduce the loss of material from the system by designing a more efficient condenser. The possibility of operating the condenser at lower temperature would be the most important factor to consider. The increase of the condensing surface would also enter but to a lesser degree.The use of solid CO_2 (-80°C.) as a refrigerant is not applicable to systems containing chloroform. Chloroform freezes at -63°C. and becomes viscous well above this temperature. The design of the condenser depends to some extent on the substances to be used in the still, but in future work it would be advisable to reduce to a minimum error from this source.

Potentiometer System

The Potentiometer employed for E.M.F. measurements was a Leeds and Northrup Type K. The specifications and circuit diagram for this instrument appear in the Leeds and Northrup Bulletin No. 755. The potentiometer had two sensitivity ranges with one ten times as sensitive as the other. On the high sensitivity scale micro volts could be read and the low sensitivity scale allowed E.M.F.s as high as 1.5 volts to be measured directly to a precision of 10 microvolts. Since the thermocouple calibration was independent of absolute values of the E.M.F. produced, the accuracy of the temperature measurements depended only on the uniformity of the potentiometer scale and the constancy of the reference E.M.F.

An Eppley unsaturated cadmium cell was used as a secondary standard. Cells of this type have a low temperature coefficient if the cell is at thermal equilibrium, but are sensitive to rapid or irregular changes in temperature. To prevent variations from this source the cell was enclosed in a thermally and electrically insulated metal container and submerged in a thermostated oil bath used for the barostat volume. The E.M.F. of this cell was compared at weekly intervals with the E.M.F. s of five saturated cadmium cells which served as primary standards. The saturated cells have a higher temperature coefficient than the unsaturated ones but are more stable with respect to time. The cells were calibrated at 250°C. by Eppley and checked by Buehrer (M.I.T. Laboratory of Phys.Chem.). The calibrated values and the values of Buehrer appear below.

Cell #	67	72	92	224	251	t=25°C.
E.M.F.(volts)	1.01806	1.01810	1.01806	1.01805	1.01805	(Eppley)
"	1.01807	1.01813	1.01810	1.01803	1.01805	(Buehrer)

The average of these values was assumed to be correct and the value of the secondary standard obtained on this basis with the saturated cells.in an auxillary thermostat maintained at 25°C. The five saturated cells were then transferred to the barostat bath which was regulated at 31.95°C. and their E.M.F.s redetermined by comparison with the secondary standard. These values obtained are given below.

Cell #	67	72	92	224	251	t=31.95°C.
E.M.F.(volts)	1.01788	1.01788	1.01790	1.01785	1.01785	

The thermocouple calibrations are based on these values of the primary standards and depend only on the constancy of these values and not on their absolute values.

The galvanometer was a Leeds and Northrup type R mounted on a Julius(25) suspension damped with oil cups. Galvanometer deflections were detected by means of an illuminated slit and a ruled ground glass scale. The distance between the galvanometer mirror and the scale was about 2 meters. A deflection of 2 m.m./microvolt was observed on the high sensitivity range. The slit was illuminated by means of a 6 volt electric bulb and a condensing lens. The image of the slit was focused on the scale by a lens placed in front of the galvanometer mirror.

The working current was supplied from a lead storage cell of the high capacity low discharge type (Willard D-D 11). The cell was surrounded by a layer of insulating material to prevent rapid temperature changes.

Thermocouples

The individual thermo-junctions of the twenty junction thermocouple were made from silk covered copper wire (#36) and constantan wire (#30). The junctions were made in a manner prescribed by Prentiss(26). Prentiss used cellulose acetate to insulate the leads and junction heads of the individual junctions. Later Benedict(27) found that a couple of this type insulated with bakelite enamel was more reliable. The heads and leads of the individual thermo-junctions of the thermocouple used were insulated with four coats of bakelite enamel. Each coat was allowed to dry thoroughly in air before being baked on at 125° for 12 hours.

An idea of the arrangement of the thermocouple and still can be obtained from Plate I which shows the thermocouple inserted in the thermometer well of the still. The bakelite support consisted of a 1/2 inch bakelite panel bolted flatly between two 1/4 inch panels. The three panels were 16 inches long and 4 1/4 inches wide which made the overall dimensions of the support 16" x 4 1/4" x 3/4". A rectangular hole concentric to the edges was cut out of the center of the 1/2 inch panel to permit the passage of the lead wires. Two holes were drilled vertically in the bottom of the center bakelite panel for the insertion of the glass tubes to conduct the leads away from the support. The holes were drilled so that the hot and cold junctions were 12 inches apart which allowed ample space for the manipulation of the ice point without interfering with the still.

The calibration by comparison with a platinum resistance thermometer was carried out in a thermostated oil bath of about 5 gallons capacity. The resistance thermometer and thermocouples were placed side by side in the bath, and temperature of the bath adjusted to the desired value. When the bath temperature became constant as indicated by resistance thermometer readings, alternate E.M.F. and resistance measurements were taken until five E.M.F. and four resistance readings were obtained. The time required for this procedure was in the neighborhood of 20 minutes. The maximum variation of bath temperature during this period was .004°C., but was in many cases not greater than .001°C. The corresponding values of the E.M.F. and resistance were taken as the average of these series of values. This comparison was carried out over a temperature range of 25°C. to 100°C. The results of this comparison appear in the first part of Table I.

The International Temperature scale is defined over this range of temperature in terms of the resistance of a platinum thermometer by the equation

$$t°C.(\text{Int.}) = \frac{R_t - R_o}{\alpha R_o} + S\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)$$

where R_t is the resistance of the thermometer at temperature t and α, R_o and S are constants. The values of these constants were determined by other workers (8,9) in this laboratory by calibration at three fixed points; the ice point (0°C.), the steam point (100°C.) and the sulfur point (444.6°C.)

Table I

Calibration of 20 Junction Thermocouples

Part I, Platinum Resistance Thermometer (#103)

R_t	t°C.	E obs. (volts)	(E obs.-E calc) millivolts
28.44135	25.2679	.020133	-.049
28.44170	25.2714	.020141	-.044
29.49727	35.6281	.028748	-.013
30.08296	41.3874	.033582	-.024
30.63757	46.8520	.038255	-.000
31.16729	52.0789	.042742	-.005
31.96362	59.9482	.049615	+.020
33.34848	73.6877	.061800	+.004
34.16840	81.8470	.069220	+.031

Part II, Vapor Pressure of Water

p m.m.	t°C.	E obs. volts	(E obs.-E calc.) millivolts
177.023	63.715	.052928	+.019
213.960	67.975	.056723	+.038
280.645	74.294	.062371	+.030
310.299	76.701	.064552	+.038
360.052	80.337	.067853	+.039
401.767	83.074	.070370	+.060
452.374	86.089	.073102	+.026
576.181	92.006	.078577	+.031
693.087	97.439	.083622	+.001
758.820	99.956	.085989	+.000

$$E(\text{calc.}) = .0007779t + 8.24 \times 10^{-7}\, t^2$$

The values of the constants used for resistance thermometer #103 are given below.

R_0 = 25.85235 ohms.

α = .003919567 $(°C.)^{-1}$

δ = 1.4942°C.

The use of the platinum resistance thermometers and wheat stone bridge was made possible by the cooperation of Prof. Beattie and Drs. Blaisdell and Kaminsky. They discuss the precision of temperature and resistance measurements in a recent publication(28).

An independent recalibration was made against the vapor pressure curve of water. In this case the thermocouples were inserted in the thermometer well of the still and were subject to the same conditions under which temperatures were eventually to be measured. The still was filled with conductivity water and a series of pressure, E.M.F. measurements made. The results of this second calibration appear in the second part of Table I. This calibration could not be carried below 60°C. because the results at pressures lower than that correspondong to this temperature became unreliable apparently as a result of irregular boiling in the still.

Temperatures were calculated from the observed pressures from the vapor pressure, temperature relation for water vapor given by Smith, Keyes and Gerry(10). The equation holding over the given temperature range is

$$\log_{10} \frac{p_c}{p} = \frac{x}{T} \; \frac{a + b\,x + c\,x^3}{1 + d\,x}$$

$\log p_c = 5.2196026 \quad p_c$ m.m.

