THE EFFECT OF CALCIUM CHLORIDE ON THE SEPARATION

OF ACETIC ACID AND WATER BY DISTILLATION

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SUMMARY

In an attempt to explore more effective methods of separating acetic acid and water by distillation, the effect of adding a third substance was investigated. The selection of calcium chloride for this purpose was made on the basis of existing vapor-liquid equilibrium data and solubility data.

It was found, experimentally, that the addition of calcium chloride to acetic acid-water mixtures reverses the relative volatility of the system, allowing the acid to be distilled overhead, leaving the water behind. Approximately forty vapor-liquid equilibrium runs were made on the system acetic acid-water-calcium chloride, covering the entire acid-water range and including salt concentrations ranging from 0 to 60 weight percent.

Reversal of the relative volatility of acetic acid and water takes place at approximately 8% calcium chloride content in the liquid phase. It appears, from the results obtained, that a fractionating tower, operated with about 30% calcium chloride in the liquid phase (a very rough estimate of the economic optimum) would permit the removal of the acetic acid overhead with a fewer number of plates and smaller heat requirements than are required for existing distillation processes. A final appraisal of the commercial possibilities of the method would involve a detailed economic comparison with existing separation procedures. Actual pilot plant studies would also have to be made before a final decision could be reached.

Data are presented on the boiling points of acetic acid-water mixtures at 760 mm pressure.

INTRODUCTION

Acetic acid is recovered from pyroligneous liquors obtained from the destructive distillation of hardwood wastes. The acid is usually available in dilute solution in water both from the original production from wood and from the process for making cellulose acetate. As a result, the separation of acetic acid and water has received considerable economic study. The separation of acetic acid and water by distillation is quite difficult because of the small relative volatility of the system, particularly in the water-rich composition region. Large fractionating towers are necessary and heat requirements are high because the water distills overhead. The existing methods of recovering acetic acid from water have been summarized in the literature:[8]

1. Ordinary fractional distillation is difficult and expensive because of the large number of plates required in the fractionating tower.

2. Transformation of the acetic acid to the calcium salt has been used.

3. Countercurrent extraction of the acid with a light solvent such as ether, chloroform, or acetone will yield about 70-90% acid. Benzene or petroleum ether will yield about 90-99% acid.

4. Extractive distillation with a heavy solvent such as dibutyl phthallate, diethyl phthallate and methyl cyclohexanone has been employed.

5. Separation by freezing out pure acid crystals at $-26^{\circ}C$, followed by subsequent distillation of the water, has been practiced.

6. Separation by forming a complex with an organic base such as quinoline or quinolidine, which complex can then be broken up after separation, finds some application.

7. Extraction with an organic solvent, followed by salting out, has been utilized in some cases.

8. Fixation of the water by hygroscopic agents is used extensively in the final concentration step. Suggested agents for this purpose are $CaCl_2$, Na_2SO_4, $MnSO_4$, $CuSO_4$ and H_3PO_4.

9. Distillation in the presence of a fixating agent such as anhydrous sodium acetate will give around 80% recovery of the acid at a concentration of 98.6%. The recovery by this operation is increased by reducing the pressure.

10. Distillation with a liquid such as xylene, benzene or ethyl acetate which will form a minimum-boiling azeotrope with the water, finds widespread use today.

It was the purpose of this investigation to find an inorganic salt which would facilitate the distillation of water and acetic acid by causing a reversal of the relative volatility, thus allowing the acetic acid to be distilled overhead while the water would pass out the bottom of the tower. The reason for this approach was based on the fact that acetic acid is usually available in dilute aqueous solution. Because large amounts of water have to be removed overhead in present-day processes, the cost of separation is quite high. A search of the literature revealed several investigations of the effect of salts on the boiling characteristics of acetic acid-water solutions.[7,9,13]

The work of McBain and Kam[9] contains acetic acid-water vapor-liquid equilibrium data involving a group of inorganic salts. The data are reproduced in Table I, along with vaporization constants calculated from these data. Vaporization constants for those salts, the use of which would be commercially feasible, are presented in Figure 1. A sample calculation of derived data from the literature information is presented in the Appendix, Section I.

In Table I the symbols have the following significance:

N_l = Normality of acid in the liquid phase

N_v = Normality of acid in the vapor phase

$R = N_v/N_l$

N_s = Normality of salt in the liquid phase

W_s = Weight percent salt in the liquid phase

X = Weight percent acid in the liquid phase (salt-free basis)

Y = Weight percent acid in the vapor phase

$K = Y/X$ = Vaporization constant

TABLE I

VAPOR-LIQUID EQUILIBRIUM
ACETIC ACID-WATER-INORGANIC SALTS

Literature data			Calculated values			
N_1	N_s	R	W_s	X	Y	K
Acetic Acid-Water						
0.05		0.662				
0.10		0.666				
0.20		0.673				
0.33		0.680				
0.50		0.685				
Acetic Acid-Water-Sodium Chloride						
0.1-0.2	0.12	0.688	0.70	0.904	0.620	0.687
0.1-0.2	0.21	0.708	1.22	0.905	0.637	0.704
0.1-0.3	0.29	0.721	1.67	1.202	0.866	0.721
0.1-0.3	0.41	0.742	2.36	1.210	0.890	0.736
0.13	0.661	0.790	3.77	0.791	0.616	0.780
0.076	1.04	0.830	5.85	0.465	0.378	0.813
0.078	1.38	0.904	7.66	0.482	0.423	0.878
0.077	2.30	1.076	12.38	0.485	0.498	1.025
Acetic Acid-Water-Potassium Chloride						
0.22	0.2-0.3	0.7146	1.88	1.33	0.943	0.709
0.254	0.4673	0.7389	3.46	1.55	1.127	0.729
0.2157	0.70	0.7741	5.13	1.32	1.000	0.758
0.2053	0.9228	0.8121	6.70	1.27	1.000	0.790
0.22	1.17	0.8383	8.40	1.37	1.108	0.810
0.2194	1.953	0.9363	13.60	1.40	1.233	0.880
Acetic Acid-Water-Potassium Thiocyanate						
0.2-0.23	0.2-0.34	0.6900				
0.2673	0.5590	0.7297				
0.2366	1.663	0.7693				
0.2595	2.451	0.8710				

TABLE I (CONTINUED)

Literature data			Calculated values			
N_1	N_s	R	W_s	X	Y	K

Acetic Acid-Water-Sodium Sulphate

0.22	0.07	0.669	0.50	1.326	0.883	0.666
0.22	0.13	0.674	0.92	1.325	0.890	0.672
0.25	0.22	0.674	1.55	1.508	1.010	0.670
0.25	0.35	0.683	2.44	1.505	1.025	0.681
0.27	0.61	0.710	4.18	1.630	1.150	0.705
0.29	1.10	0.762	7.34	1.762	1.328	0.754
0.21	1.40	0.807	9.19	1.280	1.016	0.794
0.22	1.54	0.839	10.10	1.345	1.080	0.804

Acetic Acid-Water-Lithium Chloride

0.2-0.22	0.2-0.25	0.7143	0.95	1.270	0.900	0.709
0.2269	0.2799	0.7188	1.18	1.370	0.980	0.715
0.2469	0.3930	0.7450	1.65	1.491	1.104	0.740

Acetic Acid-Water-Potassium Nitrate

0.21	0.22	0.6944				
0.24	0.3-0.5	0.7198				

Acetic Acid-Water-Sodium Acetate

0.11	0.14	0.6822				
0.1-0.23	0.4-0.67	0.6948				
0.1-0.28	0.9-1.1	0.7001				
0.2900	1.810	0.7244				

The curves of Figure 1 are drawn without regard to acid concentration variation, since this variation is extremely limited.

