

**428.** *The Ionization of Acetic, Propionic, n-Butyric, and Benzoic Acid in Water, from Conductance Measurements up to 225°.*

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The results reported are from conductance measurements up to 225° with dilute electrolyte solutions in a platinum-Teflon cell. Acid dissociation constants for acetic, propionic, n-butyric, and benzoic acid have been derived. Between 25° and 225° values of  $K_a$  for the weak acids decrease by approximately a power of ten, and above 100° the results fit a simple linear plot of  $\log K_a$  against  $1/DT$  which allows reliable extrapolation to higher temperatures. Above about 100° the decreases in ionization reflect mainly the changes in the electrical contribution to the free-energy of ionization, caused by the rapid decrease in the dielectric constant of water.

The present conductance results for potassium chloride, hydrogen chloride, and acetic acid solutions are in good agreement with work by Noyes some fifty years ago. Within about  $\pm 1\%$  the conductance results at 225° for potassium chloride and hydrogen chloride fit the Onsager equation for concentrations up to about 0.005m.

IN the study of natural hydrothermal chemical processes in volcanic areas it is often important to be able to predict the dissociation constants of weak acids and bases in water solutions above 100°. There is at present little quantitative information on the behaviour of aqueous weak electrolyte systems at elevated temperatures. The present work is an introductory study in which the changes in the dissociation of four simple organic acids with temperature have been compared by means of conductance measurements up to 225° on dilute solutions of potassium chloride, hydrochloric acid, and the weak acids and their potassium salts.

The early publication by Noyes and his co-workers<sup>1</sup> gave results for the electrical conductance of many common electrolyte solutions, and dissociation constants were derived for acetic and sulphuric acid and for ammonia solutions at temperatures up to 306°. Noyes's results were published before the modern theories of electrolytes were developed and consequently the methods of interpretation need modification. Their measurements, made with a pressure vessel in which the solutions were in contact only

<sup>1</sup> Noyes, "The Electrical Conductivity of Aqueous Solutions," Publication No. 63, Carnegie Institute of Washington, 1907.

with platinum and quartz, are believed to be of high precision and provide a useful comparison for part of the present work. Symon,<sup>2</sup> and recently Whitehead,<sup>3</sup> gave more limited information on the conductance of sodium chloride, sulphuric acid, potassium chloride, and sodium phosphate solutions at temperatures up to about 230°. Other publications have been concerned with conductance measurements about<sup>4,5</sup> and considerably above<sup>6,7</sup> the critical temperature of water.

In the present study the "external" method of MacInnes<sup>8</sup> was applied to derive dissociation constants for acetic, propionic, n-butyric, and benzoic acid. The degree of dissociation  $\alpha$  of a weak-acid solution of molal concentration  $m$  was taken as being equal to the ratio  $\Lambda/\Lambda'$ , where  $\Lambda$  is the molar conductance of the weak-acid solution and  $\Lambda'$  is the sum of the molar conductance of the hydrogen ion and that of the weak-acid anion at concentration  $\alpha m$ . To obtain  $\Lambda'$  it was assumed that the ionic conductances were additive and also that hydrochloric acid, potassium chloride, and the potassium salts of the weak acids were completely dissociated under the conditions of the experiment. The latter assumption will be justified in the discussion below.

For each temperature and concentration the acid dissociation constant  $K_a$  was obtained from the equation  $K_a = \alpha^2 m \gamma_{\pm}^2 / (1 - \alpha)$ , where  $\gamma_{\pm}$  is the mean molal activity coefficient of the ions at the ionic strength of the weak-acid solution. The activity coefficient of the undissociated acid was taken to be unity. Values of  $\gamma_{\pm}$  were calculated from the Debye-Hückel equation

$$-\log \gamma_{\pm} = 1.812 \times 10^6 (\rho m)^{\frac{1}{2}} (DT)^{-\frac{3}{2}} / [1 + 50.288 \times 10^8 (DT)^{-\frac{1}{2}} (\rho m)^{\frac{1}{2}}]$$

Where  $\rho$  is the density of the solution, values of  $D$  the dielectric constant of water at each temperature were taken from Akerlof and Oshry,<sup>9</sup> and a constant value of  $\text{\AA} = 5 \text{\AA}$  was used throughout.