$a = 3.2437814 \qquad b = 5.86826 \times 10^{-3}$

$c = 1.1702379 \times 10^{-8} \qquad c = 2.1878462 \times 10^{-3}$

$x = (T_c - T) \qquad T_c = (374.11 + 273.16)$

where p is the pressure in m.m. of Hg., p_c the critical pressure, T_c the critical temperature, and T the temperature. The temperatures in the above equation were measured on the International scale.

For these two calibations the E.M.F. was expressed as deviations (E obs.-E.calc.) from a quadratic function of the temperature (°C.).

$$E \text{ calc. (volts)} = .0007779t + 8.24 \times 10^{-7} t^2$$

The deviations in millivolts are plotted as ordinates against the temperature (°C.) as abscissae in figure (1). The circles indicate the points obtained with the platinum resistance thermometers and the flaged circles those obtained from the vapor pressure curve of water. The scattering of the points is with but two exceptions not greater than .01°C. The E.M.F.s corresponding to smooth values of the temperature calculated at five degree intervals by using the deviation curve are given in Table II.

The single junction copper-constantan thermocouples used to measure the temperature of the manometer mercury and

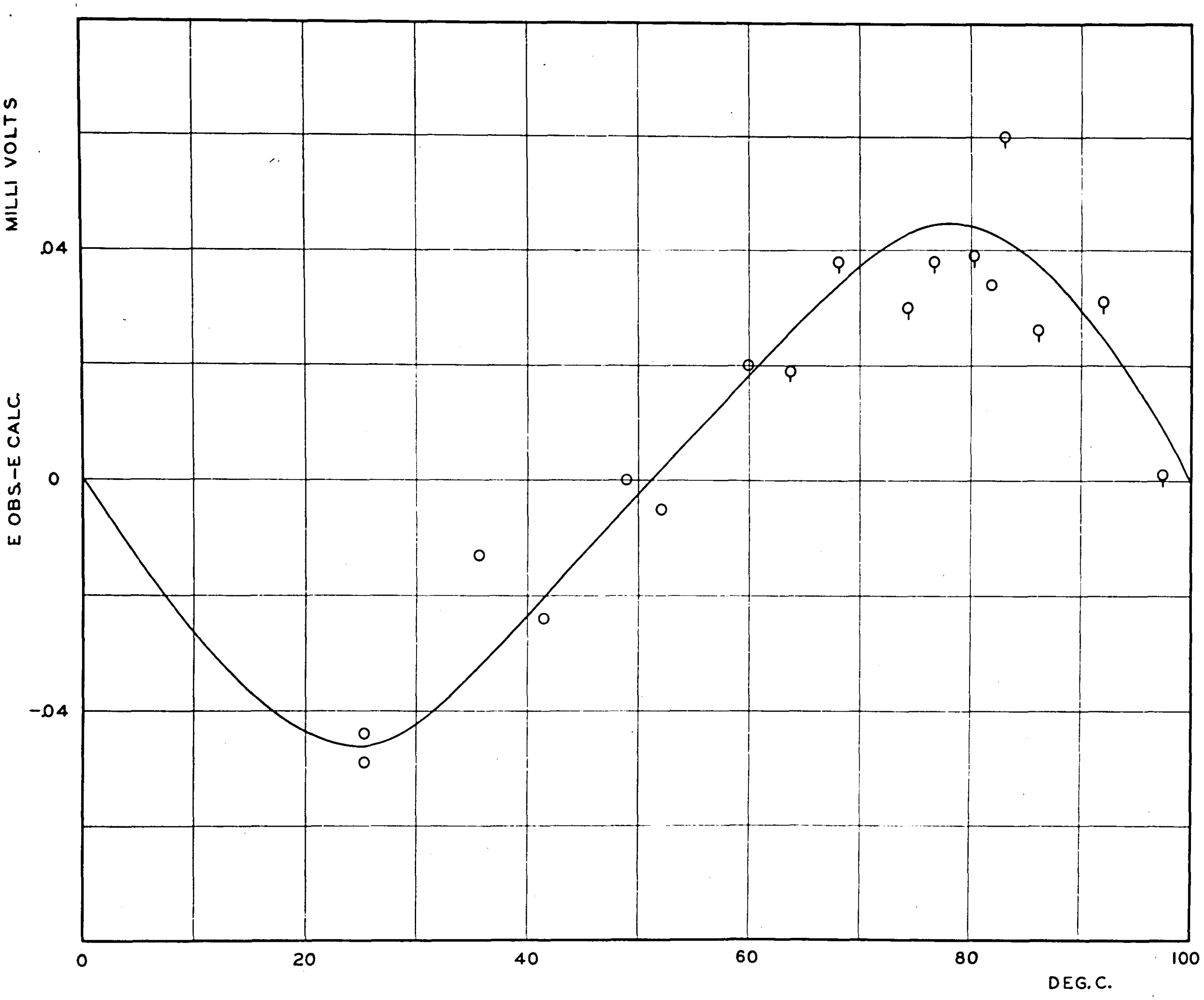


FIG. I

manostat both were calibrated against platinum resistance thermometer #103 in a manner similar to the 20 junction couple over a range of 26°C. to 35°C. Since the wire used in the construction of each of the single junctions came from the same source, only one of the junctions was calibrated and the values obtained assumed to be correct

Table II

Smoothed values of the E.M.F. calculated by using the deviation curve, figure (1).

t°C.	(E obs.-E calc.) millivolts	E.M.F. volts
30	-.041	.024038
35	-.032	.028204
40	-.022	.032412
45	-.012	.036663
50	-.002	.040953
55	+.009	.045287
60	+.018	.049658
65	+.027	.054072
70	+.036	.058527
75	+.043	.063021
80	+.046	.067552
78	+.046	.065735
62	+.020	.051417

for the others. A temperature difference of .02°C. produced an E.M.F. of about .8 of a microvolt. Hence the sensitivity of the couples was ± .02°C. The results of the calibration apprear in Table III.

Table III

Calibration of Single Junction Thermocouples

R_t(#103)	t°C.(obs.)	E.M.F.	(t obs.-t calc)°C.
28.57821	26.6090	.001065	.0013
28.81787	28.9585	.001164	-.0113
29.12447	31.9668	.001289	.0145
29.12807	32.0021	.001291	.0021
29.38588	34.5337	.001397	.0045

