EQUILIBRIUM IN THE GASEOUS PHASE BETWEEN ACETIC ACID, ALCOHOL, ETHYL ACETATE AND WATER.

BY

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Equilibrium in the Gaseous Phase between Acetic Acid, Alcohol, Ethyl Acetate and Water.

Presented by-
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INTRODUCTION

The most common method of preparing esters is to heat together the acid and the alcohol. The reaction is, however, a reversible one and therefore a condition of equilibrium is obtained when a certain ratio exists between the amount of ester and water and that of free acid and alcohol. The point of equilibrium varies with the conditions of the experiment, namely, the nature and relative quantity of acid and alcohol and the temperature. M. Berthelot (1799) was the first to call attention to the effect of quantity. He showed that the amount of chemical change c is proportional to the product and the quantity of the reacting substances a and b and their affinity K. This is known as the law of mass action and is represented by the equation:

$$c = K \times ab \qquad (1)$$

The only change introduced since Berthelot's time is in the meaning of a and b, which now stand for molecular proportions and not molecular weights. Gulberg and Waage (1867) showed that K can be determined by studying the conditions of equilibrium in the following way. Suppose a curve is drawn of the action of an equal number of gram-molecules of ethyl alcohol and acetic acid , the quantity being transformed into ester and water plotted on the absissa and time an the ordinate. (The mixture kept in a thermostat, a little removed from time to time

and titrated for free acid). It will be found that, as the quantity of free acid and alcohol diminish, the velocity also diminished until there is no further change. This is the equilibrium point. If the reaction is begun from the other end and a mixture of an equal number of gram molecules of the ester and water is taken, the free acid will make its appearance, and the reaction will slow down until the same equilibrium point is reached. This equilibrium point is reached when two thirds of a gram-molecule ester and water and one third of a gram-molecule of acid and alcohol are present. The reaction may be represented by the following equation:

$$\begin{array}{ccccccc} C_2H_5OH & + & CH_3COOH & = & CH_3COOC_2H_5 & + & H_2O \\ 1/3 & & 1/3 & & 2/3 & & 2/3 \end{array} \qquad (2)$$

We may consider that the equilibrium point is reached when the velocites of the opposing reactions are equal, that is, when

$$V_1 = V_{22}$$

According to the kinetic theory the velocity of a reaction is determined by the number of collisions between molecules; but the number of collisions in unit time is proportional to the number of molecules in unit volume(Concentration).

Let a and b equal the number of molecules of the reacting substances in unit volume and c the number of molecules of the products in unit volume. The velocities

of the two reactions will be:

$$V_1 = K_1\, ab, \qquad \text{and } V_2 = K_2\, cd$$

At equilibrium $V_1 \quad V_2$ and $K_1\, ab = K_2\, cd$

$$\text{or} \quad \frac{K_1}{K_2} = \frac{cd}{ab} \qquad \text{replacing } \frac{K_1}{K_2} \text{ for } K$$

$$K = \frac{cd}{ab}$$

and for equation (2)

$$K = \frac{c \text{ ester} \times d \text{ water}}{a \text{ alcohol} \times b \text{ acid}} = \frac{2/3 \times 2/3}{1/3 \times 1/3} = 4$$

Equilibrium in the liquid phase for reaction (2) may be represented by the above equation and the numerical value for K being practically independant of the temperature change. Since the free energy change in evaporating a liquid at its equilibrium pressure is equal to zero, it follows that the vapor in equilibrium with the liquid equilibrium mixture must represent the equilibrium between the components in the gaseous phase. (Berthelot found that at 10°C. 65.2% of alcohol and acid are changed into ester, and at 220.0°C. 66.5% of the mixture is transformed into ester, an increase of 210° produces hardly any displacement of the equilibrium).

Preparation of Materials

ABSOLUTE ALCOHOL was prepared from 95% ethyl alcohol in the following manner. The alcohol was allowed to stand with quick lime in a closed flask for five days, shaking several times a dayduring that period. It was then distilled into a flask containing quick lime which was heated on a bath of boiling water, from this flask the vapors were condensed again and received in a bottle containing freshly prepared anhydrous copper sulphate. Specific gravity 0.7948 Boiling point 78.4°C.