#### EXPERIMENTAL

*Apparatus.*—The conductance cell (Fig. 1) is a 2 in. external diameter stainless steel vessel lined with a rigid platinum insert and closed by a simple Teflon squash seal. A central platinum-rhodium electrode is attached to the head and electrically insulated by a Teflon and natural quartz assembly held under compression. The electrical resistance was measured between the central wire electrode and the body of the cell, and the contained solution came in contact only with platinum, quartz, and Teflon. Thermal expansion of Teflon would cause slight movements of the central electrode up and down the central line of symmetry of the cell but would have a negligible effect on the cell constant. Although the cell capacity was 15 ml., it was normally only filled with 11 ml. to allow for the thermal expansion of the liquid. Changes in the degree of filling between 10 and 15 ml. had no measurable effect on the cell constant when the cell was inverted in its normal operational position. The central wire electrode was recoated with platinum black after each run and the platinum liner recoated after about six runs.

The cell was heated at the centre of a 3 in. internal diameter electric tube furnace, 3 ft. long, insulated against heat losses by a surrounding 5 in. thickness of Perlite, and closed at both ends. Chromel-alumel thermocouples at each end of the cell usually registered temperatures consistent within  $\pm 1^\circ$ . The furnace could be maintained indefinitely within  $\pm 1^\circ$  at any temperature in the range of interest.

Resistance measurements were made with a capacity-compensated 1000 cycle a.c. Wheatstone bridge, corrections being made for the small resistances of the two lead wires from the cell to the bridge.

*Method.*—The cell containing the electrolyte solution was allowed to come to thermal

<sup>2</sup> Symon, *J. Royal Technical College of Glasgow*, 1931, **2**, 395.

<sup>3</sup> Whitehead, *J. Appl. Chem.*, 1961, **11**, 136.

<sup>4</sup> Fogo, Benson, and Copeland, *J. Chem. Phys.*, 1954, **22**, 212.

<sup>5</sup> Pearson, Ph.D. Thesis, University of Southern California, 1960.

<sup>6</sup> Franck, *Z. phys. Chem. (Frankfurt)*, 1956, **8**, 92, 107, 192.

<sup>7</sup> Franck, *Angew. Chem.*, 1961, **73**, 309.

<sup>8</sup> MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.

<sup>9</sup> Akerlof and Oshry, *J. Amer. Chem. Soc.*, 1950, **72**, 2846.

equilibrium at 25° by immersion up to the head bolt in a water thermostat. The conductance of the solution at this temperature was then measured after inverting the cell. This provided a check on the cell constant for each run, for although the value was always about 0.20 cm.<sup>-1</sup> small variations occurred through the wire electrode's sometimes being slightly bent when the cell was being opened. After being brought to temperature in the furnace, at least an hour was allowed for thermal equilibrium to be established between the cell and its contents. Measurements of resistance were made at approximately 25° intervals between 75° and 225°, a run usually lasting two days but often longer to check the stability of the solutions at elevated temperatures.

Many measurements were also made at a series of temperatures as the cell was cooled but it was usually not possible to make measurements below 100° on the cooling cycle owing to leakage

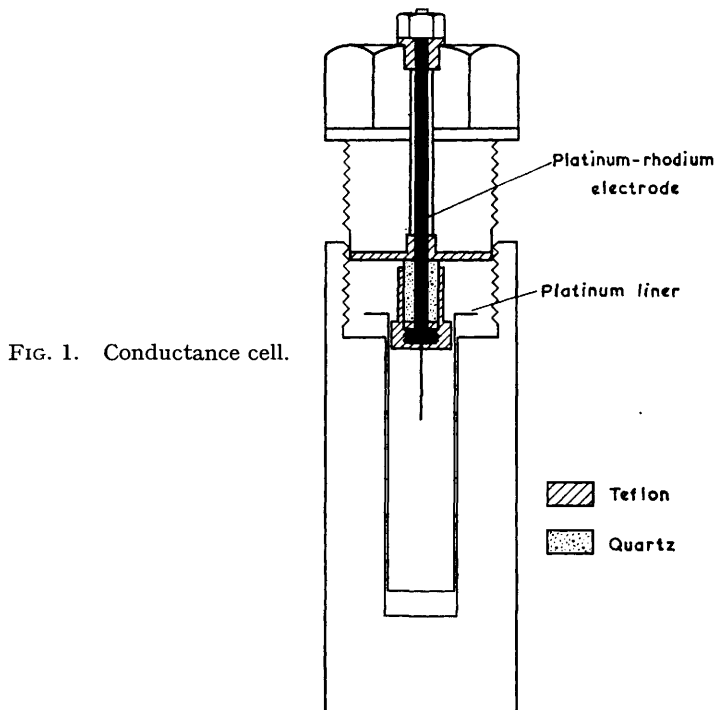


FIG. 1. Conductance cell.

which developed about the contracting Teflon seal. As examples, molar conductance results for two runs with 0.01m-hydrochloric acid and potassium chloride are given in Table 1. The

TABLE 1.