$$t°_c(\text{calc.}) = 32.00+2.386 \times 10^4 \ (\text{E.M.F.}-.001291)$$

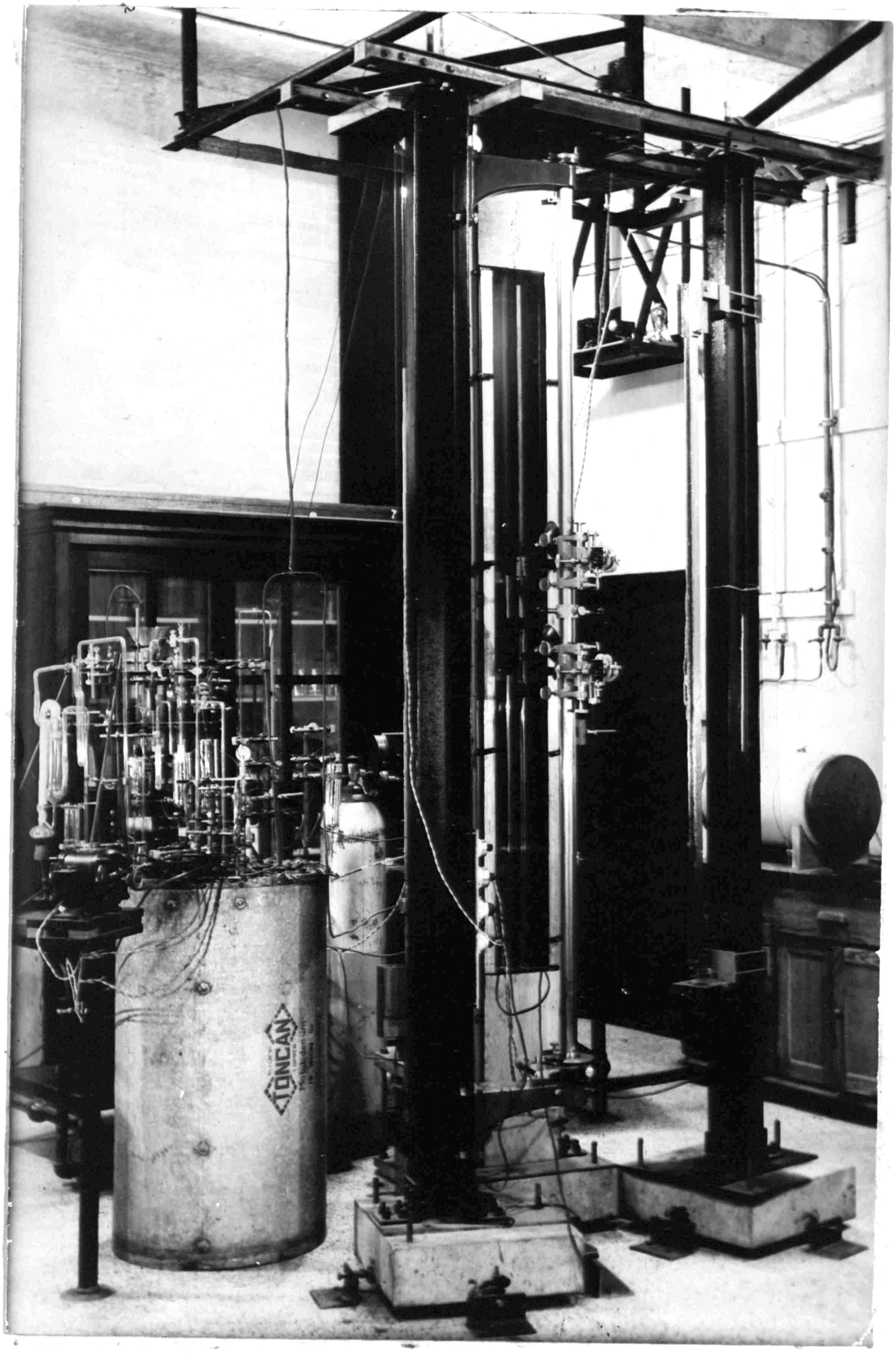
Since the deviations of the observed values of t from the values calculated from the above expression were all less than the sensitivity, the values of t (calc.) were assumed to be correct.

The reference temperature in all thermocouple measurements was 0°C. The ice point was made up in a 1 quart Dewar Flask in a manner recommended by Kaminsky(8) and Blaisdell(9). They found the ice point temperature made up in this manner to be reproducible to less than .001°C.

Manometer System

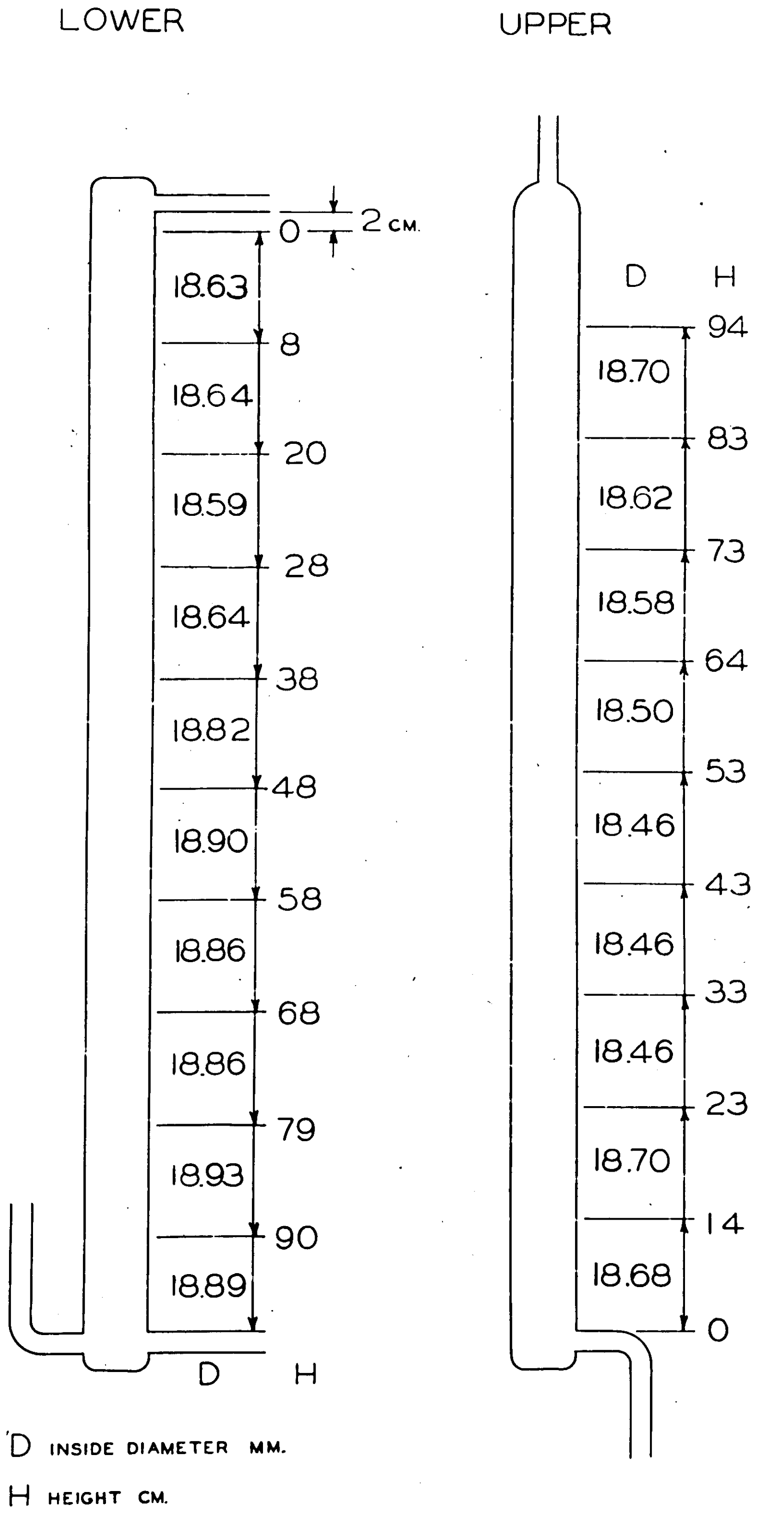
The essentials of the different parts of the apparatus and the general arrangement of the manometer system are shown in the photograph in Plate II. The three main parts of the manometer system appear in the foreground; the manometer, the cathetometer and the graduated scale. The levels of mercury menisci are measured by first adjusting the cross hairs of the cathetometer telescopes on the crowns of the menisci, and then by rotating the cathetometer bar reading the levels of the cross hairs on the scale.

Manometer: The manometer was essentially a mercury U-tube capable of measuring pressures from 80 m.m. of Hg to 2 meters. A vacuum was maintained over one arm, and hence the pressure was equal to the difference in level of the menisci in the vacuum and pressure arms. The manometer tubes were of pyrex tubing of internal diameter of 18.5 m.m. The mean diameters of 10 cm. sections of these tubes were determined along the total length of each tube by weighing the mercury contained in each section. The diameters of the tubes at different positions in each tube obtained from this calibration appear in figure (2). The two tubes forming the pressure and vacuum arms were mounted vertically between two parallel steel channel beams. These channels are about 10 feet long and are rigidly joined together and maintained parallel by three spacers at the top, bottom and center. The manometer tubes are supported by these spacers. The bottom of the



Manometer System

Plate II



CALIBRATION OF
MANOMETER TUBES
FIG. 2

upper tube rests in a pocket in the center spacer, and the lower tube is supported similarly by the lower spacer. The tops of the two tubes are held in place by circular steel rings surrounding the tubes with three radial set screws 60° apart around the circumference. The upper and lower tubes were mounted directly above one another as indicated in Part I, figure (2A) so that when the two mercury menisci are viewed with the two cathetometer telescopes, the axes of the telescopes are in a vertical plane. The scale can then be viewed by both telescopes simultaneously with but a single rotation of the cathetometer bar.