ACETIC ACID used was from new stock of "Bakers Analyzed" acetic acid testing 99.995 % pure. Boiling point 118.0°C.

ETHYL ACETATE of high degree of purity was obtained from the United States Induetral Alcohol Co. This was fractioned by distilling thru an 18 inch Hemple column, collecting only that portion distilling over at 76.0 to 78.0 degrees centigrade. When analyzed for purity it was found to be 100% ethyl acetate. (No free acid)

STANDARD SOLUTIONS of N/10 hydrodhloric acid
N /10 Barta
N/2 Sodiun hydroxide

were made up in the usual manner, protected from carbon dioxide, and carefully standardized.

Development of Apparatus

A special type of apparatus was constructed so that a very small fraction of the equilibrium mixture could be removed by distillation while the mixture was being boiled under reflux. The whole system was designed so that reflux and distillation of the vapor sample could be accomplished under reduced pressure. The volitility of the components of the equilibrium mixture. especially, ethyl acetate, made it necessary to use a very large condensing surface for the reflux. To further guard against loss of vapors the condensing surface was cooled by ice-water(produced by passing the tap water thru about forty feet of small lead pipe, cooled by an ice-salt mixture.) This cooling was especially necessary when the apparatus was put under reduced pressure. Various methods of heating the mixture were tried.

1- Ordinary water bath, water covering lower half of the flask only.

2- Entire flask submerged in the water.

3- Air bath over entire flask.

4- Direct flame under small hole in asbestos board.

5- Ni-Chrome resistance coil immersed in the liquid.

6- Platinum resistance coil immersed in the liquid.

7- Ni-Chrome resistance coil placed in quartz tube and adjusted in lower part of the flask at about

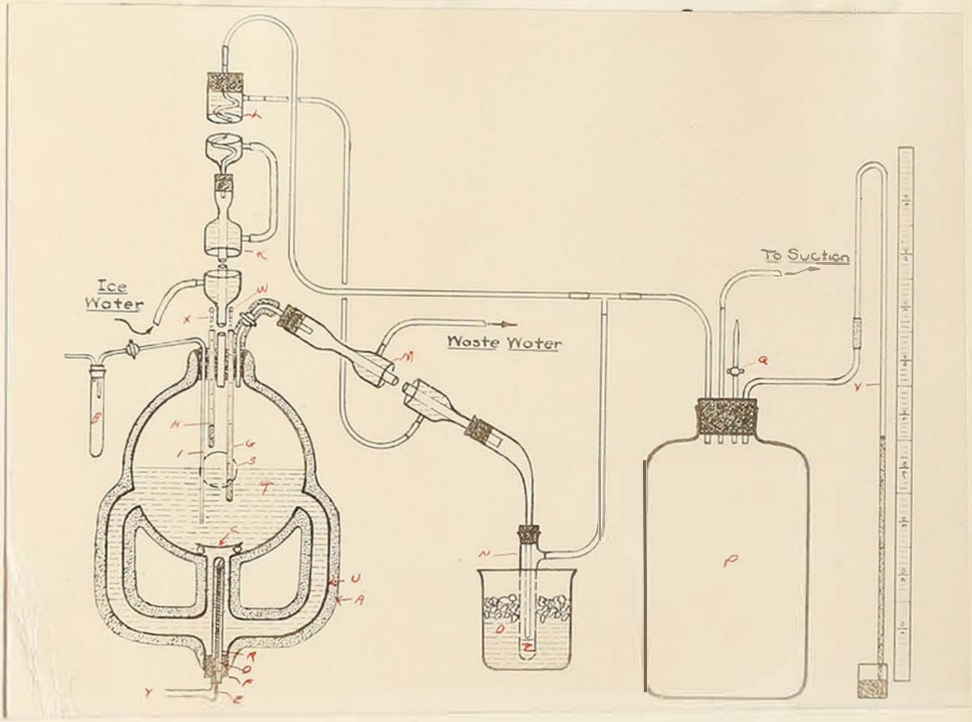
45° from the vertical axis.

8- Same heater placed in bottom of flask in line with the vertical axis. (see PLATE I.)