Quartaroli[13] has presented some data obtained from the differential distillation of acetic acid-water mixtures with salts present. These data are presented in Table II and are included in Figure 1. In Quartaroli's work 100 cc of 0.1 N acetic acid plus different weights of salt was added to a distilling flask and boiled until one-half of the volume was distilled. The recorded data give the weight percent of the acetic acid

FIGURE 1

VAPORIZATION CONSTANT OF ACETIC ACID-WATER
MIXTURES IN THE PRESENCE OF DISSOLVED SALTS
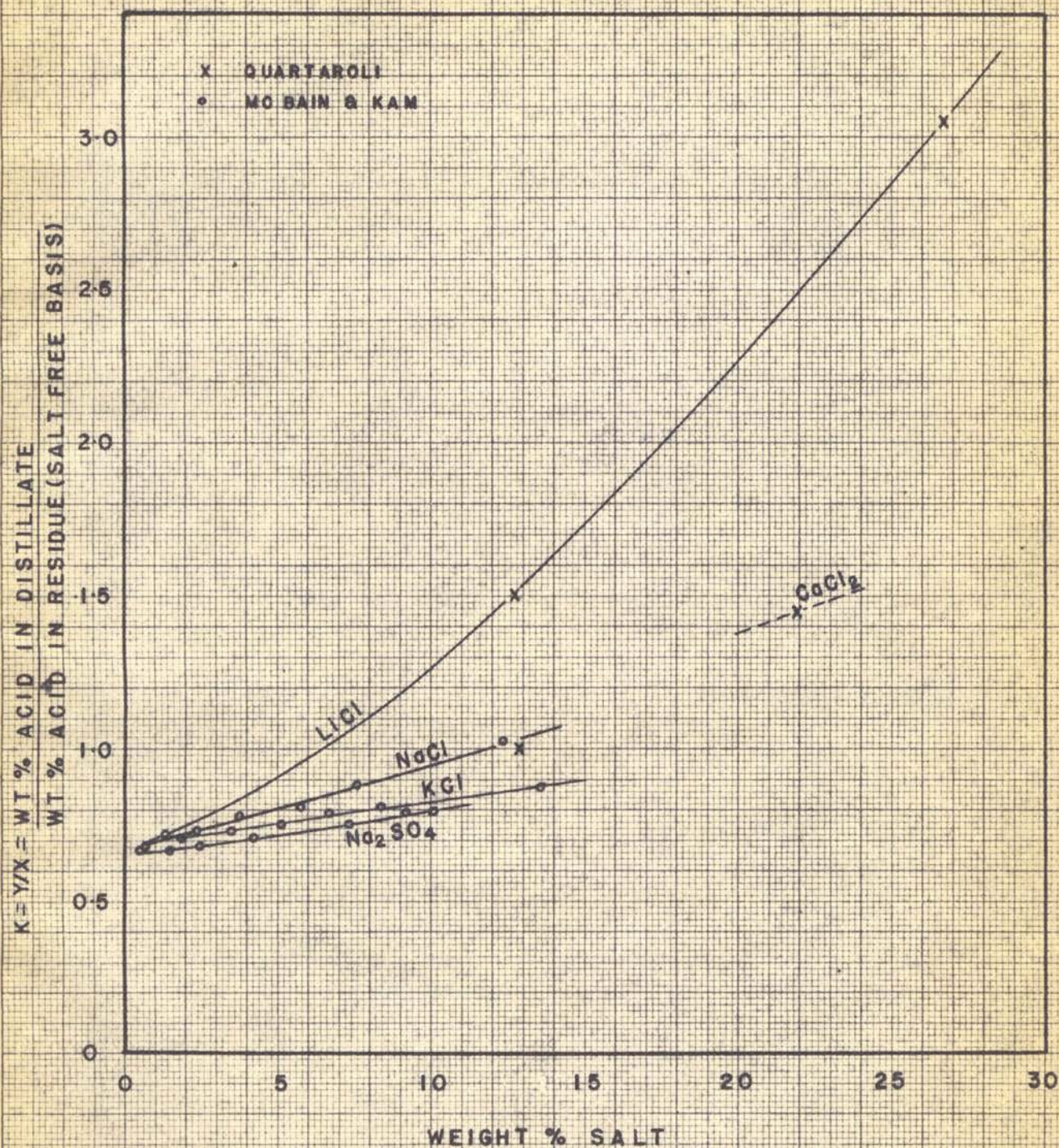
charged present in the distillate. Calculated K's were obtained from these data by the application of the Rayleigh Equation, assuming K to be constant over the range of compositions involved. A typical calculation appears in the Appendix, Section II.

In Table II the symbols have the following significance:

S = Grams of salt added

W_a = Weight percent of charged acid in the distillate

W_s(ave) = Average weight percent salt in the liquid phase

X(ave) = Average weight percent acid in the liquid phase (salt-free basis)

K = Y/X = Vaporization constant

TABLE II

VAPOR-LIQUID EQUILIBRIUM
ACETIC ACID-WATER-INORGANIC SALTS

Literature Data		Calculated Values		
S	W_a	W_s(ave)	X(ave)	K
none	32.2	0.0	0.814	0.565
10 g NaCl	51.8	12.9	0.589	1.01
25 g LiCl	88.0	26.7	0.372	3.06
10 g LiCl	64.5	12.9	0.513	1.50
19.2 g CaCl$_2$	63.3	22.0	0.520	1.44
30 g NaBr	65.0	30.3	0.501	1.58

A comparison of the data for the salt-free acetic acid-water system in Tables I & II shows the value of K calculated from Quartaroli's data to be about 15% lower than that obtained from McBain & Kam. A study of the curves presented in Figure 1 indicates that the more promising salts are lithium chloride, calcium chloride and sodium chloride. Lithium chloride appears to be the best with a volatility reversal taking place at about 7.5% salt in the liquid phase.

It was necessary to turn next to solubility data. The use of a salt for reversing the relative volatility of acetic acid and water requires that the salt be present on all the trays and in solution. The salt must therefore be soluble in concentrated acetic acid. A paper by Davidson[1] gives some qualitative data on the solubilities of salts in glacial acetic acid:

1. Salts readily soluble at room temperature:
   lithium nitrate   zinc iodide
   calcium nitrate   ammonium thiocyanate
   ammonium nitrate   potassium cyanide
   copper nitrate   lithium acetate
   calcium chloride   potassium acetate
   zinc chloride   ammonium acetate
   ferric chloride   lead acetate
   antimony chloride   cadmium acetate
   barium iodide

2. Salts somewhat less soluble
   silver nitrate   mercury iodide
   aluminum chloride   cobalt chloride
   mercury chloride

3. Salts soluble to the extent of less than one part per hundred at room temperature:
   sodium chloride   ammonium bromide   potassium chlorate
   potassium chloride   ammonium iodide   sodium sulfate
   potassium bromide   sodium nitrate   ammonium sulfate
   potassium iodide   potassium nitrate   copper acetate
   ammonium chloride   barium chloride

4. Salts practically insoluble:
   silver chloride   mercury chloride
   silver bromide   calcium phosphate
   silver iodide   copper phosphate
   silver cyanide   calcium carbonate
   silver thiocyanate   sulfates of Li, K, Cu, Ag, Ba, Ca,
   lead chloride   Mg. Zn, Cd, Hg(ous & ic), Al, Pb.
                          Mn, Ni, Co, and Fe(ous & ic)

Quantitative data for some of the more promising salts are shown in Figure 2. These include calcium chloride[10], lithium nitrate[14], mercuric chloride[2], ammonium nitrate[3], mercuric bromide[2] and sodium nitrate[3].

Davidson's work shows that sodium chloride is insoluble in acetic acid. Although solubility data for lithium chloride are not available, it

might be expected that lithium chloride, also an alkali chloride, would be insoluble. Figure 2 shows calcium chloride to be quite soluble, however. It was therefore selected as the salt to work with in this investigation. Data on the solubility of calcium chloride in water are available[14]; these are presented in Figure 3. Data for the boiling points of solutions of calcium chloride in water are presented in Table III.

