

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Study of the Vapor of Propionic Acid at 45, 50, 55, 60 and 65°

By F. H. MACDOUGALL¹

Introduction

In a previous publication² the author reported measurements of the density of acetic acid vapor at temperatures ranging from 25 to 40° and at pressures from 3 to 20 mm. From these data it was possible to determine the equilibrium between the mono- and di-meric forms of acetic acid in the gas phase and to calculate the heat of dissociation of the dimer into the monomer. The results obtained have been used in a study of association due to the formation of hydrogen bonds.³ It seemed to be worth while to extend the measurements of vapor density to propionic acid.

The Preparation of Propionic Acid

The purification of propionic acid was effected by using a modification of the technique suggested by Hess and Haber⁴ in the treatment of acetic acid. About 1.5 liters of mother liquors from previous attempts at purifying Eastman Kodak Co. purest available propionic acid was treated with 3 g. of phosphorus pentoxide and shaken for one hour. The decanted liquid was distilled in a Claisson flask. The distillate was then fractionally distilled in a long-column still. The column was 100 cm. long and 10 mm. in diameter and was filled with pieces of glass tubing. It was equipped with a dephlegmator to provide good refluxing over the glass tubing. Five fractions were taken throughout the distillation range and the low fractions were redistilled until about 500 ml. was obtained of an acid boiling within 0.2° of 140.7°. This liquid was transferred by suction to an enclosed freezing vessel and was frozen by means of a dry-ice-acetone bath.

The freezing vessel consisted of a liter balloon flask fitted with two drying tubes in series, the tube nearest the flask containing magnesium perchlorate, the second one containing calcium chloride. The opening through which the mother liquor was forced after 90% of the liquid had solidified, was provided by a 6-mm. glass tube through which a smaller tube was inserted for carrying off the liquid. After removal of the liquid, the solid was melted and the freezing process repeated until six freezes and pump-offs had been made. The liquid obtained by melting the final freeze was transferred to the vacuum distillation system described in a previous paper² and was subjected to alternate condensation and sublimation until the residual pressure after a

sublimation was 5×10^{-4} mm. About half of the sample was transferred to the receiver and sealed off from the distillation system so that it could be connected with the vapor density apparatus by breaking a break-off joint.

Distillation System and Vapor Density Apparatus.—The apparatus used was essentially the same as that described in a previous paper.² Because of the higher temperatures at which the experiments with propionic acid were carried out, larger heating lamps were installed and the water of the water-bath was covered with a layer of mineral oil. In addition, all tubing leading from the reservoir to the water-bath was wrapped with nichrome wire so that the tubing could be heated to a suitable temperature.

Calibration of Bulbs and Determination of the Manometer Factor.—The volumes of the bulbs were determined using pure nitrogen as described in the previous paper.² Similarly the manometer factor, f , was redetermined, by the method previously described, for a temperature of 30° and was found to be 1.092. For other temperatures, we have $f^t_0 = 1.092(\rho_t/\rho_{30})$ where ρ_t is the density of mercury at t° . The factor f is used in converting the observed rise R of mercury in the manometer into the pressure p in the system expressed in terms of mm. of mercury at 0°C. Thus $p = Rf^t_0$.

Standardization of Barium Hydroxide.—A known weight of constant-boiling hydrochloric acid was diluted with a known weight of conductivity water free from carbon dioxide to give an acid containing 0.09702 equiv. per kilogram of solution. Four samples of this were titrated with barium hydroxide to a pH of 7.0 using phenol red as indicator. The barium hydroxide solution was found to contain 0.01049, 0.01048, 0.01046 and 0.01046 equiv. per kilogram of solution.

As a check on the purity of the propionic acid to be used in the experiments, 1.2077 g. of the best fraction was diluted to 125.71 g. with conductivity water free from carbon dioxide. Three samples of this acid were titrated with the barium hydroxide solution with *m*-cresolsulfonephthalein as indicator until a match was obtained with a buffered solution of pH equal to 8.2. The barium hydroxide solution was found in this way to contain 0.01045, 0.01045 and 0.01043 equiv. per kilogram.

Calibration of Thermometers.—The thermometers (FL 221 and Cenco 3504162) used were compared with Bureau of Standards thermometers 40316 and 40317. The FL 221 thermometer was found to require a correction of -0.09° at 45° and of -0.02° at 50°, while the Cenco thermometer required corrections of -0.01 , -0.02 and -0.05° at 55, 60 and 65°, respectively.