The methods numbered 1 to 4, inclusive, failed to produce the results desired because of the superheating of either vapor or liquid. Methods 5 and6 produced a very even temperature but were given up because of partial oxidation of the alcohol. This was suspected by the presence of a distinct odor of acetaldehyde, and later proved by positive tests for same. A black deposit also formed on the platinum wire after being heated in the liquid for a short time. The Ni-Chrome wire in method 5 was also acted upon by the acetic acid, and for this reason the platinum wire was substituded for same. Method 7 was then adopted which removed these dificulties but produced super-heating of the liquid, which was probably due to the position of the heater in the liquid, and also to the fact that the liquid was not stirred. To overcome this dificulty the tube containing the heater was placed in the bottom of the flask in line with the vertical axis. (see PLATE I) Tubes were then sealed into opposite sides of the flask, bent down so as to enter the heater tube at the bottom of same. These tubes conducted the flow of convection currents and thereby stirring the liquid and causing more even heating. The entire flask was insulated with a magnesia-asbestos composition to prevent loss of heat by radiation. Other parts of the apparatus were of the usual type used for vacuum distillation. The two thermometers used (one in the liquid and the other in the vapor) were compared with standard thermometers tested by the Bureau of

Standards. Both thermometers were fitted in wells so that they could easily be removed, or interchanged, without loss of vapors, or breaking the vacuum.

PLATE - I.



M- Straight tube condenser for condensing sample Z

N- Sample reieiver

O- Freezing mixture of ice and salt

P- 5 gallon bottle for volume

Q- Stop-cock to emit air(for controlling pressure)

R- Closed "Vitrosol tube encasing heater element D

S- "Windows" in insulation (for obserbation)

T- Liquid, U- Pyrex flask V- Hg manometer

W- Liquid thermometer, X- Vapor thermometer

Y- Electric wires to heater, Z- Sample of distillate

to PLATE I

A- Magnesia-asbestos insulation

B- Sample tube (for obtaining samples of the equilibrium mixture)

C- Watch crystal (to spread convection currents)

D- Ni-Chrome heating element

E- Small "Vitrosol" tube supporting heater element

F- Rubber stopper holding heater in flask

G- Well for thermometer W

H- " " " X

I- Tube to carry sample to tube B

J- Stop-cock opening condenser M

K- 20 inch straight tube condenser, (for reflux)

L- Spiral condenser for reflux

M- Straight tube condenser for condensing sample Z

N- Sample reieiver

O- Freezing mixture of ice and salt

P- 5 gallon bottle for volume

Q- Stop-cock to emit air(for controlling pressure)

R- Closed "Vitrosol tube encasing heater element D

S- "Windows" in insulation (for obserbation)

T- Liquid, U- Pyrex flask V- Hg manometer

W- Liquid thermometer, X- Vapor thermometer

Y- Electric wires to heater, Z- Sample of distillate

Experimental Technique (composition of mixtures)

The equilibrium proportions of the four components of the system, as given in the first part of this paper, are according to the equation;

$$K = \frac{2/3 \text{ mol ester} \times 2/3 \text{ mol water}}{1/3 \text{ mol acid} \times 1/3 \text{ mol alcohol}} = 4$$

corresponding to 11.34% water, 55.38 ester, 1[illegible].90% acid and 14.36% alcohol. This mixture wil hereafter be referred to as "Equilibrium Mixture A. Other mixtures made up by varying the proportions of the components. They are as follows:

Equilibrium Mixture B corresponding to the equation;

$$K = \frac{2/9 \text{ mol ester} \times 2\text{mols water}}{1/3 \text{ mol acid} \times 1/3 \text{ mol alcohol}} = 4$$

and containing 21.50% ester, 3960 % water, 22.00% acid and 16.90% alcohol.