TABLE III

BOILING POINT OF SOLUTIONS OF
CALCIUM CHLORIDE IN WATER (760 mm)

Weight Percent Calcium Chloride	Boiling point, °C
1.1	100.1
2.2	100.2
5.3	100.6
10.0	101.6
35.7	115.1
44.0	123.3
52.6	133.6
75.4 (saturated solution)	178.2

Vapor-liquid equilibrium data for the system acetic acid-water have been determined by several investigators[11,12]. Othmer and Gilmont[11] have studied the effect of pressure on this equilibrium. They found that a very large pressure change was necessary to cause a noticeable shift of the equilibrium curve. A reduction in pressure shifts the curve closer to the forty five degree line. From this information it can be assumed that small fluctuations in atmospheric pressure would have little effect on the equilibrium curve but it was considered advisable, nevertheless, to operate the vapor-liquid equilibrium still employed in this investigation at 760 mm pressure so as to obtain accurate boiling point data.
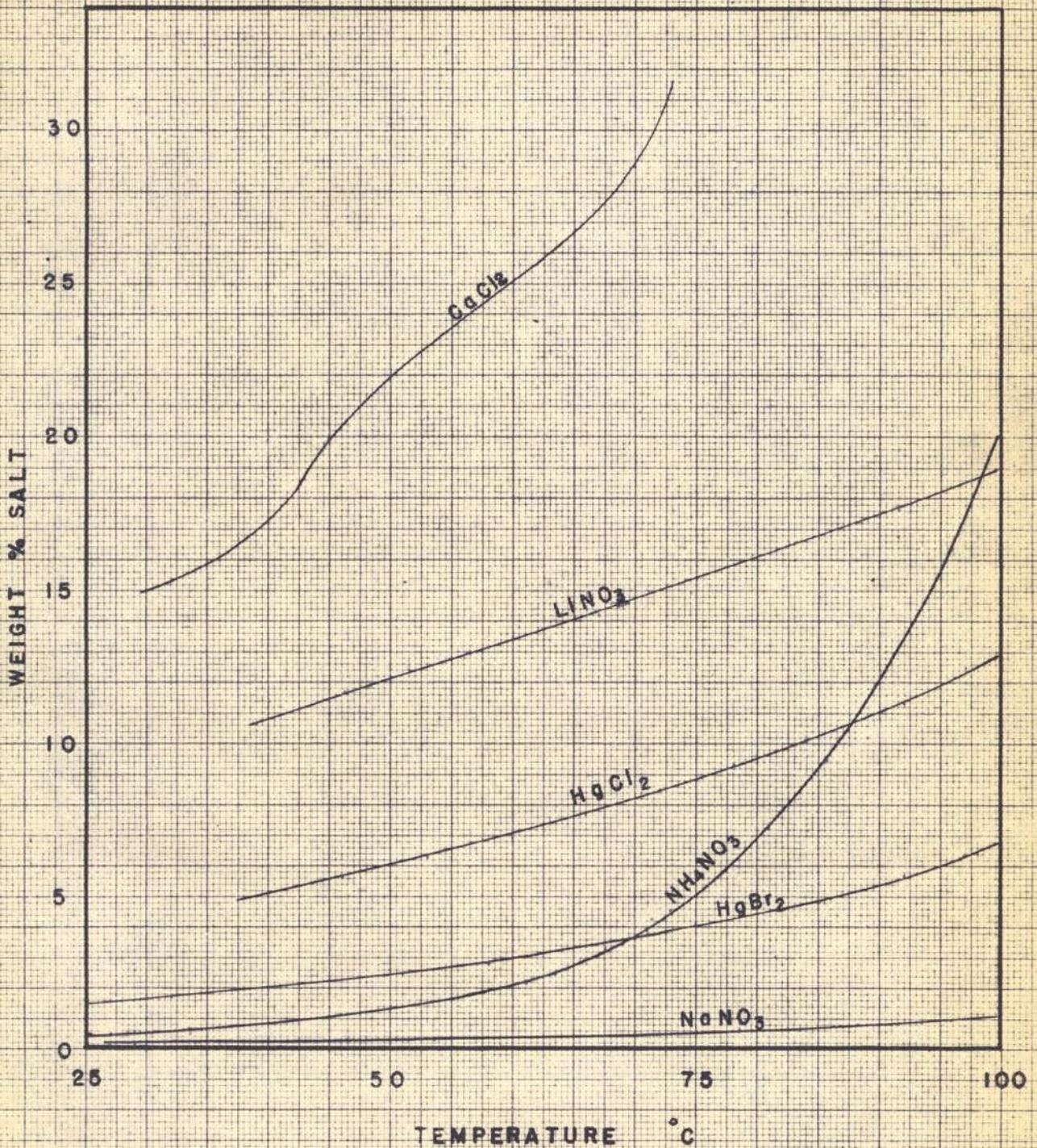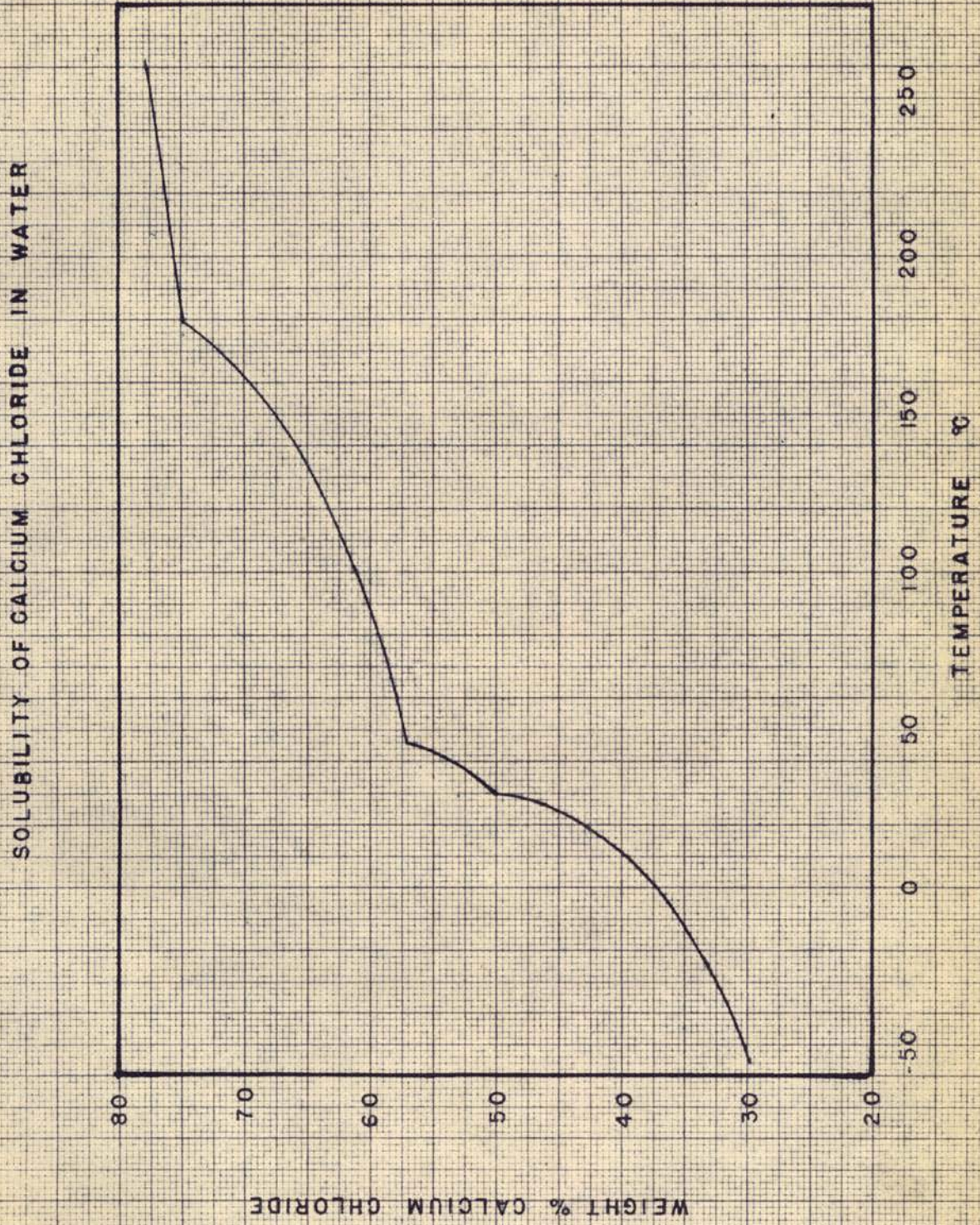
FIGURE 2