Experimental Data

In the following tables, R is the measured rise in the manometer, p is the pressure in mm., V is the volume in ml. of the bulb or bulbs containing the propionic acid vapor, g is the weight in grams of

(1) This research was made possible by grants from the Research Fund of the Graduate School of the University of Minnesota. The author takes this opportunity of expressing his appreciation of this financial assistance. The experimental work described in this paper was carried out by Mr. S. J. Jacobs.

(2) MacDougall, *THIS JOURNAL*, **58**, 2585 (1936).

(3) See for example, Edwin N. Lassette, *Chem. Rev.*, **20**, 262 (1937); G. B. M. Sutherland, *Trans. Faraday Soc.*, **36**, 891 (1940); Fox and Martin, *ibid.*, **36**, 898 (1940).

(4) Kurt Hess and Heinz Haber, *Ber.*, **70B**, 2205 (1937).

the barium hydroxide solution (0.01046 equivalent per kilogram of solution) required to neutralize the sample of propionic acid and $(pV)_M$ is

Run	<i>t</i> , °C.	R	<i>p</i>	V	g	$2(pV)_M$
XI	49.98	13.395	14.574	645.5	78.46	1.346
		8.046	8.754	1187		1.487
		4.436	4.827	2307		1.593
XXXV	59.98	14.859	16.137	645.8	74.83	1.560
		8.669	9.414	1187		1.672
		4.803	5.216	2307		1.801

Run	<i>p</i>	$2(pV)_M$	Run	<i>p</i>	$2(pV)_M$
XI	14.57	1.346	XVII	12.80	1.396
	8.75	1.487		7.51	1.507
	4.83	1.593		4.14	1.616
XII	12.31	1.407	XVIII	11.72	1.413
	7.22	1.502		6.81	1.511
	4.00	1.636		3.77	1.627
XIII	9.30	1.464	XIX	11.36	1.420
	5.43	1.575		6.62	1.523
	2.99	1.687		3.66	1.635
XIV	13.17	1.375	XX	9.03	1.472
	7.81	1.498		5.24	1.571
	4.31	1.610		2.90	1.690
XV	13.66	1.382	XXXI	6.37	1.556
	8.07	1.499		3.70	1.666
	4.46	1.612		2.02	1.770
XVI	11.39	1.428	XXXII	10.25	1.458
	6.64	1.532		5.97	1.563
	3.66	1.643		3.28	1.670

Run	<i>p</i>	$2(pV)_M$	Run	<i>p</i>	$2(pV)_M$
XXI	14.54	1.484	XXXIV	15.47	1.475
	8.50	1.595		9.03	1.584
	4.90	1.716		4.98	1.696
XXII	16.61	1.452	XLV	15.61	1.663
	9.71	1.561		9.12	1.787
	5.37	1.677		5.07	1.928
XXIII	18.45	1.422	XLVI	17.46	1.647
	10.89	1.542		10.21	1.769
	6.01	1.655		5.65	1.903
XXIV	13.06	1.499	XLVII	14.11	1.683
	7.62	1.607		8.24	1.808
	4.21	1.727		4.56	1.942
XXV	11.26	1.533	XLVIII	19.58	1.618
	6.57	1.645		11.44	1.735
	3.63	1.769		6.33	1.867
XXVI	9.19	1.570	XLIX	12.05	1.727
	5.44	1.712		7.05	1.858
	2.98	1.820		3.90	2.001
XXXIII	6.27	1.657	L	16.38	1.655
	3.66	1.780		9.56	1.776
	2.01	1.899		5.30	1.911

Run	<i>p</i>	$2(pV)_M$	Run	<i>p</i>	$2(pV)_M$
XXXV	16.14	1.560	XL	14.12	1.589
	9.41	1.672		8.25	1.707
	5.22	1.801		4.56	1.835
XXXVI	14.20	1.587	XLI	11.65	1.624
	8.29	1.704		6.78	1.738
	4.59	1.833		3.78	1.883
XXXVII	11.29	1.645	XLII	8.97	1.684
	6.59	1.766		5.23	1.806
	3.64	1.894		2.88	1.937
XXXVIII	17.70	1.550	XLIII	12.79	1.615
	10.35	1.666		7.48	1.737
	5.74	1.794		4.17	1.882
XXXIX	18.91	1.534	XLIV	7.77	1.719
	11.07	1.648		4.55	1.852
	6.12	1.773		2.51	1.983

the pressure-volume product for 74.05 g. of the acid, divided by 760 mm. × 22.414 ml. If we assume that the acid in the vapor phase occurs only as monomer and dimer, and if α is the corresponding degree of dissociation of the dimer, then

$$2(pV)_M = (1 + \alpha)T/273.18 \quad (1)$$

In Table I are given complete data for two runs, one at 50° and the second at 60°. In the presentation of the remainder of the experimental results, we give the number of the run, the temperature, the pressure and the value of $2(pV)_M$.