Equilibrium Mixture C. corresponding to the equation;

$$K = \frac{4/3 \text{ mol ester} \times 1/3 \text{ mol water}}{1/3 \text{ mol acid} \times 1/3 \text{ mol alcohol}} = 4$$

and containing 73.94% ester, 3.78% water, 12.63% acid and 9.66% alcohol.

note- (Each mixture was checked by analysis)

Experimental Techinque (procedure)

500 cc of the mixture was made up, according to the proportions given above, by weight, and placed in the boiling flask. After the thermometers were adjusted to read temperatures~~s~~ of liquid and vapor the liquid was gradually heated to boiling. The mixture was then boiled

under reflux for several hours when a sample was removed for analysis. (Boiling should not effect the composition of the mixture if the system is in equilibruim, therefore the second analysis should check the first). Also the temperature of the vapor and liquid should be the same when the system is in equilibrium. When the temperature of the liquid and vapor were found to be constant to within 0.5° the stop-cock (J) was opened and a small sample of about 5 cc from a total of 500 cc s was distilled over. The distillate was chilled by a mixture of ice and salt placed around the receiver tube . The composition of this distillate should represent the system at equilibrium in the vapor phase. After the sample at atmospheric pressure had been distilled, the apparatus was put under reduced pressure and another sample of about the same size was distilled over. In this latter case the pressure was adjusted so that the liquid would distill over at about 20 degrees lower than in the former case, at atmospheric pressure.

Method of Analysis

Two samples of less than one cubic centimeter each were remover from the two samples taken as above and placed in small glass stoppered weighing bottles (1 cc). Each bottle was accurately weihgted and dropped into the titration flasks (250 cc) containing 100 cc of ice cold distilled water and a drop of phenolphthalein as indicator. Each sample was titrated with $N/10$ $Ba(OH)_2$ and from this data the percent of acetic acid was calculated.

N/2 Sodium hydroxide was then added to the flask in excess of the amount needed to hydrolyze the ester and allowed to stand, at room temperature, for over night, or for at least ten hours. At the end of that period the excess alkali was titrated with N/10 HCl and the percent of ester calculated from the amount of alkali used. The remaining distillate of each of the two samples distilled was used for specific gravity determinations. A very small pycnometer, of the Sprengel-Ostwald type, was constructed for this purpose holding about one and one half cubic centimeters. All specific gravity determinations were made at 20° Centigrade.

Calculation of Data and K

Knowing the specific garvity of the distillate and the percentage of ester in the sample the percent of water may be read directly from the curve, which shows the percent of ester and percent of water for the corresponding specific gravity. (See PLATE II)
The acetic acid content of the distillate was so small (see Tables 1,2,& 3) that there was no apparent change in the specific gravity due to this component of the vapor sample. This small percentage of acid was subtracted from the percent of water read from the graph. The percentage of alcohol being determined by difference.

In the earlier data the alcohol was determined by hydrolyzing a five gram sample with ten percent NaOH solution in a closed flask or pressure bottle. This was then distilled thru a spiral condenser, collecting 100 cc of the distillate, and determning the specific gravity of same. The percentage of alcohol was then found from the alcohol density tables, and the percentage of alcohol for the sample calculated. The percent of water was then determined by difference. This method was given up beaause of the large sample needed and the time required to run the analysis.