Values of  $\Delta\rho$  in two runs at ascending and descending temperatures.

	0.01m-Potassium chloride						
Temp.	25°	100	125	150	175	200	225
$\Delta\rho$ (ascending $T$ )	141	358	428	496	555	603	635
$\Delta\rho$ (descending $T$ )	—	363	435	490	560	608	—
	0.01m-Hydrochloric acid						
Temp.	25°	100	125	150	175	200	225
$\Delta\rho$ (ascending $T$ )	411	775	855	915	954	972	980
$\Delta\rho$ (descending $T$ )	—	770	850	908	945	965	—

results were not always obtained at even temperature values but have been interpolated to allow easy comparison.  $\rho$  is the density of the solution at the temperature. The results at ascending temperatures are considered to be the more reliable and are quoted below, since

slight loosening of the electrode assembly must occur on cooling. Nevertheless there is reasonable agreement between values at the same temperature. Each solution was examined in consecutive runs, the first conditioning the cell, and the second giving a rather more accurate result.

Conductance blanks were obtained for distilled water and subtracted from the specific conductivities measured for the electrolyte solutions at each temperature.

### RESULTS

For the electrolyte solutions conductivities are given in terms of the product  $\Lambda\rho$ , where  $\rho$ , the density of the solution, is taken as being equal to that for water at the same temperature. By working with molal concentrations and  $\Lambda\rho$  values continual use of numerical values for water densities is avoided in the calculations.

The results of stability studies on acetic, n-butyric, and benzoic acid solutions at about 225° are shown in Table 2.

Acetic and propionic acid are quite stable at 225°, n-butyric acid solutions increased slightly in conductivity after five days, but benzoic acid solutions showed a significant change in conductance after about five hours. The results for benzoic acid were therefore obtained in eight-hour runs, results being taken only at four temperatures for each filling. Decomposition of benzoic acid should not affect the results under these conditions. The conductances of hydrochloric acid and the potassium salts remained constant, within the possible experimental error, for at least two days.

TABLE 2.

Stability of aqueous acetic, n-butyric, and benzoic acid solutions at about 225°. Results in terms of the product  $\Lambda\rho$ , where  $\rho$  is the density of the solution at the temperature.

0.1m-Acetic acid					
Time (days) .....	1	2	3	4	5
Temp. ....	225°	224	226	227	227
$\Lambda\rho$ .....	3.95	3.94	3.96	3.97	3.97
0.01m-n-Butyric acid					
Time (days) .....	1	2	5	7	
Temp. ....	225°	225	225	224	
$\Lambda\rho$ .....	9.00	8.95	9.16	9.36	
0.02m-Benzoic acid					
Time (hr.) .....	1	2	5	6	18
Temp. ....	225°	225	224	224	225
$\Lambda\rho$ .....	18.5	18.6	18.8	18.8	19.7

Formic acid showed appreciable decomposition in a few hours even at 150°, so that measurements of its dissociation constant could not be made.

TABLE 3.

The specific conductance of distilled water at various temperatures and examples of the corrections required to solution conductances.

Temp. ....	25°	50	100	150	200	225
Specific cond. ( $10^6 \text{ ohm}^{-1} \text{ cm.}^{-1}$ ) .....	1.2	2.2	3.5	7.0	15	19
Correction (%) due to blank						
for $\Lambda$ (0.001m-potassium chloride) .....	0.8	1.0	0.9	1.2	2.0	2.3
$\Lambda$ (0.01m-n-butyric acid) .....	0.8	1.2	1.6	6	9	15
$\Lambda$ (0.1m-n-butyric acid) .....	0.25	0.4	0.5	1.1	3.0	4.7

Table 3 gives the mean specific conductance values measured for the distilled water used in preparing the solutions. It was not possible to reproduce these values to better

than  $\pm 10\%$  at the highest temperatures, and the values are about three times those reported by Noyes for distilled water at the same temperatures. The extra conductance in the present work may be due to slight hydrolysis of the Teflon plastic. The blank conductance values in Table 3 were used to correct the conductances of acid, base, and salt solutions. The extent of the correction is also shown in the Table for three representative solutions, 0.001m-potassium chloride, and 0.01m- and 0.1m-*n*-butyric acid.