In Fig. 1 are plotted the experimental values of $2(pV)_M$ against *p* for each of the five temperatures 45, 50, 55, 60 and 65°. Those for 45° are pretty well scattered. They were obtained while the experimenter was getting acquainted with the apparatus and developing his technique. The values for 50, 55, 60 and 65° seem much more satisfactory. From curves drawn on a large scale

TABLE V
VALUES OF $2(pV)_M$ OBTAINED FROM GRAPHS AND OF K'_2 CALCULATED THEREFROM

<i>p</i>	50°		55°		60°		65°	
	$2(pV)_M$	K'_2	$2(pV)_M$	K'_2	$2(pV)_M$	K'_2	$2(pV)_M$	K'_2
3	1.687	0.376	1.816	0.235	1.938	0.157		
4	1.627	.381	1.751	.236	1.876	.153	1.985	0.109
5	1.585	.383	1.700	.240	1.820	.156	1.926	.112
6	1.552	.387	1.658	.247	1.775	.159	1.885	.111
7	1.521	.402	1.626	.250	1.741	.160	1.853	.109
8	1.495	.408	1.601	.251	1.712	.160	1.823	.108
9	1.473	.434	1.578	.255	1.685	.163	1.795	.109
10	1.450	.466	1.558	.259	1.662	.165	1.769	.111
11	1.429	.503	1.538	.267	1.642	.167	1.747	.111
12	1.408	.555	1.520	.275	1.624	.169	1.724	.114
13	1.387	.627	1.503	.286	1.607	.171	1.704	.116
14	1.366	.728	1.488	.296	1.593	.173	1.688	.117
15	1.344	.883	1.472	.312	1.578	.176	1.673	.118
16			1.458	.327	1.566	.178	1.658	.120
17			1.444	.346	1.554	.181	1.647	.120
18			1.432	.377	1.544	.182	1.635	.121
19					1.535	.183	1.625	.121