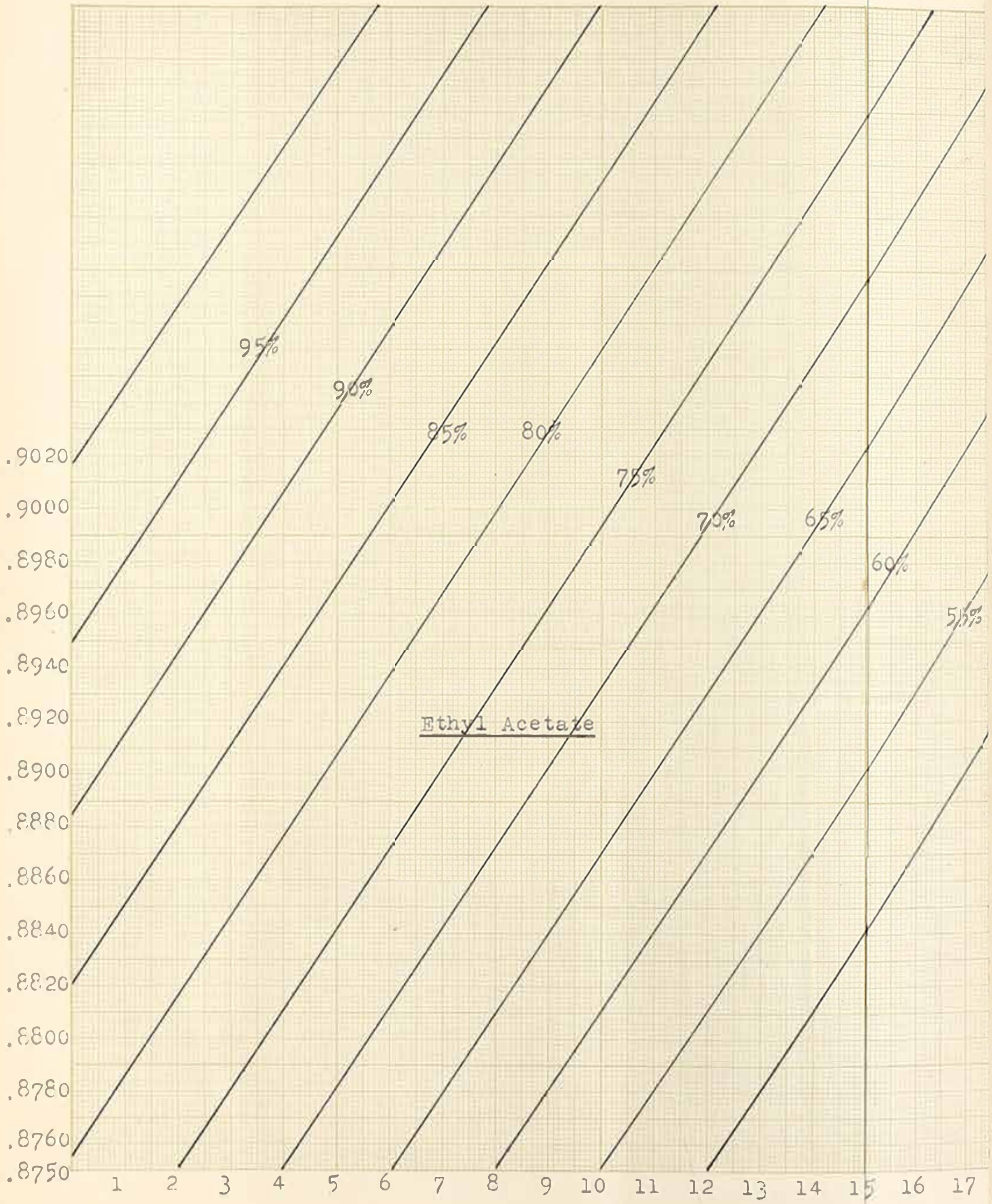
A effort was made to determine the amount of water present by the decomposition of some material by water and yielding a gas, the volume of the gas measured, and from this data the percent of water obtained. Calcium carbide yielding acetylene and metallic calcium yielding hydrogen were tried. Another method tried was to absorb the acetylene gas in a ten percent solution of silver nitrate, titrate the amount of nitric acid liberated by the reaction, and calculate the percent of water from this data. All of these methods were given up because of the difficulty found in removing all of the acetylene in solution in the liquid of the reaction flask. Low results were produced at every trial on standard solutions of water in absolute alcohol, altho this proved to be more practical than the former.

The percentage composition of the distillate being obtained, the equilibrium constant (K) for the gaseous

phase was calculated in the same manner that the constant is calculated in the liquid phase.

The equilibrium constant (K) has been calculated for the vapor phase of the equilibrium mixtures A, B, and c. which are tabulated in Tables 1, 2, and 3, respectively.