The blank correction becomes appreciable at the highest temperatures for the 0.01m weak-acid solutions and reaches a maximum of 15% for the conductance of *n*-butyric acid. As the solution species causing the major proportion of the water conductance blank are unknown, the use of an overall blank may result in over correction in the case of acid solutions. The derived  $K_a$  values, especially for 0.01m-solutions may therefore be low.

The extent to which the reported  $K_a$  values may be low can be related directly to the uncertainty over the true distilled-water blank. The possible negative errors in  $K_a$  are given in Table 4 for representative weak-acid solutions at various temperatures. The possible errors for 0.1m-*n*-butyric acid are typical for all the 0.1m-weak acids, and the

TABLE 4.

Negative percentage errors possible in  $K_a$  values through uncertainties in the distilled-water blank.

Temp.	25°	50	100	150	200	225
<i>Acid solution</i>						
0.1m- <i>n</i> -Butyric .....	0.5	0.7	1	2	4	7
0.01m- <i>n</i> -Butyric .....	1.5	2	3	7	18	30
0.01m-Acetic .....	1.5	2	3	5	13	22
0.02m-Benzoic .....	0.6	0.8	1	2	3	5

possible errors for acetic and propionic acid are similar in value. In comparison with the distilled-water blank, other possible errors can be neglected (thermal expansion of metal and plastic cover on the electrode base; temperature uncertainties).

Table 5 gives interpolated values of  $\Lambda_p$  at various temperatures for solutions of potassium chloride, hydrochloric acid, potassium acetate, potassium propionate, potassium butyrate, and potassium benzoate, at concentrations ranging from 0.001m to 0.01m. The  $\Lambda_p$  values at infinite dilution, obtained by extrapolation, are also shown.

The values of  $\Lambda_p$  shown for the potassium salts of the weak acids have been corrected for the slight hydrolysis of the salt into free acid and potassium hydroxide (up to 5% at lowest concentrations and 225°) from knowledge of the excessive conductance of the hydroxide ion over the weak-acid anion at each temperature. Noyes presented high-temperature conductance results for sodium hydroxide solutions, and a single check at 0.01m-sodium hydroxide concentration in the present cell was in good agreement. Pearson<sup>5</sup> also confirmed Noyes's results at 218° for sodium hydroxide solutions.

The values for potassium acetate attributed to Noyes were obtained from his results for sodium acetate and potassium and sodium chloride at the required concentrations. The rather poor agreement between the two sets of the 0.01m results at 200° and 225° may be due to the fact that additivity of ionic conductances at this appreciable concentration is not a good approximation.

Table 6 summarizes the results of conductance measurements on the weak-acid solutions and contains the derived acid dissociation constants rounded off to the nearest significant figure. Values of  $\Lambda'$  were obtained by successive approximation, using the infinite dilution conductances of potassium chloride, hydrogen chloride, and the potassium salt of the weak acid to get a preliminary value of  $\alpha_m$ . For acetic acid there was good agreement with values interpolated from Noyes's results which are shown in parentheses.

TABLE 5.

The variation of  $\Lambda_p$  with temperature at various solution concentrations. Values in parentheses obtained by interpolation of Noyes's results.

Temp. Concn. (m)	<i>Potassium chloride</i>					
	25°	50	100	150	200	225
0	149.5 *	226	388	540	660	697
0.001	146.5 *	221	385(382)	531(528)	647(643)	670(676)
0.002	145.5 *	219	—(377)	—(521)	—(633)	—(668)
0.005	143.1 *	215	363(366)	504(507)	608(616)	640(649)
0.01	140.8 *	212	358(362)	496(496)	603(605)	635(637)

\* Base values taken from Gunning and Gordon.<sup>10</sup>

Temp. Concn. (m)	<i>Hydrochloric acid</i>					
	25°	50	100	150	200	225
0	425 *	572	811	970	1050	1068
0.001	420 *	563	806(795)	955(950)	1020(1028)	—(1043)
0.002	418 *	562	792(792)	945(943)	1008(1016)	1020(1031)
0.005	415 *	—	—(782)	—(930)	—(999)	—(1008)
0.01	411 *	552	775(774)	914(917)	972(977)	980(988)

\* Base values taken from Owen and Sweeton.<sup>11</sup>

Temp. Concn. (m)	<i>Potassium acetate</i>					
	25°	50	100	150	200	225
0	114.1 *	178	310	435	530	560
0.001	111.4 *	172(174)	303(306)	425(428)	510(516)	550(538)
0.002	110.5 *	—(171)	294(299)	414(420)	507(507)	538(528)
0.01	106.3 *	160(165)	277(285)	394(396)	458(473)	477(495)

\* Base values taken from MacInnes and Shedlovsky's<sup>12</sup> results for sodium acetate adjusted for the difference  $\lambda(K^+) - \lambda(Na^+)$ .