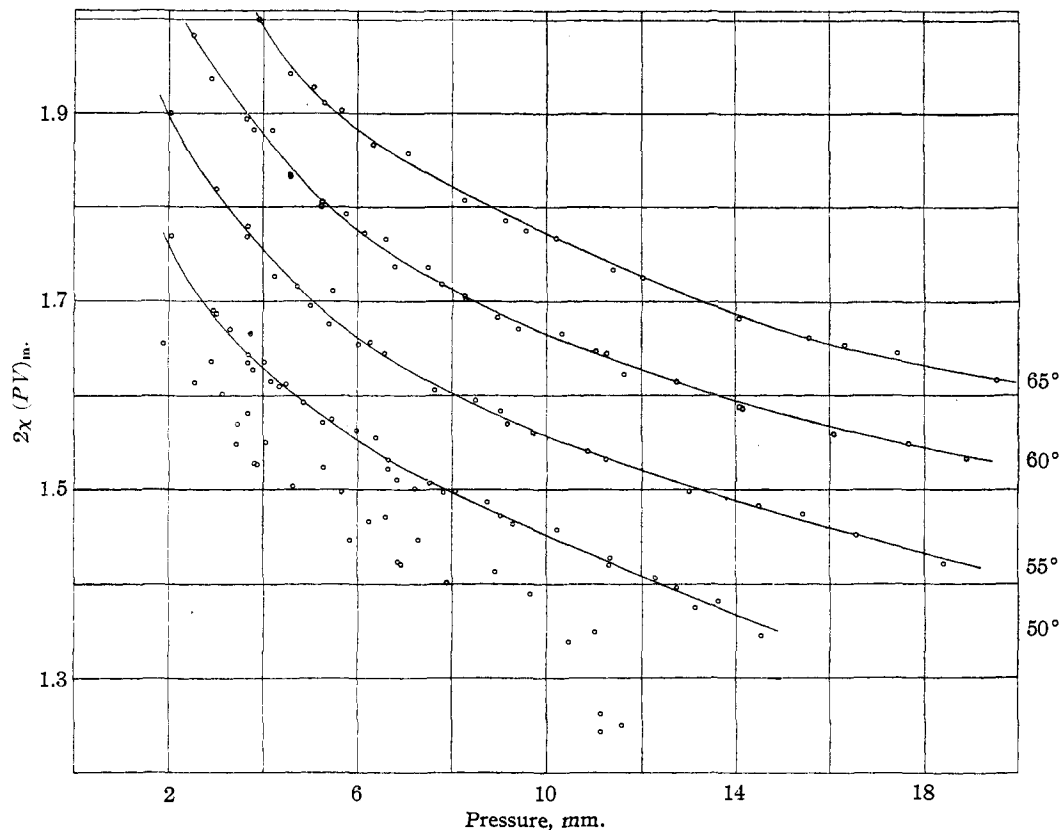


Fig. 1.—Isothermals of vapor of propionic acid.

plot, we have read off the "best" values of $2(pV)_M$ for integral values of the pressure. These values are given in Table V together with the corresponding values of K'_2 , calculated by means of equation (6) (see below).

Equilibrium among Polymers

Let A_1 be the formula for unassociated propionic acid and let A_n represent a polymer whose molecular weight is n times that of A_1 . For the equilibrium



we have

$$K_n = p_n/p_1^n, \quad (3)$$

where p_n is the partial pressure of A_n . Let p be the total pressure of a given sample of propionic acid vapor for a given temperature T and a given volume V and let p_0 be the pressure which the same mass of vapor would exert at the same temperature and volume if the vapor consisted exclusively of the monomer, A_1 . Then it follows from equation (3) that we have

$$p = p_1 + K_2 p_1^2 + K_3 p_1^3 + \dots \quad (4)$$

$$p_0 = p_1 + 2K_2 p_1^2 + 3K_3 p_1^3 \dots \quad (5)$$

Let K'_2 be the "equilibrium constant" calculated for equation (2) with n equal to 2, on the assumption that only A_1 and A_2 exist in the gas phase. This is equivalent to assuming that K_3, K_4 , etc., are equal to zero. We readily find

$$K' = \frac{p_0 - p}{(2p - p_0)^2} \quad (6)$$

(It may be noted that K'_2 is the reciprocal of the dissociation constant K_p , used in the previous paper on acetic acid vapor.)

On using our experimental data to compute the quantity K'_2 as expressed by the simple equation 6, we found it to increase systematically with increasing p but less rapidly at the higher temperatures. This is also clear from Fig. 2. It can be shown readily that this result is to be expected if appreciable amounts of the polymers A_3, A_4 , etc., occur, that is, if the equilibrium constants K_3, K_4 , etc., are not negligibly small. Again, if the heat of the reaction (2) increases numerically with n (as we can reasonably expect it to do), it follows thermodynamically that K_3 , for example, will decrease more rapidly with rising temperature than will K_2 and hence that K'_2 of equation (6) will be-

come less and less dependent on the pressure p , the higher the temperature of the experiment.

Using equation (4) we can express p_1 as a power series in p . We find

$$p_1 = p - K_2 p^2 + (2K_2^2 - K_3) p^3 - (5K_2^3 + 5K_2 K_3 - K_4) p^4 + \dots$$

Similarly p_0 , $p_0 - p$ and $2p - p_0$ can be expressed as power series in p . We finally obtain for K'_2 of equation (6)

$$K' = K_2 + 2K_3 p + 5(K_4 - 2K_2 K_3) p^2 + \dots \quad (7)$$

an equation which confirms the statements of the preceding paragraph.