The mercury column is enclosed by a housing two sides of which consist of plywood board and are removable to give access to the inside of the housing. The third side is of heavier wood and is used to secure the pressure and vacuum leads. The remaining side is a panel of plate glass which fits flush against the front flanges of the steel channel beams which are provided with rubber gaskets and serves as a window for viewing the mercury levels.

The manometer housing forms a thermostated air bath regulated by a mercury regulator of 350 c.c. capacity. There is a second glass plate fitting flush against the back flanges of the steel channel beams which are also provided with rubber gaskets so that air can be circulated by means of an electrically propelled fan up the rear of the housing and down along the length of the column. On the inside of the rear wall of the housing are mounted an electric resistance heater, cooling coils and the mercury regulator. The temperature of the mercury is measured by three single junction copper-constantan thermocouples evenly distributed along the length of the column. These thermocouples are immersed in cylindrical mercury wells. The wells are of the same diameter as the manometer tubes and are supported from the bed of one of the channel beams. The temperature of the mercury was regulated at some temperature between 28°C. and 32°C. depending on room temperature. A temperature gradient existed along the column caused by loss of heat from the thermostat to the surroundings through the front glass plate as the circulating air progressed down along the column. Under the best conditions the temperature of the top of the column was 0.1°C. higher than the bottom. The temperature difference at times attained a maximum value of 0.4°C. These values of the gradient apply for the total length of the column (2 meters); but since the pressures observed were all less than 1 atm, it is probable that the average temperature of the mercury in the section of the column used could be determined to ± 0.1°C. The thermostat operated most efficiently when it was regulated only slightly above room temperature. Since room temperature varied at times several degrees C., the thermostat was seldom operating at its greatest efficiency. The difference in temperature between the top and bottom of the room which at times also amounted to several degrees C. was also an unfavorable factor in regulating the thermostat temperature .

The mercury menisci are illuminated by diffuse light sources behind the mercury surfaces and in line with the axes of the telescopes. The light sources consist of shielded 6 V. bulbs behind blue tracing cloth. Extraneous light and reflection from the front halves of the menisci are eliminated by semi-cylindrical blackened shields which fit closely around the rear semi-circumferences of the manometer tubes. A slot was cut out of the lower edge of these shields as shown in Part I, figure (2F) so that only the center portions of the menisci are visible. The light sources and shields slide on trolleys running the length of the mercury column and can be adjusted to the desired position behind the mercury surfaces from outside the manometer housing by a system of pulleys.

The vacuum arm of the manometer is evacuated by means of a mercury diffusion pump and a Hyvac fore pump. The residual gas pressure is measured by means of a McLeod Gauge. The gauge was calibrated by measuring the total volume of the bulb and capillary and the volume of the capillary per unit length by weighing the contained mercury.

Total weight (of contained Hg. at (24°C.)= 1162.185 gr.
Total volume = 84.090 c.c.

Calibration of Capillary

W gr.(24°C.)	h cm.	dW gr.(24°C.)	d h cm.
73.0146	0	0	0
73.4735	1.7856	.4589	1.7856
73.9793	3.6119	.5058	1.8263
74.6354	6.3094	.6561	2.6975
75.5305	9.9212	.8951	3.6118
76.0854	12.1438	.5549	2.2226

W= weight of Hg + weighing bottle

h= distance from closed end of the capillary.

Average cross section of capillary = .01961 cm^2.

The vacuum arm of the manometer is shut off with a mercury seal. Part I, figure (2C) shows the arrangement of the McLeod gauge and seal. The vacuum arm was pumped out regularly at monthly intervals. The pressure at no time during these periods exceeded .001 m.m.

Scale: The scale was a 2 meter invar bar graduated in millimeters, and was made by the Société Genevoise, Switzerland. The scale was calibrated by the U.S. Bureau of Standards in October, 1934. The lengths of the sub intervals of the scale spaced every 10 centimeters are given in Table IV. The calibration was made with the scale in a horizontal position supported at the two points indicated by the arrows on the side of the bar.

For use in this work the scale is supported vertically along a steel H-beam. The arrangement of the mounting is shown in Plate II. The scale is hung from the upper support

TABLE IV

Calibration of the Subintervals:

Length of Subintervals at 20°C

Interval	Length
0 to 10 cm.	100.0021 mm.
0 to 20 cm.	200.0036 mm.
0 to 30 cm.	300.0048 mm.
0 to 40 cm.	400.0051 mm.
0 to 50 cm.	500.0053 mm.
0 to 60 cm.	600.0055 mm.
0 to 70 cm.	700.0014 mm.
0 to 80 cm.	800.0009 mm.
0 to 90 cm.	899.9992 mm.
0 to 100 cm.	1000.0000 mm.
0 to 110 cm.	1099.9988 mm.
0 to 120 cm.	1199.9991 mm.
0 to 130 cm.	1299.9995 mm.
0 to 140 cm.	1399.9991 mm.
0 to 150 cm.	1499.9996 mm.
0 to 160 cm.	1599.9998 mm.
0 to 170 cm.	1699.9958 mm.
0 to 180 cm.	1799.9947 mm.
0 to 190 cm.	1899.9940 mm.
0 to 200 cm.	1999.9957 mm.

The values of these lengths as given above are not in error by more than 0.001 mm.

which is free to rotate in perpendicular planes. The lower support does not carry any of the weight, but merely serves to adjust and hold the scale in a perpendicular position. Allowance was made at the lower support for the unequal thermal expansion of the H-beam and invar bar. The center of gravity of scale and upper support was adjusted by counter weights in order that when these two members were hanging freely, the equilibrium position would be such that the scale hang in a perpendicular position. Then no bending momoment is introduced when the scale is held rigidly perpendicular by the lower support. The correction for the elongation of the scale caused by shifting the scale from a horizontal position to a vertical position was found by Benedict(29) to be negligible for a 2 meter invar scale similar to the one described.

The scale is lighted by two 6 volt spot light reflectors, one mounted on each telescope carriage. The scale was rotated at such an angle that no directly reflected light entered the telescopes. The two lights were adjusted so that the appearance of the scale was the same through each telescope. It was found that the settings of the cross hair on a scale dimension were more reproducible if the scales lights were adjusted so that the scale-rulings appeared as bright lines on a dark background. When this condition exists, the rulings are visible largely as a result of scattered light.

Cathetometer: The cathetometer bar is 8 feet long and 1 3/4 inches in diameter. It is mounted on a vertical steel I beam by means of two ball bearing supports one at each end of the bar. The telescope carriages are keyed to the bar and slide freely along the length of the shaft. The carriages can be clamped at any desired height on the shaft by means of split collars and set screws. The bar and telescopes can be rotated as a unit around the axis of the bar.

The telescopes were tightly clamped in the carriages. On top of each telescope was mounted a floating bubble level. The axes of these levels and the telescopes were accurately adjusted to be parallel. Leveling of the telescopes was accomplished by leveling screws on the carriages.

The eye pieces of the telescopes are of the positive Ramsden type with a magnifying power of 12.5 x. The objectives have a focal length of 162 m.m. The eye pieces are fitted with stationary vertical and adjustable horizontal cross hairs. The horizontal cross hair is moved up and down vertically by means of a micrometer screw. The plane of the cross hairs is between the objective and the eye piece and coincides with the plane of the image formed by the objective when the system is properly focused. The micrometer heads were divided into 100 divisions. Each division corresponded approximately to .008 m.m. Tenths of a division could be estimated. The micrometer screws were calibrated for uniformity by comparing the number of division corresponding to a given m.m. interval on the scale for different sections of the screw. The results of this calibration appear in Table V.

Adjustment of the Manometer System: The beams supporting the mercury column, scale and cathetometer are rigidly held at each end. The bottoms are bolted to heavy slate blocks which are provided with leveling screws. The tops of the beams are pivoted to a false ceiling by means of universal joints which allow for adjustments in any horizontal direction and rotation around the axis of the support. The adjustment of a system similar to this has been taken up by Benedict(29) who discusses in detail the adjustment of the three unit parts to perpendicularity, focusing of the system, scale and manometer lighting and other critical factors in pressure measurements.