Temp. Concn. (m)	<i>Potassium propionate</i>					
	25°	50	100	150	200	225
0	109 *	172	296	416	522	560
0.001	107 *	169	289	405	507	545
0.002	105 *	165	283	395	494	530

\* Base values from Belcher's<sup>13</sup> results on sodium propionate adjusted as for potassium acetate.

Temp. Concn. (m)	<i>Potassium n-butyrate</i>					
	25°	50	100	150	200	225
0	106 *	171	296	408	504	543
0.002	103 *	165	284	390	478	515
0.01	98 *	158	270	366	448	480

\* Base values obtained as for previous solution.

Temp. Concn. (m)	<i>Potassium benzoate</i>					
	25°	50	100	150	200	225
0	106 *	166	283	401	488	512
0.001	104 *	162	275	390	470	490
0.002	103 *	159	269	381	464	486

\* Base values from Brockman and Kilpatrick.<sup>14</sup>

<sup>10</sup> Gunning and Gordon, *J. Chem. Phys.*, 1942, **10**, 126.

<sup>11</sup> Owen and Sweeton, *J. Amer. Chem. Soc.*, 1941, **63**, 2811.

<sup>12</sup> MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429.

<sup>13</sup> Belcher, *J. Amer. Chem. Soc.*, 1938, **60**, 2744.

<sup>14</sup> Brockman and Kilpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 1483.

TABLE 6.

The conductance of solutions of acetic, propionic, *n*-butyric, and benzoic acid at temperatures up to 225°, and the derived molal acid dissociation constants.

Temp.	$\Delta\rho$	$\Lambda'\rho$	$10^2\alpha$	$\gamma_{\pm}^2$	$10^5K_a$	Accepted value <sup>21, 22</sup> ( $10^5K_a$ )
<i>0.01m-Acetic acid</i>						
25°	16.2(16.2)	386	4.19	0.953	1.74(1.74)	1.754
50	21.0(21.0)	519	4.05	0.954	1.63(1.63)	1.633
100	24.4(24.6)	727	3.37	0.954	1.12(1.13)	—
150	21.6(21.6)	857	2.52	0.952	0.62(0.62)	—
200	16.2(16.1)	911	1.78	0.954	0.31(0.30)	—
225	12.6(12.2)	924	1.34	0.956	0.18(0.17)	—
<i>0.1m-Acetic acid</i>						
25°	5.20(5.10)	384	1.36	0.922	1.71(1.71)	1.754
50	6.65(6.65)	516	1.29	0.919	1.55(1.55)	1.633
100	7.83(7.91)	722	1.09	0.918	1.09(1.12)	—
150	7.05(7.00)	851	0.828	0.918	0.63(0.63)	—
200	5.25(5.25)	902	0.582	0.918	0.31(0.31)	—
225	3.95(4.00)	916	0.424	0.924	0.17(0.18)	—
<i>0.01m-Propionic acid</i>						
25°	14.0	382	3.66	0.958	1.33	1.336
50	18.2	514	3.54	0.956	1.25	1.229
100	20.8	712	2.92	0.957	0.86	—
150	18.9	839	2.25	0.955	0.50	—
200	13.9	903	1.54	0.955	0.23	—
225	10.3	924	1.12	0.958	0.12	—
<i>0.1m-Propionic acid</i>						
25°	4.40	380	1.16	0.926	1.26	1.336
50	6.00	511	1.17	0.920	1.28	1.229
100	7.05	708	0.996	0.921	0.92	—
150	6.10	833	0.733	0.922	0.50	—
200	4.62	897	0.515	0.920	0.24	—
225	3.60	915	0.394	0.924	0.14	—
<i>0.01m-n-Butyric acid</i>						
25°	14.7	378	3.89	0.957	1.50	1.515
50	18.0	512	3.52	0.956	1.23	1.302
100	20.6	713	2.89	0.956	0.82	—
150	18.0	831	2.17	0.954	0.46	—
200	12.6	886	1.42	0.955	0.20	—
225	9.0	907	0.99	0.960	0.10	—
<i>0.1m-n-Butyric acid</i>						
25°	4.65	377	1.24	0.926	1.43	1.515
50	5.80	509	1.14	0.923	1.21	1.302
100	6.50	709	0.917	0.924	0.78	—
150	5.82	826	0.704	0.922	0.46	—
200	4.19	898	0.466	0.926	0.20	—
225	3.20	900	0.356	0.927	0.12	—
<i>0.01m-Benzoic acid</i>						
25°	29.5	379	7.79	0.939	6.2	6.29
50	37.8	505	7.49	0.938	5.7	5.88
100	46.9	695	6.75	0.934	4.5	—
150	43.5	819	5.31	0.934	2.8	—
200	33.2	865	3.84	0.934	1.4	—
225	26.5	871	3.04	0.934	0.89	—
<i>0.02m-Benzoic acid</i>						
25°	20.5	377	5.44	0.929	5.8	6.29
50	26.7	504	5.30	0.928	5.5	5.88
100	32.4	694	4.67	0.923	4.2	—
150	29.8	817	3.65	0.922	2.6	—
200	22.9	864	2.65	0.924	1.3	—
225	18.5	870	2.12	0.924	0.85	—