PLATE II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80%
75%
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60%
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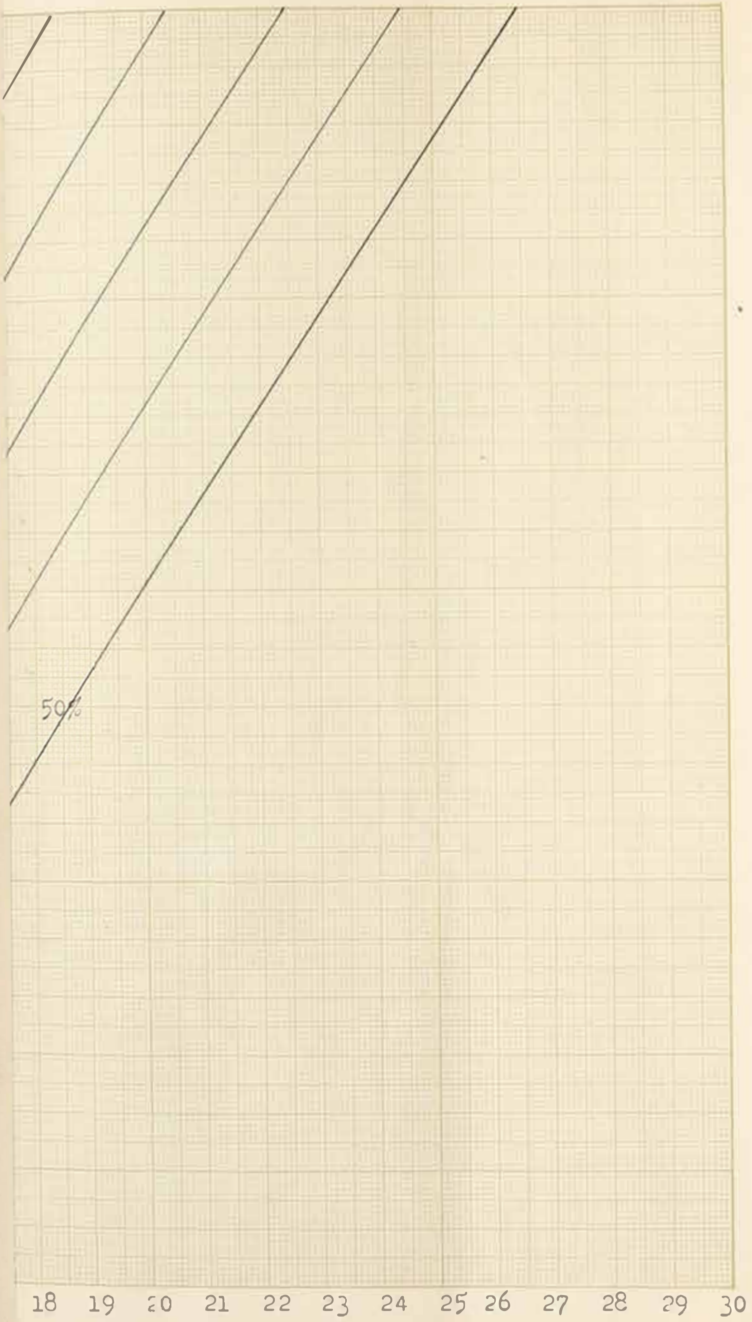
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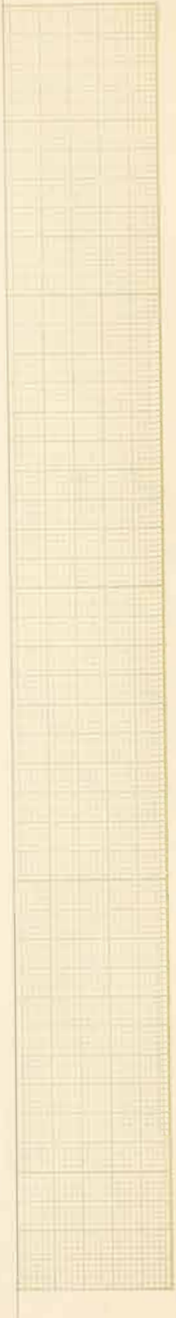

TABLE # 1

Showing the composition of Equilibrium Mixture~~s~~ A and composition of the distillate of this mixture, which represents the vapor phase of the mixture at equilibrium.