TABLE V

Calibration of Micrometer Screws for Uniformity

Upper Telescope			(V_2-V_1)	Lower Telescope		(V_2-V_1)
Scale division vernier settings	103.8	103.9	1 m.m.	78.7	78.8	1 m.m.
	0.0	121.6	121.6	0.3	119.3	119.3
	5.3	126.9	121.6	5.3	124.4	119.1
	9.8	131.2	121.4	10.1	129.4	119.3
	15.0	136.5	121.5	15.3	134.5	119.2
	19.5	141.0	121.5	20.1	139.3	119.2
	24.6	146.2	121.6	25.1	144.3	119.2
	30.1	151.8	121.7	30.1	149.1	119.0
	35.1	156.8	121.7	35.5	154.7	119.2
	40.5	161.9	121.4	39.7	158.8	119.1
	44.3	165.9	121.6	45.7	164.8	119.1
	49.5	171.1	121.6	49.9	168.9	119.0
	55.1	176.7	121.6	54.8	174.0	119.2
	60.1	181.6	121.5	60.2	179.2	119.0
	65.8	187.3	121.5	64.9	184.1	119.2
	70.7	191.3	121.6	70.2	189.3	119.1
	75.2	196.8	121.6	74.9	194.0	119.1
	79.8	101.3	121.5	79.9	199.0	119.1
	85.8	7.3	121.5	85.1	204.3	119.2
	90.0	11.6	121.6	90.1	209.3	119.2
	95.2	16.8	121.6	94.7	213.8	119.1

Pressure Corrections

The observed mercury heights were corrected for capillary depression and calibration and thermal expansion of the scale. The differences in corrected heights were reduced to pressures in m.m. of Hg. at 0°C. and standard gravity. These observed pressures were further corrected for static head caused by the weight of the gas between the levels of the thermometer well spiral of the still and the mercury meniscus in the pressure arm of the manometer.

The pressure in terms of the observed levels of the crowns of the mercury menisci in the vacuum and pressure arms of the manometer is

$$P_{m.m.} = (L'' - L' + h_o'' - h_o^1 + \delta'' - \delta^1)\,F + h_1 + h_2$$

where the quantities appearing are defined as follows:

$P_{m.m.}$ = corrected pressure

L'' = scale height of upper meniscus crown

L' = " " " lower " "

h_o'' = capillary depression of upper meniscus

h_o' = " " " lower "

δ'' = scale calibration and thermal expansion for upper level

δ' = scale calibration and thermal expansion for lower level

F = factor for reduction to standard gravity and pressures (0°C.).

h_1 = static head

h_2 = " "

Capillary Depression: Capillary depressions were calculated from the Lohnstein(30) formula. The measured values of the capillary depressions of Cawood and Patterson(31) for tubes of 14 m.m. to 18 m.m. in diameter were found by Benedict(29) to agree with the calculated values to .005 m.m. if the surface tension of Hg. was taken as 476 dynes/cm. The capillary depression is given by

$$h_0 = \frac{8\mu h}{1+\sqrt{1-\frac{\mu h^2}{2a^2}}} \,\text{exp.}\left[-\frac{R\sqrt{2\mu}}{a} - 2 + \sqrt{1-\frac{\mu h^2}{2a^2}}\right]$$

h_0 = capillary depression in m.m.

h = meniscus height " "

R = radius of the tube " "

μ = .8 (dimensionless)

$a = \frac{1}{\sqrt{\frac{\rho g}{2\sigma}}}$ ρ = density of Hg. at 25°C. σ = surface tension of Hg.

σ = 476 dynes cm^2 (Int. Critical Tables, IV, 144)

ρ = 13.521 gr/cm^3 (" " " II, 458)

g = 980.397 cm./sec^2

The values of h_0 were calculated at .1 m.m. intervals for meniscus heights from .5 m.m. to 1.9 m.m. Since the diameters of the manometer tubes were not uniform, the value of h_0 depended on the position of the meniscus in the tube. The values of h_0 for each meniscus height(h) were calculated at 10 cm. intervals along the lengths of the tubes. The

h_0	.5	.6	.7	.8	.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
0-100	.0178	.0212	.0246	.0280	.0313	.0344	.0375	.0406	.0434	.0462	.0489	.0513	.0538	.0561	.0582
100	.0176	.0210	.0244	.0278	.0310	.0341	.0372	.0402	.0430	.0458	.0484	.0509	.0533	.0556	.0577
200	.0180	.0214	.0249	.0283	.0316	.0348	.0379	.0409	.0439	.0467	.0494	.0519	.0532	.0566	.0588
300	.0180	.0214	.0249	.0283	.0316	.0348	.0379	.0409	.0439	.0467	.0494	.0519	.0532	.0566	.0588
400	.0178	.0212	.0246	.0280	.0313	.0344	.0375	.0406	.0434	.0462	.0489	.0513	.0538	.0561	.0582
500	.0181	.0216	.0251	.0285	.0318	.0351	.0383	.0413	.0443	.0471	.0498	.0524	.0549	.0572	.0593
600	.0189	.0225	.0262	.0298	.0332	.0366	.0399	.0431	.0462	.0492	.0520	.0547	.0573	.0597	.0619
700	.0191	.0227	.0265	.0300	.0336	.0370	.0403	.0435	.0466	.0497	.0525	.0542	.0568	.0602	.0625
800	.0189	.0225	.0262	.0298	.0332	.0366	.0399	.0431	.0462	.0492	.0520	.0547	.0573	.0597	.0619
900	.0189	.0225	.0262	.0298	.0332	.0366	.0399	.0431	.0462	.0492	.0520	.0547	.0573	.0597	.0619
1000	.0187	.0223	.0260	.0295	.0329	.0363	.0396	.0427	.0458	.0487	.0515	.0542	.0567	.0591	.0613
1150	.0186	.0222	.0258	.0293	.0328	.0361	.0394	.0425	.0456	.0485	.0513	.0539	.0565	.0588	.0610
1250	.0197	.0235	.0274	.0311	.0347	.0382	.0417	.0450	.0482	.0513	.0543	.0571	.0598	.0623	.0646
1350	.0197	.0235	.0274	.0311	.0347	.0382	.0417	.0450	.0482	.0513	.0543	.0571	.0598	.0623	.0646
1450	.0197	.0235	.0274	.0311	.0347	.0382	.0417	.0450	.0482	.0513	.0543	.0571	.0598	.0623	.0646
1550	.0196	.0233	.0271	.0308	.0344	.0379	.0413	.0446	.0478	.0508	.0538	.0566	.0592	.0617	.0640
1650	.0192	.0228	.0266	.0302	.0337	.0372	.0405	.0438	.0469	.0499	.0528	.0444	.0581	.0605	.0628
1750	.0190	.0226	.0263	.0299	.0334	.0368	.0401	.0433	.0464	.0494	.0523	.0550	.0575	.0600	.0622
1850	.0186	.0222	.0258	.0298	.0328	.0361	.0394	.0425	.0456	.0485	.0513	.0539	.0565	.0588	.0610

Capillary Depression of Hg. (h_0)