SOLUBILITY OF SALTS IN GLACIAL ACETIC ACID

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FIGURE 3

SOLUBILITY OF CALCIUM CHLORIDE IN WATER

TEMPERATURE °C

WEIGHT % CALCIUM CHLORIDE

PROCEDURE

Analytical Technique

The distillate, consisting of water and acetic acid, was analyzed by titration of a five ml sample with approximately 1 N sodium hydroxide. The sample was diluted with distilled water to approximately 25 cc before titration. The indicator used was phenolphthalein. The caustic was standardized against dry potassium acid phthalate. The weight percent acetic acid in the distillate was determined from its normality, obtained by titration, through the use of standard conversion tables.[4]

The residue samples, when free of calcium chloride, were analyzed by the same method as the distillate samples. The acid analysis of water-acetic acid-calcium chloride mixtures was made by straight titration with caustic. Comparison tests showed that calcium chloride, even when present to the extent of 40% in the original sample, produced no measurable effect on the caustic titration. All titrations were run in duplicate and were reproducible to 0.05 ml, on the average. The chloride content of the residue was obtained by titrating the same sample, already titrated to a neutral point with caustic, with standard silver nitrate (0.1 N) using sodium chromate as an indicator (Mohr's Method). It was only necessary to discharge the pink phenolphthalein color with a fraction of a drop of acetic acid prior to titrating with silver nitrate. This method was found to be accurate by a series of comparison tests on solutions of known calcium chloride content containing varying amounts of sodium acetate and made barely acidic to phenolphthalein. The preparation of the residue samples for analysis consisted of weighing a sample of approximately 25 grams into a 100 ml volumetric flask and diluting to mark. Measured aliquot portions of 5 to 30 cc, depending on the concentration range, were titrated and the

weight percent acetic acid and calcium chloride calculated. All reagents used were analytical grade.

Operational Technique

The apparatus used in the equilibrium distillation work is shown in Figure 4. It was approximately 15 inches in overall length. It was designed initially by Jones, Schoenborn, and Colburn.[6] Several modifications were made in the original design. These included the addition of glass beads to the condensate chamber to reduce the liquid hold-up, thus shortening the time necessary to reach equilibrium, the installation of a side arm at the upper end of the flash reboiler, and the substitution of a wick of glass wool for the spiral of wire in the flash reboiler. Preliminary runs showed a tendency for the liquid to momentarily hold up in the flash boiler, subjecting the glass to thermal shock and causing the glass to break. Considerable trouble was experienced from this source until the glass wool wick was introduced.

The heated surfaces, i.e., the flash boiler, the residue chamber, and the vapor section were covered with asbestos paper and then wrapped with 84, 80, and 30 inches, respectively, of number 24 Chromel A heating wire. The flash boiler was controlled with a Varitrans transformer and the other two heaters were controlled with variable slide wire resistances connected in series with the heaters. The power requirements for normal operation on the flash boiler, residue chamber, and vapor section were approximately 350, 40, and 10 watts, respectively.

The pressure on the still was maintained at 760 mm of mercury by the use of a Model No. 5 Industrial Cartesian Manostat, available through The Emil Greiner Company, New York City. The pressure source used to operate the manostat was compressed nitrogen gas. The controller maintained the pressure constant to about 0.5 mm of mercury.
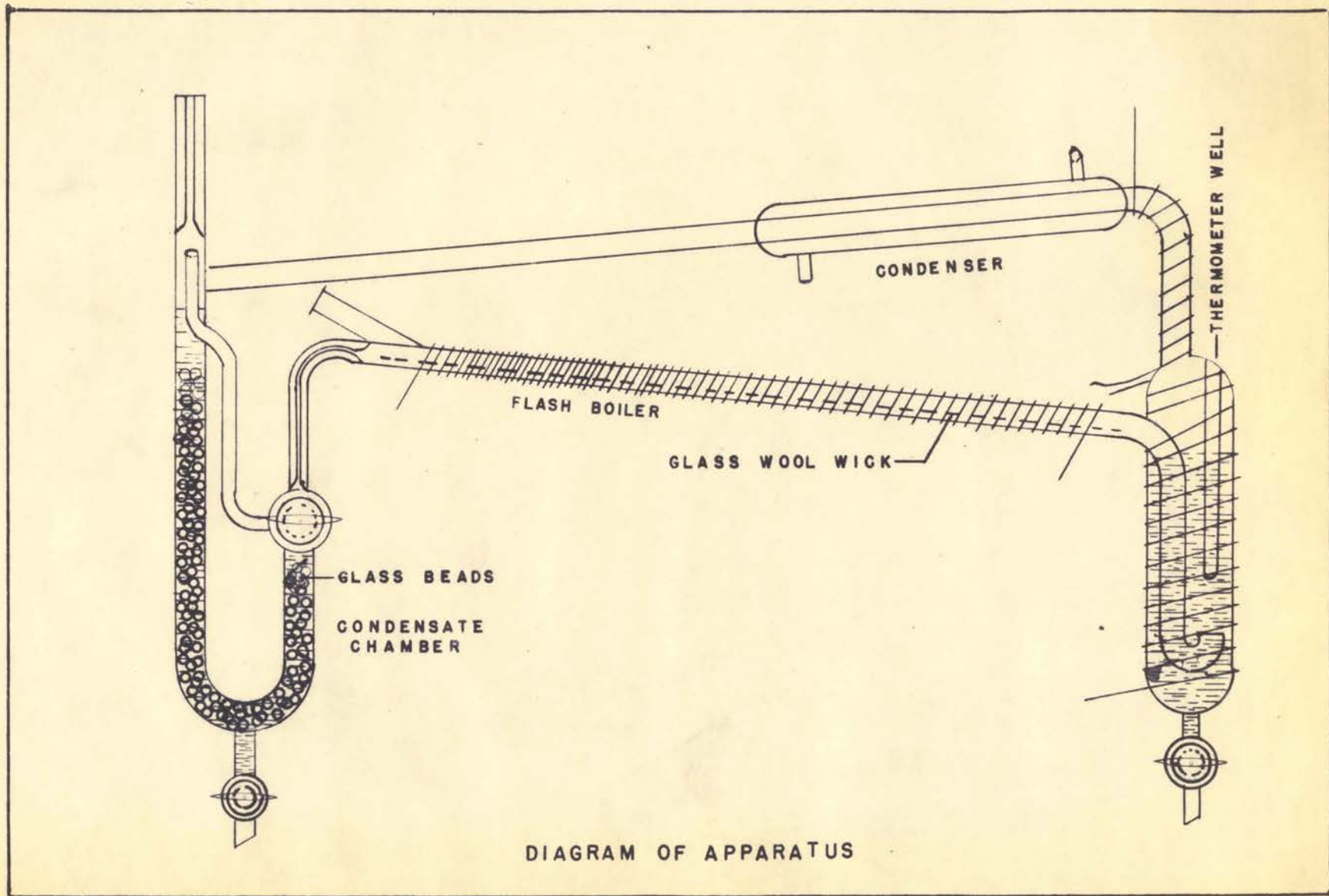
FIGURE 4

THERMOMETER WELL

CONDENSER

FLASH BOILER

GLASS WOOL WICK

GLASS BEADS

CONDENSATE
CHAMBER

DIAGRAM OF APPARATUS

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The temperature of the boiling liquid was obtained with a mercury thermometer inserted in the thermometer well. The temperature was estimated to $0.1^{o}C$. Glycerine was used as the contact liquid in the well. It was attempted earlier to use a thermocouple for this temperature measurement, but the potentiometer available was not sufficiently sensitive.