## DISCUSSION

**Conductance Results.**—Brief discussion of Noyes's high-temperature conductance results in liquid water has been given in an earlier paper.<sup>15</sup> The molar conductance results (Noyes's as well as the present values) for the potassium salts and hydrochloric acid are now interpreted by means of the Debye-Hückel-Onsager equation in the following form

$$\Lambda\rho = \Lambda^\circ\rho - (\alpha\Lambda^\circ\rho + \beta\rho)\rho^{\frac{1}{2}}m^{\frac{1}{2}}$$

Values of the constants  $\alpha$ ,  $\beta$ , and  $\rho$  are given in Table 7.

The value of  $\Lambda$  for the electrolyte at infinite dilution ( $\Lambda^\circ$ ) at each temperature was obtained by extrapolation along the slope predicted by the above equation on graphs of

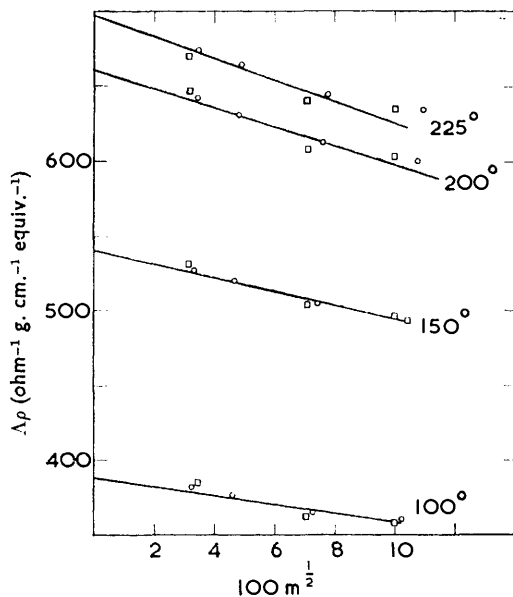


FIG. 2. Conductance results for potassium chloride in terms of  $\Lambda\rho$  plotted against  $m^{\frac{1}{2}}$ , compared with the theoretical Onsager slopes at each temperature.  $\square$  Present values;  $\circ$  Noyes's results.

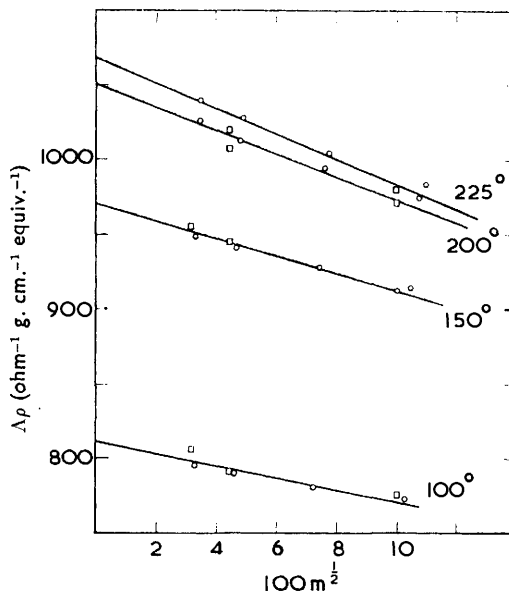


FIG. 3. Conductance results for hydrochloric acid in terms of  $\Lambda\rho$  plotted against  $m^{\frac{1}{2}}$ , compared with the theoretical Onsager slopes at each temperature.  $\square$  Present values;  $\circ$  Noyes's results.