Table VI

δ	20	21	22	23	24	25	26	27	28	29	30	31	32
100	.0021	.0023	.0024	.0026	.0027	.0029	.0030	.0032	.0033	.0035	.0036	.0038	.0039
200	.0036	.0039	.0042	.0045	.0048	.0051	.0054	.0057	.0060	.0063	.0066	.0069	.0072
300	.0048	.0052	.0057	.0061	.0066	.0071	.0075	.0080	.0084	.0086	.0093	.0098	.0102
400	.0051	.0057	.0063	.0069	.0075	.0081	.0087	.0093	.0099	.0105	.0111	.0117	.0123
500	.0053	.0061	.0068	.0075	.0083	.0091	.0098	.0106	.0113	.0121	.0128	.0136	.0143
600	.0055	.0064	.0073	.0082	.0091	.0100	.0109	.0118	.0127	.0136	.0145	.0154	.0163
700	.0014	.0025	.0035	.0046	.0056	.0067	.0077	.0088	.0098	.0109	.0119	.0130	.0140
800	.0009	.0021	.0033	.0045	.0057	.0069	.0081	.0093	.0105	.0117	.0129	.0141	.0153
900	-.0008	.0005	.0019	.0032	.0046	.0059	.0073	.0086	.0100	.0113	.0127	.0140	.0154
1000	.0000	.0015	.0030	.0045	.0060	.0075	.0090	.0105	.0120	.0135	.0150	.0165	.0180
1100	-.0012	.0004	.0021	.0037	.0054	.0070	.0087	.0103	.0120	.0136	.0153	.0169	.0186
1200	-.0009	.0009	.0027	.0045	.0063	.0081	.0099	.0117	.0135	.0153	.0171	.0190	.0207
1300	-.0005	.0014	.0034	.0053	.0073	.0092	.0112	.0131	.0151	.0170	.0190	.0209	.0229
1400	-.0009	.0012	.0033	.0054	.0075	.0096	.0117	0138	.0159	.0180	.0201	.0222	.0243
1500	.0004	.0018	.0041	.0063	.0085	.0108	.0131	.0153	.0176	.0198	.0221	.0243	.0266
1600	-.0002	-.0018	.0046	.0070	.0094	.0118	.0142	.0166	.0190	.0214	.0238	.0262	.0286
1700	-.0042	-.0017	.0009	.0034	.0060	.0085	.0111	.0136	.0162	.0187	.0213	.0238	.0262
1800	-.0053	-.0027	.0001	.0028	.0055	.0082	.0109	.0136	0163	.0190	.0217	.0244	.0271
1900	-.0060	-.0032	-.0003	.0025	.0054	.0082	.0111	.0139	.0168	.0196	.0225	0253	.0282
2000	-.0043	-.0013	.0017	.0047	.0075	.0107	.0137	.0167	.0197	.0227	.0257	.0287	.0317

Calibration and Temperature Correction of Invar Scale (δ)

Table VII

diameters of the manometer tubes are given in the calibration chart shown in figure (2). Since the relative positions of the manometer tubes and scale are fixed, any level in the tubes can be interpreted as a corresponding height on the scale. The values of h_o at different meniscus heights and scale levels appear in Table VI. The table was doubly interpolated for intermediate values.

Thermal Expansion and Calibration of the Scale:

These corrections were grouped together and applied as a single correction (δ) as has already been indicated. The thermal expansion correction at any scale height is $L\alpha(t-20)$ where α is the linear coefficient of thermal expansion and t the temperature of the scale in °C. The value of this quantity was calculated for even scale heights at 10 cm. intervals.over a range in temperature from 20°C. to 32°C. at 1° intervals. The values of the calibration correction at these scale heights can be obtained from table IV. The sum of these two corrections at different scale heights and temperatures appear in table VII. This table was also doubly interpolated for intermediate values.of t and L. The value of α for Invar is 1.5×10^{-6} deg $C.^{-1}$.

Static Head Corrections: The value of the pressure is desired at the level of the thermometer well spiral of the still. The pressure is actually measured at the level of the mercury in the pressure arm of the manometer. These two pressures differ by the pressure head caused by the weight of the gas included between these two levels.

The total static head correction is the sum of two parts h_1 and h_2. The first part (h_1) is the pressure head between the levels of the mercury in the pressure arm and of the vapor, gas interface in the still condenser. The second part (h_2) is the pressure head of the vapor between this interface and the thermometer well spiral.

The level of the vapor gas interface was assumed to remain constant and was measured to be 13 cm. above the thermometer well spiral. Hence h_1 varied with the pressure in the system, the height of pressure arm and room temperature. Room temperature was assumed to be constant at 25°; and since the pressure depended only on the pressure arm height, the value of h_1 could be expressed in terms of this height alone. The vapor, gas interface was at a scale level of 63 cm. When the mercury in the pressure arm was at this level the value of h_1 became 0. The value of h_1 was calculated from the following equation

$$h_1 \text{ (m.m. Hg)} = \frac{d \times P \text{ m.m.}}{13.53 \times 760}$$

13.53 gr/cm^3 = density of Hg. at 25°C.

d = " of gas in manometer system.at 25°C. and 760 m.m.

P.m.m= pressure in the system.

d (He) = .000164

d(N_2) = .001148

The values of h_1 at even heights of the pressure arm appear in Table VIII.

Table VIII

Static Head Correction (h_1)

Short Arm Height	H_e	N_2	N_2 cond. at -80°C.
0 m.m.	-.0201 m.m.	-.1405 m.m.	-.1223 m.m.
50	-.0176	-.1229	-.1056
100	-.0153	-.1064	-.0900
150	-.0130	-.0910	-.0755
200	-.0110	-.0767	-.0621
250	-.0091	-.0636	-.0499
300	-.0074	-.0515	-.0388
350	-.0058	-.0405	-.0287
400	-.0044	-.0308	-.0199
450	-.0031	-.0220	-.0120
500	-.0021	-.0145	-.0047
550	-.0012	-.0080	.0002
600	-.0004	-.0027	.0046
650	.0002	.0016	.0076
700	.0007	.0047	.0100
750	.0010	.0067	.0112
800	.0011	.0076	.0112
850	.0010	.0073	.0100
900	.0010	.0071	.0089
950	.0005	.0035	.0044

The second part of the correction (h_2) varied with the pressure, temperature in the still and the composition of the vapor. The values of h_2 were calculated from the expression

$$h_2 \text{ (m.m. of Hg)} = \frac{d_1 \times 298 \times l \times P_{m.m.}}{760 \times 13.53 \times (t+273)}$$

d_1 = density of the vapor at 25°C. and 760 m.m.

t = temperature in the still.

p m.m. = pressure in the system.

l = 130 m.m.

The densities of mixtures of chloroform and ethanol vapors were taken as a linear function of the composition .

$$d_1 = .004895 - .003007\ y$$

where y is the mole fraction of ethanol in the vapor.

d_1 (water vapor) = .000738 gr./cm^3

d_1 (alcohol vapor) = .001888 gr./cm^3

d_1 (chloroform vapor) = .004895 grm./cm^3

$$h_2 = \frac{3.767 \times d_1 \times P_{m.m.}}{(t + 273)}$$

Reduction to Pressures at 0°C. and Standard Gravity: These two corrections both appear as multiplying factors applied to the difference in corrected mercury levels. The product of the two factors are combined and are represented by F. The factor for the reduction to pressures at 0°C. is the ratio of the density of mercury at 0°C. to the density at the temperature of the manometer mercury. The gravity correction enters as a constant factor and is equal to the ratio of the value of standard gravity to the value of gravity at the location where pressures are measured. The values of F have been calculated by Benedict(29) over a range in temperature from 20°C. to 32°C. at 0.1° intervals, and were later revised by Kaminsky(8) and Baisdell(9). These values of F appear in Table IX. Values at .01°C. intervals were obtained by interpolation. The calculation of this table was based on the value of gravity of

980,400 cm/sec^2 in room 6-231 of this laboratory and the value of standard gravity of 980.866 cm/sec^2. The pressure measurements in this work were carried out in room 6-232. An error of ± 0.1°C. in the temperature of the manometer mercury produces an error of approximately ± .01 m.m. in the reduced pressure at a pressure of 1 meter.

Factor for Reduction of Pressures

to m.m. of Hg. at 0°C. and Standard Gravity (F)

Table IX

F	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
20	.9961110	.9960930	.9960749	.9960569	.9960388	.9960208	.9960028	.9959847	.9959667	.9959486
21	.9959306	.9959126	.9958945	.9958765	.9958584	.9958404	.9958224	.9958043	.9957863	.9957682
22	.9957502	.9957322	.9957141	.9956961	.9956780	.9956600	.9956420	.9956239	.9956059	.9955878
23	.9955698	.9955518	.9955338	.9955157	.9954977	.9954797	.9954616	.9954436	.9954256	.9954075
24	.9953895	.9953715	.9953535	.9953354	.9953174	.9952994	.9952814	.9952633	.9952453	.9952273
25	.9952093	.9951912	.9951732	.9951552	.9951372	.9951191	.9951011	.9950831	.9950651	.9950471
26	.9950290	.9950110	.9949930	.9949750	.9949570	.9949389	.9949209	.9949029	.9948849	.9948669
27	.9948489	.9948308	.9948128	.9947948	.9947768	.9947588	.9947408	.9947228	.9947048	.9946867
28	.9946687	.9946507	.9946327	.9946147	.9945967	.9945787	.9945607	.9945427	.9945247	.9945066
29	.9944886	.9944706	.9944526	.9944346	.9944166	.9943986	.9943806	.9943626	.9943446	.9943266
30	.9943086	.9942906	.9942726	.9942546	.9942366	.9942186	.9942006	.9941826	.9941646	.9941466
31	.9941286	.9941106	.9940926	.9940746	.9940566	.9940386	.9940206	.9940026	.9939846	.9939667
32	.9939487									

Procedure for Measuring the Pressure

The manometer light sources were adjusted behind the mercury levels. The cathetometer bar was rotated until the vertical cross hairs of the upper and lower telescopes were in the center of the upper and lower minisci. Each telescope was adjusted vertically until the crown of the meniscus was at the center of the field of view. The shields were lowered behind the mercury surfaces until the distance between the crown of the menisci and the lower edges of the shields appeared in the telescopes to be about 1 m.m. This distance was accurately reproducible by the aid of a vertical scale in the plane of the cross hairs which appeared directly beside the image of the meniscus in the field of view. The telescopes had two parallel horizontal cross hairs which appeared to be about 1 m.m. apart. The upper cross hair was used as a reference line and the lower one as an additional aid in adjusting the heights of the shields.