The solutions prepared for obtaining the necessary vapor-liquid equilibrium data covered the complete acid-water concentration range. These concentrations were approximately 10, 25, 40, 60, 75, and 90% acid (salt-free basis). Anhydrous calcium chloride in successively larger amounts was added to each one of these acid solutions to produce salt mixtures charged to the still residue chamber. The liquid volumes in the residue and condensate chambers during operation were approximately 65 and 15 cc respectively.

The charging of the still consisted of drawing the water-acid-salt mixture into the residue chamber to the level indicated in Figure 4 and then drawing a sample of salt-free acetic acid-water solution of the same relative composition as the material in the residue chamber into the condensate chamber. Since the heat of vaporization during normal operation of the still is supplied in the flash boiler, the purpose of the heating coil on the residue chamber was primarily to compensate for radiation and convection losses. When the still was started up, however, it was also used to bring the liquid up to the boiling point.

Starting up the still is the most critical part of the operation. When condensate begins to collect and feed through to the flash boiler, the stop-cock feeding the flash boiler must be regulated until the boiling action becomes steady. Then the stop-cock may be opened full and the heat on the residue chamber cut back to the operating level. Carelessness at this point of the starting procedure can result in a cracked flash boiler

if excessive liquid is allowed to flow into it.

The still was allowed to operate for a period of three hours before the taking of the equilibrium samples. Preliminary tests with water and acetic acid showed no detectable difference between samples taken after 3 hours' running time and ten hours' running time. Since these tests were made before the capacity of the condensate chamber was approximately halved by the addition of glass beads, there is very little doubt but that equilibrium was reached at the end of three hours' operating time.

The samples were taken by closing the stop-cock feeding the flash boiler and withdrawing the residue and distillate fractions as quickly as possible. After the samples were taken the heat was cut off or left on if another run was to be made immediately following. The process of draining the residue sample when in the concentrated salt range required the use of a Bunsen burner to unfreeze the drain cock before the sample would flow out. The samples were run into stoppered Erlenmeyer flasks and were analyzed the same day or the following.

RESULTS

The first series of runs was made on the system acetic acid-water and the data obtained are presented as weight percent water in the vapor versus weight percent water in the liquid in Figure 5 and in the first part of Table IV. In Figure 5 are also plotted the data of Othmer & Gilmont[11] and those in Perry.[12] The curve obtained in this investigation lies between the other two curves and is very close to that published in Perry.

Experimental data for the system acetic acid-water-calcium chloride appear in Table IV. Smoothed data for this system appear in Table V and are presented in Figure 6 as lines of constant weight percent salt in the liquid phase. These lines were obtained by first drawing the best smooth curve for zero percent calcium chloride, then taking the points at approximately 10% calcium chloride, relocating them to exactly 10% by means of interpolation or extrapolation (with reference to the zero percent calcium chloride line) along a line perpendicular to the 45° line, drawing the best 10% line through these relocated points, relocating the points for the 20% calcium chloride line by linear interpolation from the previously constructed smooth 10% curve, etc. The boiling liquids in runs number 30 and 34 were very nearly saturated with respect to salt. On the strength of this indication it was felt that the lines of constant salt concentration of 40 and 50% should be terminated before reaching the origin. A line termed an "approximate saturation line" has been drawn in Figure 6. The 40 and 50% curves terminate at this line. If data were available on the solubility of calcium chloride in acetic acid at the boiling point, then this approximate saturation line could be located with somewhat greater precision.

It can be seen from Figure 6 that the desired reversal of the volatility of acetic acid-water mixtures is attained with a salt concentration

TABLE IV

SYSTEM ACETIC ACID-WATER-CALCIUM CHLORIDE
VAPOR-LIQUID EQUILIBRIUM AND BOILING POINT DATA
PRESSURE = 760 mm MERCURY

Run #	S	X	Y	T
1A	0.0	91.9	93.9	100.2
2A	0.0	74.5	81.5	100.9
3E	0.0	61.9	71.9	101.3
4A	0.0	44.2	56.5	101.9
5A	0.0	23.6	34.6	104.4
6A	0.0	10.6	17.4	108.0
7	9.3	85.3	83.7	102.0
8	10.1	76.5	73.5	102.4
9	9.7	62.5	59.7	103.2
10	9.4	41.3	39.6	105.0
11	9.6	26.5	25.4	107.6
12	9.5	11.8	11.5	111.6
13	19.7	88.8	79.9	104.2
14	19.3	79.2	65.7	104.8
15	20.0	66.8	49.4	106.2
16	19.8	45.1	30.2	109.0
17	19.0	28.1	18.8	112.0
18A	18.4	15.3	11.0	115.0
19	29.8	93.5	81.5	110.0
20	29.2	83.6	59.7	110.2
21	31.0	79.8	51.3	111.1
22	30.4	48.7	25.0	115.0
23	31.6	32.1	16.0	120.3
25A	37.6	91.0	67.8	115.3
26	40.1	85.0	50.8	116.8
27	35.6	71.7	39.2	114.0
28	39.1	55.1	25.4	118.9
29A	36.8	36.5	16.4	121.6
30	36.2	18.4	7.2	127.2
31	44.7	84.8	47.8	121.2
32	45.1	85.5	48.6	120.9
33	45.8	73.4	33.0	121.9
34	49.5	57.1	20.0	128.0
36	53.4	90.4	51.8	127.9
37	53.2	88.6	47.5	127.5
38	60.3	97.0	65.0	132.3
39	60.5	98.5	80.7	138.9
40	61.0	91.2	50.8	136.0

S = Weight percent calcium chloride in liquid.
X = Weight percent water in liquid (salt-free basis).
Y = Weight percent water in vapor.
T = Temperature, °C.

TABLE V

SYSTEM ACETIC ACID–WATER–CALCIUM CHLORIDE
SMOOTHED VAPOR-LIQUID EQUILIBRIUM AND BOILING POINT DATA
PRESSURE = 760 mm MERCURY