$\Lambda\rho$  against  $m^{\frac{1}{2}}$ . The conductance results and the theoretical slopes are shown by Figs. 2 and 3 for potassium chloride and hydrochloric acid respectively. The results of Noyes,<sup>1</sup> where available, were taken into consideration when drawing lines of theoretical slope through the experimental points. These lines were used to interpolate values of  $\Lambda$  for calculations of  $K_a$ . As the ionic concentrations of the weak-acid solutions were in the

TABLE 7.

Values of the constants  $\alpha$ ,  $\beta$ , and  $\rho$  of the Onsager equation at various temperatures.

Temp.	25°	50	100	150	200	225
$\alpha$	0.229	0.241	0.272	0.324	0.392	0.437
$\beta$	60.2	99.7	201	326	474	543
$\rho$	0.997	0.988	0.958	0.917	0.865	0.834

<sup>15</sup> Ellis and Fyfe, *Rev. Pure Appl. Chem.*, 1957, **7**, 261.



range  $1 \times 10^{-4}$ — $4 \times 10^{-4}$ m this is unlikely to introduce more than a 2% error into  $K_a$  at 225°.

At 225° the Onsager equation was obeyed within the possible experimental error of the measurements up to concentrations of about 0.005m for hydrochloric acid and the potassium salts. The dielectric constant of water at 225° is 30.5 which is comparable with that for methanol ( $D = 31.5$ ) at 25°. For the latter solvent the theoretical Onsager slope is obeyed to better than 1% for solutions of salts such as potassium chloride up to concentrations of about 0.003m (conductance data from Butler, Schiff, and Gordon<sup>16</sup>).

At 225° there is no tendency for the conductance values at higher concentrations to fall appreciably below the line of theoretical slope as would be expected if ion association of hydrochloric acid or the potassium salts were important. A further check on the extent of ion association of these electrolytes is provided by Bjerrum's theory. Pearson<sup>5</sup> produced a convenient graph of the variation in association constants with dielectric constant and temperature, and from this graph, for a mean distance of approach of ions ( $\lambda$ ) of 2 Å, degrees of dissociation of 99.2% and 93% are predicted for 0.001 and 0.01m-solutions. For  $\lambda$  equals 4 Å the predicted figures are 99.8% and 96% respectively.

Walden's rule  $\Lambda\eta = \text{constant}$  ( $\eta$  is the viscosity of the solvent) also demonstrates that the hydrogen chloride and potassium salts at concentrations of about 0.01m are essentially dissociated at 225°. Values of  $\eta$  for water were taken from Dorsey<sup>17</sup> (Table 8).

TABLE 8.

Values of  $\Lambda\eta$  at a temperature relative to  $\Lambda\eta = 1$  at 25° for various electrolytes at infinite dilution and at 0.01m.

Solution	Temp.	25°	50	100	150	200	225
Infinite dil. KCl.....		1	0.94	0.82	0.82	0.77	0.68
0.01m-KCl .....		1	0.94	0.81	0.80	0.75	0.68
Infinite dil. HCl.....		1	0.84	0.60	0.52	0.43	0.38
0.01m-HCl .....		1	0.84	0.60	0.51	0.42	0.36
Infinite dil. KOAc.....		1	0.97	0.86	0.86	0.81	0.74
0.01m-KOAc .....		1	0.95	0.84	0.84	0.77	0.69

There is little difference between the ratio  $\Lambda\eta(T)/\Lambda\eta(25^\circ)$  at infinite dilution and at 0.01m for potassium chloride and hydrochloric acid, and only a small difference for potassium acetate. The degree of dissociation of each salt must therefore be similar at 0.01m and infinite dilution.

Complete dissociation of hydrochloric acid and the potassium salts can be safely assumed for temperatures up to 225° at the ionic strengths between  $10^{-3}$  and  $10^{-4}$ m used in the determination of the weak-acid dissociation constants.

Where there is overlap of results, the present conductance values for strong electrolytes are in good agreement with those of Noyes who fitted his results to the equation

$$c(\Lambda^\circ - \Lambda) = K(c\Lambda)^n$$

where  $n$  was adjusted to give the best fit and was usually in the range 1.4—1.5, and  $c$  is the concentration in moles per litre. The resulting infinite-dilution values were 0.5—1% higher than those reported here.

*Weak-acid Dissociation Constants.*—The change in acid dissociation constants with temperature has in the past been expressed by equations of several types, each of which shows the dissociation first to increase with rising temperature, reach a maximum value, and then steadily decrease.