The Equilibrium Constant K_2

If our assumption is correct that the variation of K'_2 with the pressure is due to the occurrence of higher polymers, then K_2 can be found by extrapolating K'_2 to zero pressure. A study of Fig. 2 leads to the conclusion that the accuracy of extrapolation will be greatest for 65° and 60°, less for 55° and still less for 50°. The error in the value of K_2 found by extrapolation ranges probably from 2% at 65° to around 10% at 50°. We find these results

$$\begin{aligned} \text{For } t = 64.95^\circ, K_2 &= 0.105 \text{ (mm. Hg.)}^{-1} \\ \text{For } t = 59.98^\circ, K_2 &= 0.15 \end{aligned}$$

The Equilibrium Constants K_2 and K_3

In view of equation 7, it seemed natural to attempt to fit an equation of the form $K'_2 = a + bp + cp^2 + \dots$ to the experimental data, using the method of least squares. In addition, an equation of the form $K'p = ap + bp^2 + cp^3 + \dots$ also was used. In these equations, the physical interpretation of the constants would be: $a = K_2$, $b = 2K_3$, etc. It may be stated immediately that in all cases, except for the data at 60°, one result of employing an equation with the three constants a , b and c , was to lead to a negative value of b . The following procedures were therefore adopted.

For the data at 65°, it is clearly seen from Table V or Fig. 2 that in the range $p = 4$ to $p = 8$ the values of K'_2 are fairly constant. In fact, the best straight line for this range has a slight *negative* slope. It seemed best therefore to fit equations

of the form $K'_2 = a + bp$ (and $K'_2 p = ap + bp^2$) to the data at 65° in the range $p = 8$ to $p = 19$.

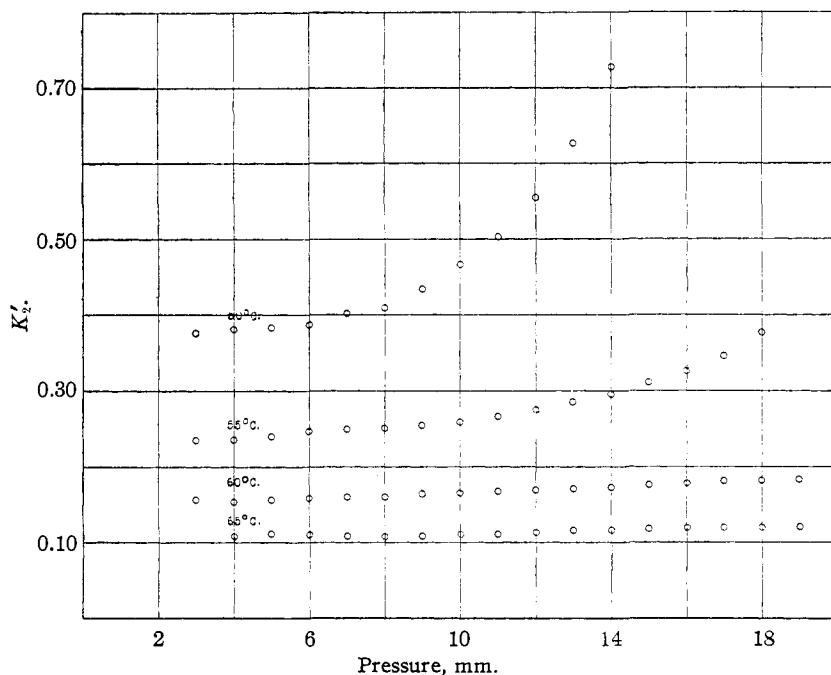


Fig. 2.—The "equilibrium constant" K'_2 .

Both equations gave $a = 0.0983$ and $b = 0.00128$.

Applied to the data at 60°, the equations $K'_2 = a + bp$ and $K_2 p = ap + bp^2$ gave $a = 0.1452$, $b = 0.00202$ and $a = 0.1447$ and $b = 0.00206$, respectively. Similarly for the data at 55°, the two equations were applied in the range $p = 4$ to $p = 10$, giving $a = 0.2229$, $b = 0.00361$ and $a = 0.2217$, $b = 0.00350$, respectively. At 50°, satisfactory results can only be obtained by restriction to the range $p = 3$ to $p = 8$. For the two equations were found $a = 0.3537$, $b = 0.00646$ and $a = 0.3510$ and $b = 0.00690$, respectively. We give in Table VI a summary of the results.

$t, ^\circ\text{C.}$	$K_2 \text{ (mm. Hg.)}^{-1}$	$K_3 \text{ (mm. Hg.)}^{-2}$
64.95	0.0983	0.00064
59.98	.1450	.00102
54.99	.2223	.00178
49.98	.3524	.00333

If ΔH_2 and ΔH_3 are, respectively, the quantities of heat absorbed in the formation from the monomer of one mole of the dimer and one mole of the trimer, we find, by applying the Clausius-Clapeyron equation to the data of Table VI, these results

60-65°, $\Delta H_2 = -17,500$;	$\Delta H_3 = -21,000$ cal.
55-60°, $\Delta H_2 = -18,560$;	$\Delta H_3 = -24,200$ cal.
50-55°, $\Delta H_2 = -19,370$;	$\Delta H_3 = -26,300$ cal.
50-65°, $\Delta H_2 = -18,500$;	$\Delta H_3 = -23,900$ cal.