| S	X	Y	T	S	X	Y	T
0.0	5.0	8.5	111.0	30.0	5.0	2.4	
0.0	10.0	16.5	108.2	30.0	10.0	4.9	
0.0	20.0	30.3	105.1	30.0	20.0	10.0	
0.0	30.0	41.8	103.4	30.0	30.0	15.1	119.6
0.0	40.0	52.5	102.3	30.0	40.0	20.6	116.8
0.0	50.0	62.2	101.7	30.0	50.0	26.5	114.5
0.0	60.0	70.7	101.2	30.0	60.0	33.8	112.8
0.0	70.0	78.2	100.8	30.0	70.0	42.6	111.5
0.0	80.0	85.5	100.5	30.0	80.0	53.6	110.6
0.0	90.0	92.8	100.2	30.0	90.0	71.5	110.2
0.0	95.0	96.3	100.0	30.0	95.0	84.5	110.3
10.0	5.0	4.5		40.0	30.0	12.0	125.0
10.0	10.0	9.0	112.8	40.0	40.0	16.5	122.1
10.0	20.0	18.2	109.3	40.0	50.0	21.7	120.0
10.0	30.0	27.6	107.0	40.0	60.0	27.7	118.3
10.0	40.0	37.2	105.4	40.0	70.0	35.0	116.9
10.0	50.0	46.8	104.2	40.0	80.0	44.6	116.3
10.0	60.0	56.8	103.5	40.0	90.0	61.5	117.0
10.0	70.0	67.0	102.8	40.0	95.0	76.5	117.8
10.0	80.0	77.5	102.3	50.0	60.0	21.0	127.5
10.0	90.0	88.2	102.0	50.0	70.0	26.9	125.5
10.0	95.0	93.8	101.8	50.0	80.0	36.5	124.8
20.0	5.0	3.3		50.0	90.0	53.2	125.1
20.0	10.0	6.5		50.0	95.0	69.0	126.2
20.0	20.0	13.0	114.6	60.0	90.0	46.5	134.7
20.0	30.0	19.6	112.1	60.0	92.5	52.0	135.0
20.0	40.0	26.2	110.1	60.0	95.0	59.2	136.5
20.0	50.0	33.7	108.4	60.0	97.0	67.0	138.0
20.0	60.0	42.3	107.0	60.0	99.0	81.0	140.0
20.0	70.0	53.2	105.9				
20.0	80.0	67.0	104.9				
20.0	90.0	81.6	104.4				
20.0	95.0	90.0	104.5				

S = Weight percent calcium chloride in liquid.
X = Weight percent water in liquid (salt-free basis).
Y = Weight percent water in vapor.
T = Temperature, °C.

FIGURE 5

VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM
ACETIC ACID-WATER   PRESSURE 760 mm

FIGURE 6

VAPOR-LIQUID EQUILIBRIUM IN THE SYSTEM ACETIC
ACID-WATER-CALCIUM CHLORIDE   PRESSURE 760 mm
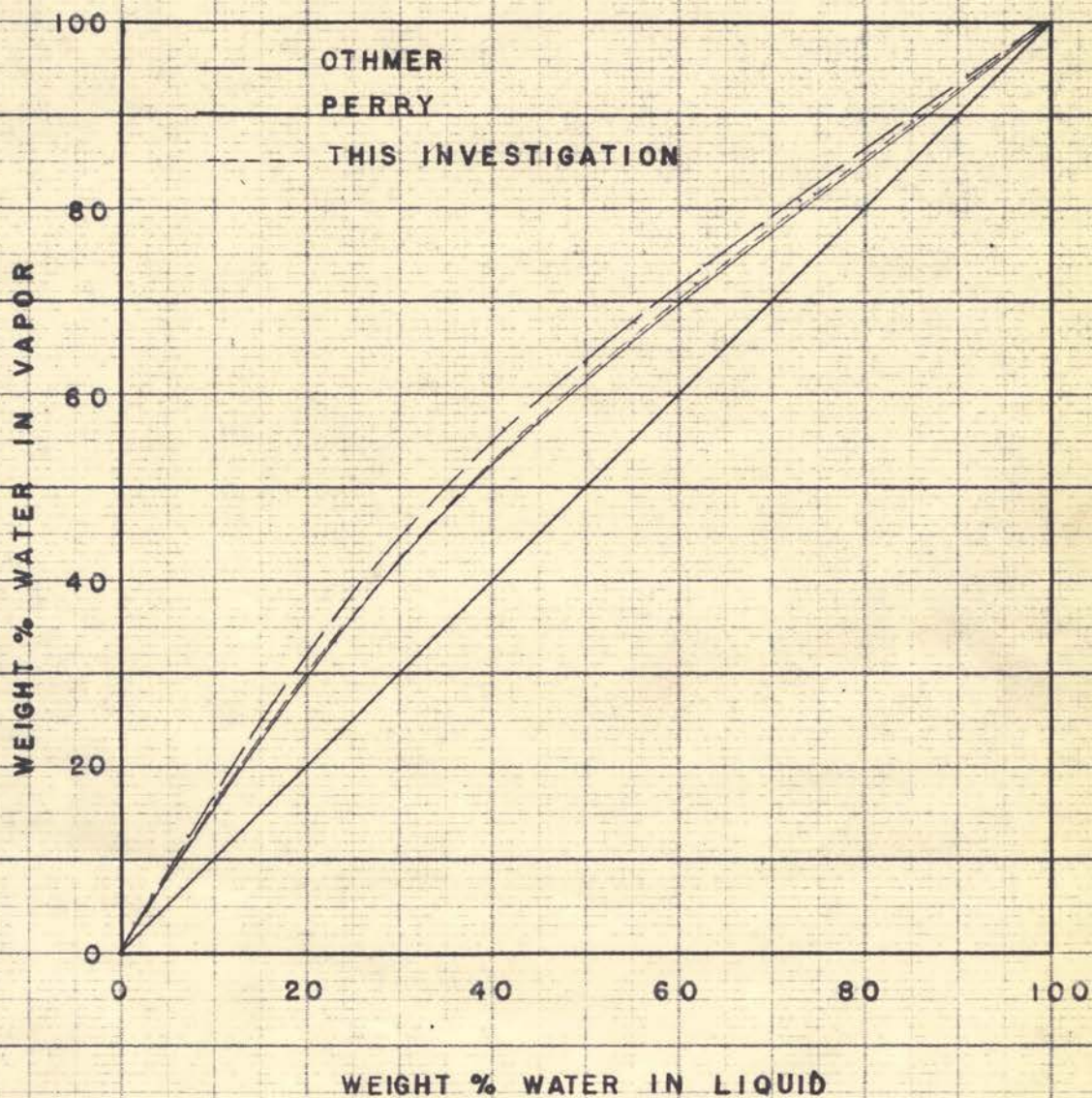
in the liquid phase of approximately 8% calcium chloride and that the effect of salt addition decreases slowly as its concentration level is increased. The curves are quite symmetrical at the lower salt concentrations but show a tendency toward greater volatility reversal at the water-rich ends of the more concentrated salt mixtures. In the region of 60% salt concentration three points were determined and the curve extends only as far as these points allow.

The reliability of the temperature data is indicated by a comparison in Table VI of the boiling points of acetic acid-water mixtures at even percentages in the liquid phase with the data of Othmer & Gilmont[11] and those in Perry.[12]

TABLE VI

SYSTEM ACETIC ACID-WATER
BOILING POINT VERSUS CONCENTRATION
PRESSURE = 760 mm

	T		
X	Othmer & Gilmont	Perry	This Investigation
0	118.0	118.1	
10	108.6	108.2	108.2
20	105.1	105.1	105.1
30	103.4	103.4	103.4
40	102.3	102.3	102.3
50	101.6	101.6	101.7
60	101.1	101.1	101.2
70	100.7	100.7	100.8
80	100.4	100.4	100.5
90	100.2	100.2	100.2
100	100.0	100.0	100.0

X = Weight percent water in liquid.
T = Temperature, $^{\circ}C$.

Boiling point curves, based on the data of Table IV, and smoothed by the linear interpolation method described above, are plotted in Figure 7.

The curves in Figure 7 represent constant percentages of salt with the boiling point plotted as a function of the weight percent water on a salt-free basis. The solid line portions of the curves indicate the extent of the actual data while the dashed line portions at the high water concentrations are extrapolations to the known boiling points of water-calcium chloride mixtures (Table III). Data are not available on the boiling points of acetic acid-calcium chloride mixtures. Hence, extrapolation in the other direction was not possible. Also, for the same reason, a saturation curve terminating the lines of constant percent calcium chloride between values of pure acetic acid and pure water could not be drawn.

The boiling point curves show a tendency to reach a minimum at 80 to 90% water on a salt-free basis except for the 0 and 10% calcium chloride curves.