The upper horizontal cross hair of each telescope was first set on the line of intersection of the mercury meniscus and wall of the manometer tube. This level was detected by shining a light on the manometer tube opposite the mercury surface. The cross hair was set at the point where light ceased to be reflected from the cylindrical mercury surface. This level was assumed to be the bottom of meniscus. The value of this level was read to .01 m.m. but was uncertain to .05 m.m. The micrometer head was then rotated noting the number of complete revolutions of the screw, until the cross hair was set on the crown of the meniscus. Three separate settings were made on the crown of the upper and lower mercury menisci. The three separate settings usually agreed within .002 m.m. and seldom deviated more than .004 m.m. The manometer lights should be switched off immediately after finishing observations on the mercury surfaces in order to prevent unnecessary fluctuations in the manometer thermostat as a result of the heat generated by the light filaments.

When the levels of the crowns and bottoms of both the upper and lower menisci had been observed, the cathetometer bar was rotated until the vertical cross hairs were in the center of the scale. The micrometer head of each telescope was rotated until the reference cross hair coincided with the next lowest m.m. scale dimension. Three separate settings were made at this level, and the values usually agreed within .002 m.m. The micrometer head was then rotated until the reference cross hair had traveled down the scale.1 m.m. and coincided with the next lowest m.m. scale division. Three separate settings were made at this level. This procedure gave the number of divisions of the micrometer head of each telescope per m.m., and served to check the screw calibration at various positions on the scale.

The temperature of the scale was measured by a mercury thermometer graduated in 0.1°C. intervals suspended beside the scale at about its midpoint. The temperature of the manometer mercury was determined by measuring the E.M.F.

Table X

	vernier reading lower telescope		vernier reading upper telescope	
bottom of meniscus	62.4		16.6(1)	
Crown of meniscus	60.1		85.8	
	60.4		85.9	
	60.2		85.9	
scale setting	30.5		45.0	
	30.5	845 m.m.	45.1	1153 m.m.
	30.4		44.9	
calibration setting	11.2(1)		23.9(1)	
	11.1	844 m.m.	24.0	1152 m.m.
	11.2		24.0	

Scale Temperature = 27.2

E.M.F of thermo junctions

lower	.001125 volts
center	.001127 "
upper	.001128 "

of the three thermo junctions in the manometer housing.

An example of the manner of recording readings taken for a pressure measurement appears in Table X. The super script (1) added to a micrometer head setting indicates a rotation of more than one complete revolution of the screw. The corrected pressure was calculated in the following manner.

Lower mercury level.

screw calibration $=130.5 - 11.2 = 119.3$ divisions/m.m.

$$\text{meniscus height} = \frac{160.2 - 62.4}{119.3} = .83 \text{ m.m.}$$

$$L = 845 + \frac{60.2 - 30.5}{119.3} = 845.248 \text{ m.m.}$$

Upper mercury level.

$$\text{screw calibration} = 145.0 - 24.0 = 121.0 \ \frac{\text{divisions}}{\text{m.m.}}$$

$$\text{meniscus height} = \frac{185.9 - 16.6}{121.0} = 1.40 \text{ m.m.}$$

$$L'' = 1153 + \frac{85.9-45.0}{121.0} = 1153.338 \text{ m.m.}$$

$L''-L' = 1153.338 - 845.248 = 307.990$ m.m.

$$P_{m.m.} = (307.990+h_o'' - h_o' + \delta'' - \delta')F + h_1+h_2$$

At this point the analysis of the distillate gave a value of $y = .8838$ The mean mercury temperature of the manometer mercury for this pressure was taken as the average of center and lower thermo junction temperatures.

Average E.M.F = .001126

" $t°C. = 32.00x2.3860x10^{4}(.001126-.001291)$

" " $= 28.06°C.$

$h_o'' = .049$ m.m. $h_o' = .031$ m.m.

$\delta'' = .011$ " $\delta' = .009$ "

$h_1 = .007$ "

$h_2 = .008$ "

$F = .9946579$

corrected $P_{m.m.} = 306.379$ m.m.

It was necessary to measure pressures below 160 m.m. with only one telescope. The construction of the telescope carriages prevent the axes of the two telescopes from being moved closer together. In this procedure alternate readings were taken on the upper and lower menisci by sliding the telescope up and down on the bar. It was necessary to level the telescope before each meniscus and scale reading. The pressures measured in this manner had an uncertainty of .05 m.m. caused mainly be error in leveling of the telescope. Mechanical imperfections in the bearings of the cathetometer bar may also be a source of error in this procedure.

Materials

The distillations necessary in the purifications of both ethanol and chloroform were carried out in a vacuum jacketed Vigreux fractionating column with controlled reflux. The boiler and receiver of the still had a capacity of 2 liters. The parts of the still were entirely of glass and were assembled by means of ground glass joints. The vent communicating with the atmosphere passed through a calcium chloride drying tube. Heat was furnished by means of an electrically heated air bath surrounding the still boiler. The rate of distillation was controlled by a variable resistance in series with the heater.

Ethanol: Commercial absolute alcohol was purified in 2 liter quantities. Purified iodine crystals (1 gr./liter) were added to the alcohol and the mixture allowed to stand for 24 hours. The mixture was introduced into the still and after refluxing for 2 hours was allowed to distil at the rate of 150 c.c. per hour. The first and last quarters of this distillation were rejected. The middle fraction was refluxed over zinc wool for about 12 hours to remove the iodine that came over during the first distillation. After being certain of the removal of all the dissolved iodine as indicated by the disappearance of the yellow color, the alcohol was allowed to distil at the rate of 75 c.c. per hour; and the middle third collected.

The pure alcohol was immediately transferred to 100 c.c. stoppered glass bottles.