The ΔH_2 values probably are uncertain to the extent of 2000 calories; the ΔH_3 values are still more uncertain. If we assume that in the dissociation of the dimer and of the trimer to form the monomer two and three hydrogen bonds, respectively, must be broken, we may infer from the magnitude of the ΔH_2 and ΔH_3 values that the "strength" of a hydrogen bond in the vapor of propionic acid is about 9 ± 1 kcal.

Summary

1. We have determined values of pV for the

vapor of propionic acid at 50, 55, 60 and 65° and at pressures ranging from 3 to 20 mm.

2. Under the conditions of the experiments the vapor is associated to a considerable degree. There are indications that not only the dimer but also higher polymers occur.

3. The equilibrium constants for the reactions $2A_1 = A_2$ and $3A_1 = A_3$ have been determined. From the calculated heats of association, we find the "strength" of a hydrogen bond in this case to be 9 ± 1 kcal.

MINNEAPOLIS, MINNESOTA

RECEIVED JULY 14, 1941

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Equilibrium Diagram of the System Carbon Tetrachloride-*t*-Butyl Chloride as Revealed by Dielectric Constant Measurements

BY W. P. CONNER AND C. P. SMYTH

It was thought to be of interest to investigate the effect of changing environment upon the rotation of molecules in a crystal. With this end in view, a continuous series of solid solutions was sought in which the molecules of at least one component would rotate. The rather symmetrically-shaped molecules of *t*-butyl chloride had been found to rotate over a considerable range of temperature in the crystal and their possession of a dipole moment made dielectric constant measurements a suitable method of observing the freedom of molecular rotation.¹ The similarity of molecular shape and size of the *t*-butyl chloride and carbon tetrachloride molecules and their isotropic lattices in the region just below the freezing point made it seem probable that these two substances would form a series of solid solutions. This was confirmed by the freezing point measurements of Mr. J. V. D. Hoffman, carried out in this Laboratory,² which showed that the two substances formed a continuous series of solid solutions from pure carbon tetrachloride on the one hand to pure *t*-butyl chloride on the other. The temperature-time cooling curves run in this investigation also showed the expected lowering of the rotational transition of each substance by the presence of the other. These curves represented a tentative step toward the establishment of an equilibrium diagram for the system, and showed the system to be suitable for the investigation of the effect of the

presence of the carbon tetrachloride molecules upon the rotation of the *t*-butyl chloride molecules.

Experimental Measurements

The carbon tetrachloride and *t*-butyl chloride were carefully purified in the usual way.³ The dielectric constant measurements were made upon the mixtures with a capacity bridge coupled to a variable oscillator in the general fashion previously described.^{1,3} The rate of change of temperature with time was normally less than 5° an hour. The dielectric constants and specific conductances of the mixtures were measured at frequencies of 50, 5 and 0.5 kilocycles, but, as the conductances in the solid state were of the order of 10^{-10} mhos, and as any anomalous dispersion was negligibly small, the conductances are not reproduced here and the dielectric constant data used are those obtained at 50 kc. In order to save space, the numerical values of the results are not reproduced, but the dielectric constants of the different mixtures are plotted against temperature in Fig. 1, the individual points being too numerous to indicate. Each curve in Fig. 1 is marked with the molar percentage of *t*-butyl chloride in the mixture which it represents, and the curves obtained with falling temperature are given in the upper half of the diagram marked (I). The curves for the same mixtures obtained with rising temperature are in the lower half marked (II). The temperatures of the breaks in the curves are plotted against composition in Fig. 2 to obtain an equilibrium diagram. A few points in Fig. 2 are obtained from curves which have been omitted from Fig. 1 to prevent overcrowding.

Discussion of Results

In considering the behavior of the dielectric constants of these mixtures, it must be borne in

(1) Baker and Smyth, *THIS JOURNAL*, **61**, 2798 (1939).

(2) Turkevich and Smyth, *ibid.*, **62**, 2468 (1940).

(3) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).