A comparison might be made of the K values for dilute aqueous solutions of acetic acid calculated from the work of McBain & Kam, and Quartaroli, and that obtained in this investigation. These values are 0.67, 0.57, and 0.70, respectively. The McBain & Kam and Quartaroli values are thus approximately 5 and 20% below that found in the present work. For a calcium chloride concentration of about 22% in the liquid phase, there is obtained, from the data of Quartaroli, a value of K of approximately 1.45 (Figure 1). This is about 25% below the value of approximately 2.0 found in this investigation for the same concentration region (Figure 6).

A proposed process for separating water and acetic acid by distillation in the presence of calcium chloride is illustrated in Figure 8. The water-calcium chloride stream coming from the bottom of the fractionating column would be fed to a multiple-effect evaporator for concentration to approximately 60 to 70 weight percent calcium chloride. Part of this concentrated liquid would be fed to a spray dryer to produce anhydrous calcium

FIGURE 7

BOILING POINTS AT 760mm OF ACETIC ACID—WATER—CALCIUM CHLORIDE MIXTURES

LINES OF CONSTANT WT (%) CALCIUM CHLORIDE
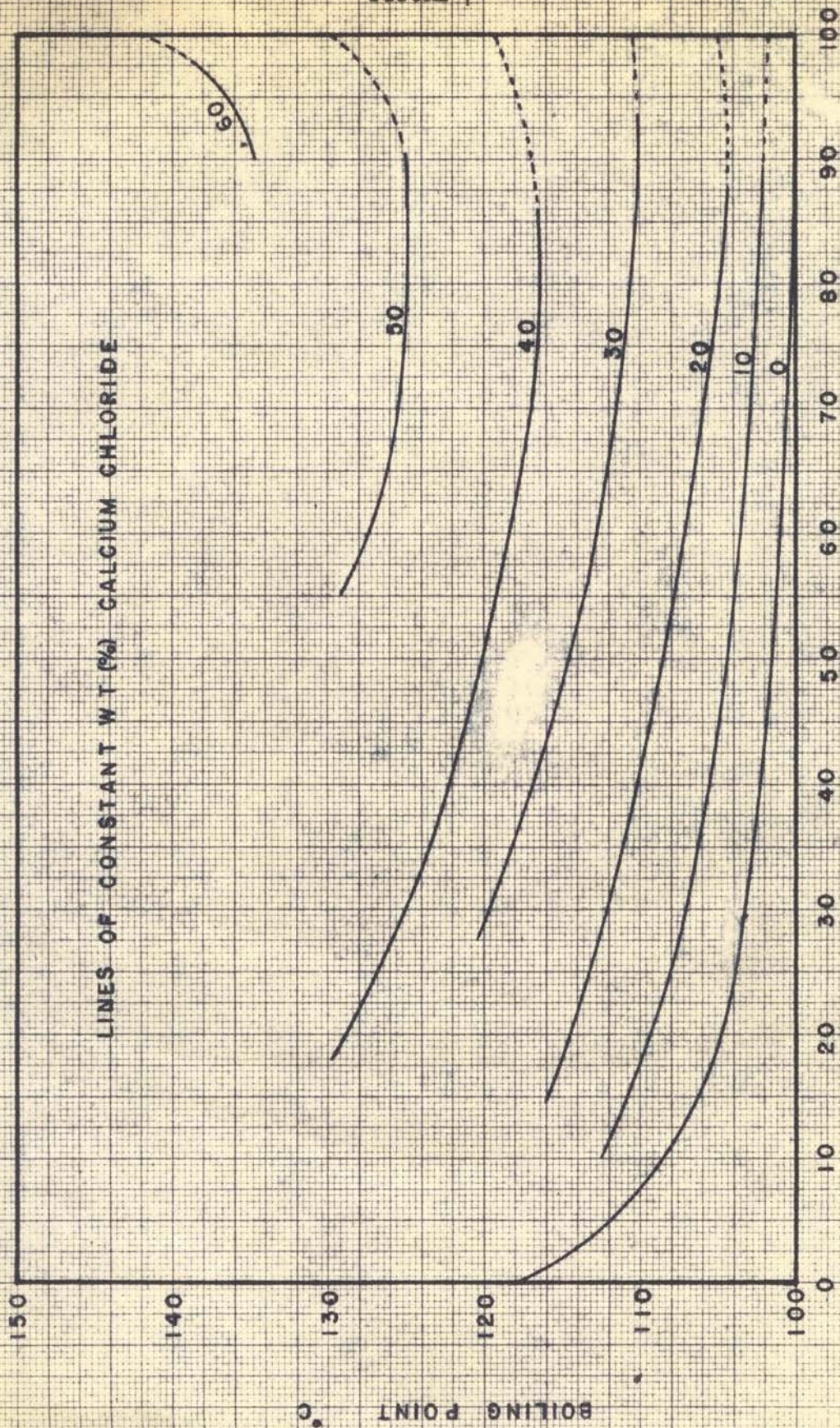
WEIGHT (%) WATER (SALT—FREE BASIS)

BOILING POINT °C

chloride. This would be dissolved to the extent of approximately 30% in the acetic acid reflux returning to the column. The rest of the concentrated salt solution could be introduced directly with the feed. Thus the calcium chloride would be continuously recycled, water would be continuously rejected from the evaporator and the spray dryer, and pure acetic acid would be continuously obtained as the distillation column overhead product. No deposits of salt would be expected in the column since the solubility of calcium chloride increases with the water content of the acid.

The materials of construction suitable for handling both acetic acid and calcium chloride in the towers and heat exchange equipment are stoneware, Karbate, and steel lined with Hastelloy B or C, tantalum, silver, or glass. The distillation towers might well be of the packed variety, with stoneware or carbon packing. Aluminum is commonly used for concentrated acid storage tanks.
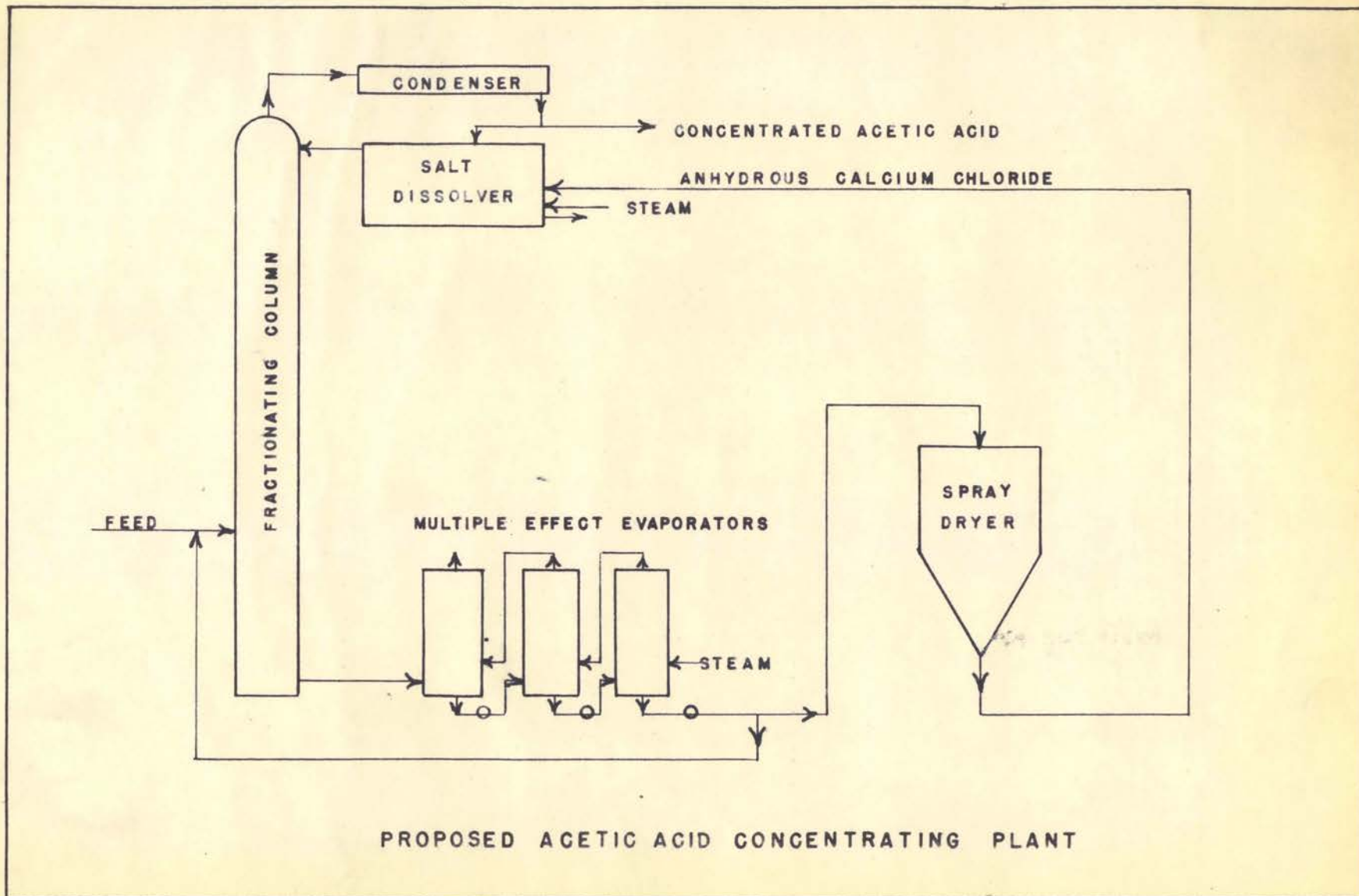
PROPOSED ACETIC ACID CONCENTRATING PLANT