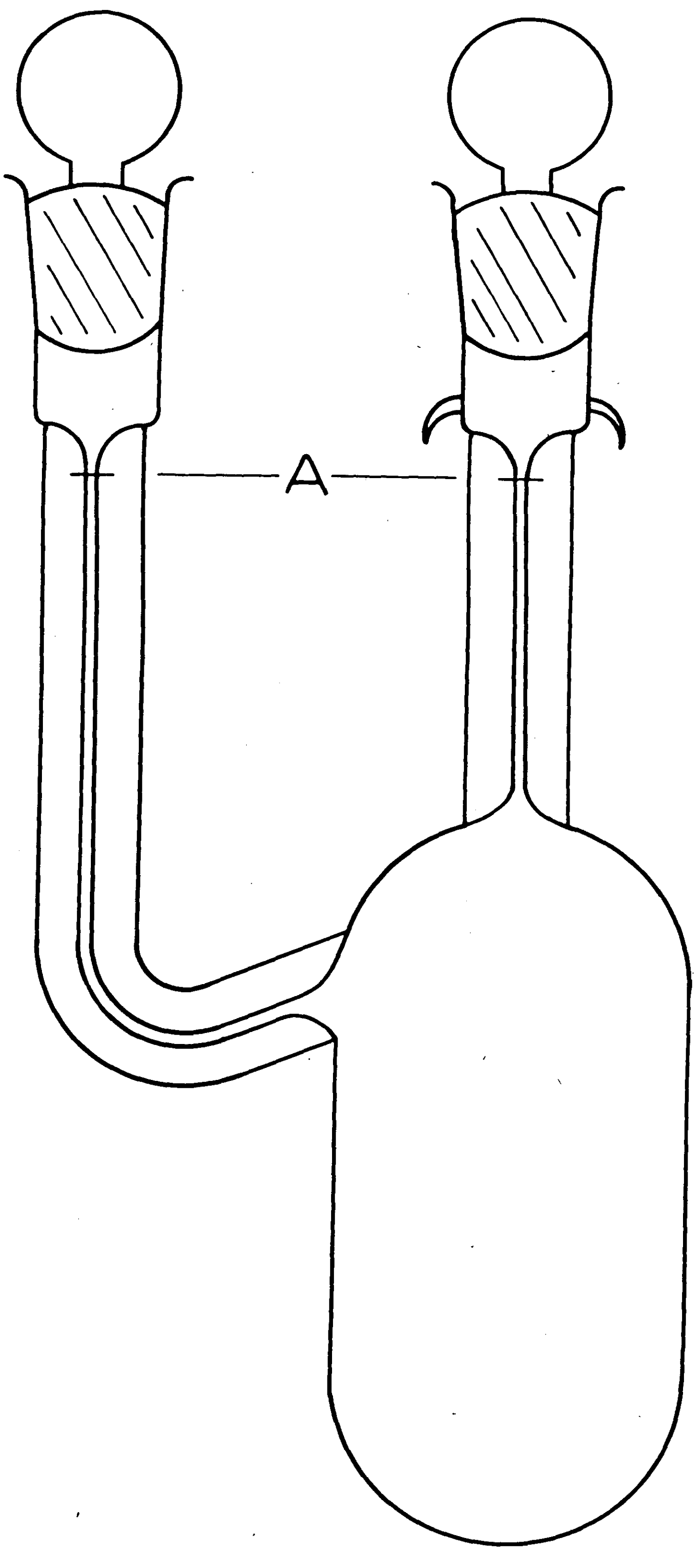
Chloroform: Chloroform was also purified in 2 liter quantities. It was first refluxed for 12 hours over phosphoric anhydride and then allowed to distil at about 150 c.c. per hour. The first and last quarters were rejected. The middle fraction was redistilled over anhydrous sodium carbonate at a rate of 75 c.c. per hour, and the first and last thirds rejected. These distillations were carried out in the dark. The necessary measurements on pure chloroform were made as quickly as possible after the purification process. About 1% by volume of ethanol was added to pure chloroform that was to be stored and the mixture transferred to 100 c.c. glass stoppered bottles. This mixture of chloroform and ethanol was stored in the dark.

Density Measurements

A diagram of the pycnometers used is shown in figure (3). Two similar pycnometers were used, one for analysis of the distillate sample and the other for the liquid sample. The bulbs had a volume of approximately 11.5 c.c. The capillaries had a bore of .6 m.m. Each capillary was provided with a fine file scratch (A) which served as a reference level. On the tops of the capillaries were mounted short lengths of glass tubing which were sealed by means of ground glass stoppers. Ample space was allowed between the stoppers and the mouths of the capillaries to take care of any expansion of the liquid that might occur.

Density measurements and the pyconometer calibrations were carried out at 25°C. A small thermostated water bath was used to maintain this temperature. The temperature of the bath was measured by a Beckmann thermometer which was set by comparison with platinum resistance thermometer #103. The temperature of the thermostat during a density measurement was constant at 25.00 ± .01°C.

Before each density determination the pycnometers were thoroughly dried by placing them in an evacuated bell jar for about 1/2 hour. They were then weighed after they had been dipped in water and dried with a damp cloth. The liquid was introduced into the pycnometers through the side arm capillary from a 25 c.c. pipette. After filling the stoppered pycnometers were suspended in the thermostat for



PYCNOMETER

FIG. 3

10 minutes. At the end of this period the level of the liquid in the capillaries was adjusted to the reference marks by removing the excess liquid with filter paper. The filled vessels were then removed from the bath, dryed with a damp cloth and weighed. It was found that better weighings could be obtained if the vessels were wiped with a slightly damp rather than a dry cloth. The static charge induced on the surface by wiping with a damp cloth is probably smaller than that induced with a dry one.

A glass tare of size and shape comparable to each of the pycnometers was used on the weight pan of the balance as a counter poise. This tare was subject to the same treatment as the pycnometers. The loss of weight of the vessels resulting from evaporation of the liquid through the ground glass joints was negligible during the time required for weighing.

The two pycnometers were designated by the symbols p_1 and p_2. P_1 had a single file scratch on both capillaries while p_2 had two scratches on the center capillary. In p_2 the upper of these two scratches was used as a reference level. Weighings were made by suspending the pycnometers from the pan support of the balance by means of a loop of copper wire. The different weights to be considered then combine as follows:

$$\begin{array}{l} W_p \text{ (empty)} + W \text{ (wire)} = W \text{ (tare)} + W' \text{ (weights)} \\ \underline{W_p \text{ (full)} + W \text{ (")} = W \text{ (")} + W'' \text{ (")}} \end{array}$$

$$W\text{(liquid)} = (W''-W') \text{ weights (in air)}$$

These weights of the liquid in air were reduced to weight in vacuum by correcting for the buoyancy effect as a result of the air displaced by the liquid and brass weights. The values of $(W''-W')$ were sufficiently large to justify neglecting the buoyancy effect of the fractional gram weights. The density of brass was taken as 8.0 gr./cm^3.

The largest difference observed between observed values of W_p (empty) was .5 m. gr. The values of W (liquid) for pure liquids could be checked to within 1 m. gr.

The two pycnometers were calibrated by determing the weight of water contained at 25.0°C. The calibration values are given below.

$$W_p = 11.43921 \text{ gr.} \qquad \text{volume } p_1 = \frac{11.43921}{.997044} = 11.47313 \text{ c.c.}$$

$$W_{p_2} = 11.29631 \text{ "} \qquad \text{volume } p_2 = \frac{11.29631}{.997044} = 11.32980 \text{ "}$$

On Jan. 6, 1937 it was necessary to repair a small crack which developed in the side wall of p_2. P_1 and p_2 were both recalibrated at this time. It was found that p_2 had changed its volume slightly but p_1 had not. The values for the recalibrations of p_2 are given below.

$$W_{p_2} = 11.28828 \text{ gr.} \quad \text{volume } p_2 = \frac{11.28828}{..997044} = 11.32175 \text{ c.c.}$$

All density measurements made later than Jan. 6, 1937 are based on this value of the volume of p_2.

The accuracy of the analysis of chloroform, ethanol mixtures as carried out in this work appears to be limited by errors arising from changes in composition resulting from evaporation while handling the mixtures rather than by the error in the actual density measurements.

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(14) Vapor pressure data for chloroform and ethanol	3E	129
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(17) " " 35°C. " "	4E	29
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The calculations involved in the application of the Gibbs-Duhem equation are given in tables which are supplementary to the notebooks.

Biographical Sketch

Charles L. Raymond was born on May 18, 1911 in Schenectady, New York. He attended Howe Grammar School through the seventh grade and transferred at the beginning of the eighth grade to Central Park Intermediate School. He graduated from this school in June 1925 after having completed work through the first year of high school. He attended Nott Terrace High School for three years and graduated in the Scientific course in June 1928. He entered Union College in September 1928 and during a four year period pursued the course of study prescribed by the Chemistry Course. He graduated in June 1932 with a degree of B.S. in Chemistry. He was elected an associate member of Sigma Xi, and was affiliated with the Phi Gamma Delta Fraternity. He returned to Union College for a year's graduate work and received the degree of M.S. in Chemistry in June 1933. The results of the work included in the Thesis presented for the degree appear in the Journal of Physical Chemistry, 38, 663 (1934). He was admitted to the Graduate School of the Mass. Inst. of Tech. in September 1934 and has since been pursuing a course of study leading to a degree of Ph.D. in Physical Chemistry. He was elected to membership in Sigma Xi in May 1936.