		%acid	%ester	%water	%alcohol	(K)	Sp.Gr.
Start		18.90	55.38	11.34	14.36	4	
A.P.		.345	71.70	5.40	22.50	88.7	
" "		.309	67.80	7.00	24.90	107.8	
" "		.432	79.52	5.67	14.38)	125.0	.8931
" "		.434	79.55	5.65	14.44)		
" "	x	.218	83.40)	6.53	9.97	422.2	.8994
" "	x	.231	83.14)				
" "	x	.224	83.27	6.73	9.87	431.0	.8997
R.P.	x	.126	84.73))	5.97	9.38	721.0	.8994
" "	x	.134	84.32)				
" "	x	.136	84.73)	6.12	9.23	942.7	.8995
" "	x	.134	84.32)				

Boiling point of mixture at atmospheric pressure (A.P.)

Vapor 74.0
Liquid 74.4

Boiling point of mixture under reduced pressure (R.P.)

Vapor 53.0
Liquid 53.5

x indicates runs made using ice water in condensers.

TABLE # 2.

Showing the conposition of equilibrium mixture B and composition of the distillate of this mixture, which represents the Vapor Phase of this mixture at equilibrium.

		%acid	%ester	%water	%alcohol	(K)	Sp.Gr.
start		22.00	21.50	39.60	16.90	4	
A.P.		.326	64.45	8.60	27.63	114.3	
" "		.402	70.51	8.80	20.27	126.9	
" "		.432	71.67	7.92	19.93)	118.5	
		.415	72.17	7.77	19.66)		
" "		.429	71.27	8.16	20.17	119.5	
" "		.405	72.17	7.70	19.73	121.15	
" "		.260	74.41	7.89	17.44	220.4	
" "		.259	75.73	9.00	15.01	305.9	
" "	x	.155	76.74	8.35	14.79	485.6	.8996
" "		.199	79.11)	8.10	12.38	452.0	.8995
	x	.202	79.53)				
" "	x	.233	79.53	7.86	11.70	401.6	.8999
" "	x	.291	84.33)	5.81	9.77	300.7	.8998
	x	.290	84.04)				
R.P.	x	.208	79.58	8.00	12.07	442.2	.8992
" "	x	.370	83.94)	6.05	10.05	250.5	.8992
	x	.332	84.16)				
" "	x	.450	79.77	7.55	12.23	190.7	.8993

Boiling point at atmospheric pressure (A.P.) Vapor 77.5° C.
Liquid 77.8

" " " reduced pressure (R.P.) Vapor 56.2
Liquid 56.4

x indicated runs made using ice water in condensers.

TABLE # 3.

Showing the composition of Equilibrium Mixture C and composition of the distillate of this mixture, which represents the Vapor Phase of the mixture at equilibrium.

		%acid	%ester	%water	%alcohol	(K)	Sp.Gr.
Start		12.63	73.94	3.78	9.66	4	
A.P.		.199	73.20	6.67	18.93	259.6	
" "		.579	75.29	7.69	16.44	105.6	
" "		.200	73.72	7.02	19.06	236.8	
" "		.370	77.01	8.09	14.53	207.9	
" "	x	.230	81.50	7.73	9.93	490.0	.9002
" "	x	.228	81.21	6.32	12.24	319.2	.8967
" "	x	.230	81.49	6.17	12.10	314.2	.8965
" "	x	.0734	84.02	6.68	9.23	1275.0	.9008
R.P.	x	.156	84.20	5.35	10.30	489.0	.8974
" "	x	.155	84.27	3.46	12.11	270.0	.8920
" "	x	.156	84.10	3.54	12.20	273.0	.8920
" "	x	.0523	82.87	7.09	9.98	1966.0	.9000

Boiling point at atmospheric pressure (A.P.) Vapor 72.4° C.
Liquid 72.8

" " " reduced pressure (R.P.) Vapor 52.0
Liquid 52.4

x indicated runs made using ice water in condensers.

Equilibrium in the Vapor Phase (Object)

As stated before it has been assumed that the the analysis of the distillates of the equilibrium mixtures represented the vapor phase of the mixture at equilibrium. In an attempt to prove , or confirm, this assumption mixtures were made up to represent the average distillate of either mixture A and B. A calculated and weighted amount of these mixtures was heated to 96° C. in highly evacuated sealed flasks for a period of 36 days.