FIGURE 8

26

CONCLUSIONS

From the data obtained in this investigation it may be concluded that:

1. Calcium chloride reverses the relative volatility of acetic acid-water mixtures. This reversal takes place at approximately 8% calcium chloride in the liquid phase.

2. It appears likely that the separation of acetic acid and water (with the acetic acid as overhead product) can take place readily in a column of a small number of theoretical plates, with decreased heat requirements, through the use of calcium chloride dissolved in the liquid phase. Because the calcium chloride so employed must be recycled, its recovery from the aqueous bottoms stream must be considered in the overall economics of the proposed process. A simplified flow sheet incorporating the recycling feature has been presented.

For further work it is recommended that:

1. The boiling point curves for acetic acid-water-salt mixtures in the high acetic acid range be obtained. This would complete the boiling point curves obtained in the investigation.

2. An experimental fractionating column be operated on a laboratory scale to confirm the practical value of acetic acid concentration by the use of calcium chloride.

3. A detailed economic study be made to compare the cost of separating acetic acid from water by the proposed process with the cost of existing commercial methods.

BIBLIOGRAPHY

1. Davidson, A. W., J. Am. Chem. Soc., 50, 1890-5 (1928).

2. Davidson, A. W., Chappell, W., J. Am. Chem. Soc., 60, 2043-6 (1938).

3. Davidson, A. W., Geer, H. A., J. Am. Chem. Soc., 55, 642-9 (1933).

4. Handbook of Chemistry and Physics, Chemical Rubber Publishing Co. 26th Edition, p. 1454 (1942).

5. International Critical Tables, Vol III, McGraw-Hill Book Company Inc., p. 325 (1928).

6. Jones, C. A., Schoenborn, E. M. & Colburn, A. P., Ind. Eng. Chem., 35, 666-72 (1943).

7. Larson, E., Svensk Kem. Tid., 41, 130-41 (1929).

8. Mayor, Y., Rev. Prod. Chim. 38, 260-4 (1935).

9. McBain, J. W. & Kam, J., J. Chem. Soc., 115, 1332-46 (1919).

10. Menschutkin, B. N., Z. anorg. Chem. 54, 89 (1907).

11. Othmer, D. F. & Gilmont, R., Ind. Eng. Chem., 36, 1061-4 (1944).

12. Perry, J. H., Chemical Engineers Handbook, McGraw-Hill Book Company Inc., 2nd Edition, p. 1360 (1941).

13. Quartaroli, A., Ann. Chimi. Applicata, 33, 141-6 (1943).

14. Seidell, A., Solubilities of Inorganic & Metal Organic Compounds, D Van Nostrand Company Inc., Vol I, 3rd Edition, p. 280 (1940).

15. Ibid., p. 928.

APPENDIX

Section I

Sample Calculation for Table I

$$N_1 = 0.077$$
$$N_s(NaCl) = 2.30$$
$$R = 1.076$$

Distillate Composition

$$N_v = 0.077 \times 1.076 = 0.0829$$
$$0.0829 \times 60 = 4.98 \text{ grams acid/liter solution}$$
$$Y = 4.98 \times \frac{100}{1000} = 0.498 \text{ (approximation)}$$

Residue Composition

Salt: $2.3 \times 58.4 = 134.4$ grams salt/liter solution
sp. gr. of sol'n (assuming water and salt only)
$= 1.088$ (approximately)
(Ref. 4, p. 1528)

$$W_s = \frac{134.4}{1.088} \times \frac{100}{1000} = 12.4$$

Acid: $0.077 \times 60 = 4.62$ grams acid/liter solution

$$\frac{4.62}{1.088} \times \frac{100}{1000} = 0.425 \text{ weight } \% \text{ acid}$$

$$X = 0.425 \times \frac{100}{87.6} = 0.485$$

Therefore $K = Y/X = 1.028$

Section II

Sample Calculation for Table II

Charged: 100 cc of 0.1 N acetic acid + 10 g sodium chloride

$$100 \text{ cc } 0.1 \text{ N acid} = 0.1 \times 60 \times \frac{100}{1000} = 0.60 \text{ g acid}$$

Therefore water $= 99.4$ g (by difference) (approximately)

Information Available:
100 cc 0.1 N acid plus 10 g NaCl at start
50% of the volume distilled off
51.8 wt.% of total acid in the distillate

Charge:

$$W_{s-i} = \frac{10}{110} \times 100 = 9.09 \text{ (approximation)}$$

$$X_i = 0.6$$

Distillate:

50 cc = 50 g (approximately)
0.518 x 0.6 = 0.311 g acid

$$Y = \frac{0.311}{50} \times 100 = 0.622$$

Residue:

Weight = 110 - 50 = 60 g

Contains: 10 g salt
             0.60 - 0.311 = 0.289 g acid
             49.7 g water (by difference)

$$W_{s-f} = \frac{10}{60} \times 100 = 16.7$$

$$X_f = \frac{0.289}{50} \times 100 = 0.578$$

Substituting in the Rayleigh equation and assuming that Henry's Law holds ($Y = KX$),

$$\ln \frac{W_i}{W_f} = \int_{X_f}^{X_i} \frac{dX}{Y - X} \quad ; \quad \ln \frac{W_i}{W_f} = \frac{1}{K - 1} \ln \frac{X_i}{X_f}$$

$$K - 1 = \frac{\ln X_i/X_f}{\ln W_i/W_f} \quad ; \quad K = 1 + \frac{\ln 0.6/0.578}{\ln 2/1}$$

$$K = \frac{0.0038}{0.694} + 1 = 1.005$$

$$W_s(ave) = \frac{W_{s-i} + W_{s-f}}{2} = 12.90$$

$$X(ave) = \frac{X_i + X_f}{2} = 0.589$$

W = grams of salt-free mixture
Subscript i = before differential distillation
Subscript f = after differential distillation

Typist: Harold A. Coonrad