(procedure)

Weighted amounts of the liquids were introduced into 500 cc Pyrex boiling flasks which had been highly evacuated and cooled by being packed in an ice-salt mixture. The flasks were then sealed and kept in a water-jacketed oven for 36 days at a temperature of 96 degrees centigrade. The liquid was entirely in the vapor state during the whole period of heating. Before opening the flasks they were again packed in ice and salt and after the vapors were driven from the neck of the flasks by heating, they were opened with extreme care to prevent the loss of any of the material. Ice cold water was then added to the flasks and the contents analyzed for acid and ester. The specific gravity of the liquid being known, the amounts of water and alcohol were then determined. Data showing the resusts of this investigation are found ~~on~~ in TABLE # 4.

(sealing the flasks)

500 cc long neck, round bottom, Pyrex boiling flasks were used to hold the material and were constricted about two inches from the mouth so as to facilitate easy sealing.

The mouth of the flask was fitted with a two hole rubber stopper holding a 2 cc burette (specially constructed for the purpose) and a small el of glass tubing to connect to the vacuum pump. The burette was filled with the liquid and weigh~~t~~ed, placed in position in the stopper, and the flask evacuated. The calculated portion of theliquid was run in, the flask sealed, the burette removed and weighted.

TABLE # 4.

	% acid	% ester	% water	% alcohol	K
B dis. start	0.200	79.47	8.58	11.79~~8~~	840.0
36 days	0.753	76.00	9.25	14.00	116.33
C dis. start	0.052	82.87	7.098	9.98	1966.0
36 days	0.550	78.81	8.35	12.29	169.0

Discussion of Results

The evident trend in the values of the equilibrium constant (K) as tabulated in tables 1,2, and 3 may be due to one or all of a number of causes. In the first data there was a wide variation in the values, or percentages, of ester and acid obtained, and consequently in the percent of alcohol and water, which was obtained by difference. In this first data the apparent loss of ester was probably due to vaporization occurring during the analysis. In an effort to correct this the technique of analysis was changed and reasonable good checks, on the same sample, were obtained. Also the metod of analysis was tried out on a known concentration of ester, the results obtained proving that thedetermination of adid and ester were correct, which might indicate that the loss in ester was not due to vaporization (at least not for the later analysis).

The determination of alcohol by the first method used depended on the accurcy of the measurement of the specific gravity. The method was that commonly used for the determination of alcohol in alcoholic liquors(see Government Bulletin No.). This would have been satisfactory if a sample of sufficient size could have been used. A large sample could not be obtained as the removal of a considerable amount of the liquid by distillation would change the composition of the equilibrium mixture remaining in the boiling flask. Values for alcohol and water as determined by use of specific gravity, ester, water chart (PLATE II) were obtained by the use of a very small sample, and proved to be more satisfactory.

After the apparatus was changed so that ice water could be run thru the condensers the values for acid percent were decreased considerably and in like manner, the percent of ester was very much increased. This change in values for acid and ester influenced the values for alcohol and water and in some cases doubled or trebled the values of the equilibrium constants (K), as obtained when the warmer tap water was used in the condensers.

The increase in the percentage of ester would possibly indicate that, heretofore, a large amount of ester had been lost by volitization due to ineffecient condensing surface. But the decided lower precentage of acid makes it apparent that a partial hydrolysis of the ester had taken place in the former case, thereby increasing the acid percent and lowering the ester content.

Altho there is a very large trend of the values of equilibrium constants for the reaction in the vapor phase it is obvious that the values of K are very much higher in this phase than in the liquid phase.

The data tabulated on page 21, Table 4, shows that during the 36 hour period of heating there was a partial hydrolysis of the ester, resulting in a marked increase in the amount of acid. Thers results seem very inconsistant in that the loss of ester greatly overbalances the gain in acid. The data therefore, is of only qualitative value.

SUMMARY

1- The equilibrium constant (K) was found to be very much larger in the gaseous phase than in the liquid phase.

2- No definite numerical value for the equilibrium constant (K) could be found from the data obtained.

3- Colder condensing surface shifted the percentage composition of the equilibrium distillate, resulting in very much higher values for the gaseous equilibrium constant.

4- Data given in TABLE #4 shows a decided shift in the equilibrium from right to left.,indicating that the mixtures made up were not in equilibrium in the gaseous phase.