<sup>16</sup> Butler, Schiff, and Gordon, *J. Chem. Phys.*, 1951, **19**, 752.

<sup>17</sup> Dorsey, "Properties of Ordinary Water-substance," Amer. Chem. Soc. Monograph No. 81, 1940.

Harned and Embree<sup>18</sup> suggested the approximate equation

$$\log K_a - \log K_a^m = -p(t - t_m)^2 \quad (1)$$

which fits the variations in dissociation constants for many weak electrolytes up to about 60°, where  $K_a^m$  is the maximum dissociation constant at temperature  $t_m$ , and  $p$  is a universal constant. Equations of the form:

$$\log K_a = -(A/T) - B \log T + D, \quad (2)$$

and

$$\log K_a = -(A/T) - CT + D \quad (3)$$

reproduce the variations with temperature rather more closely where A, B, C, and D are constants. The former equation assumes that the change in heat capacity on ionization,  $\Delta C_p^\circ$ , does not vary with temperature, while the latter equation implies that  $\Delta C_p^\circ$  is proportional to temperature. To date there has not been sufficient information on dissociation constants over a wide range of temperature to decide whether either of these assumptions is correct.

TABLE 9.

Values of the constants of equation 5 for interpolating values of  $\log K_a$  for acetic, propionic, butyric, and benzoic acid between 0° and 220°.

	A	B	C	D
Acetic acid .....	-2785	-22.96	$2.15 \times 10^{-3}$	60.76
Propionic acid .....	-1041	-0.409	$-1.135 \times 10^{-3}$	3.02
Butyric acid .....	71	12.57	$-1.908 \times 10^{-3}$	-30.48
Benzoic acid .....	-1929	-12.39	$-3.24 \times 10^{-3}$	33.88

Pitzer<sup>19</sup> produced a useful general approximate equation of the form

$$\log K_a = (A/T) + 53.78 - 20 \log T \quad (4)$$

This was based on the fact that the average entropy change on ionization ( $\Delta S^\circ$ ) for many weak acids was about -22 e.u., and  $\Delta C_p^\circ$  was about -40 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. For acetic acid at 250° the values of  $K_a$  calculated from this equation are within a factor of about two of Noyes's experimental value.<sup>15</sup>

The present results were fitted to an equation of the following type

$$\log K_a = (A/T) + B \log T + CT + D \quad (5)$$

Table 9 gives values of the constants A, B, C, and D for the four acids investigated. In the temperature range 0—220° this equation reproduces the mean experimental curves shown in Fig. 4 within  $\pm 0.03$  in  $\log K_a$ —usually within 0.01—0.02 at temperatures below 100°. The equation cannot, however, be used for extrapolation to higher temperatures as the calculated values of  $\log K_a$  become higher than those given by experiment. For example the equation for acetic acid predicts a value of  $\log K_a$  equal to -6.23 at 306°. Noyes's experimental value at this temperature was -6.88.

There is need for a simple equation which would allow both the interpolation of  $\log K_a$  results within the present experimental range, and reasonable extrapolation to higher temperatures. Equations (1)—(4) suffer from long-range inaccuracies similar to those of eqn. (5).

Baughan<sup>20</sup> suggested that the free-energy of the ionization process  $HA + H_2O \longrightarrow H_3O^+ + A^-$  could best be considered in two parts, a chemical part  $\Delta G_c^\circ$  due to the proton

<sup>18</sup> Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1050.

<sup>19</sup> Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

<sup>20</sup> Baughan, *J. Chem. Phys.*, 1939, **7**, 951.

shift, and an electrical part  $\Delta G_e^\circ$  due to the creation of a new electrical field about the ions:

$$\Delta G^\circ = \Delta G_c^\circ + \Delta G_e^\circ.$$

From Born's equation, for univalent ions,  $\Delta G_e^\circ = Ne^2/2Dr$  where  $D$  is the dielectric constant of water and  $r$  is the mean ion radius,  $\frac{1}{r} = \left(\frac{1}{r_+} + \frac{1}{r_-}\right)$ . It follows that

$$\begin{aligned} \log K_a &= \log K_c + \log K_e \\ &= \log K_0 - (Ne^2/9 \cdot 150rDT), \end{aligned} \quad (6)$$

FIG. 4. Changes with temperature in the values of  $\log K_a$  for four acids. A, benzoic; B, acetic; C, propionic; D, butyric.  $\circ$ , 0.1m-solutions;  $\Delta$ , 0.01m-solutions;  $\square$ , 0.02m-solutions.

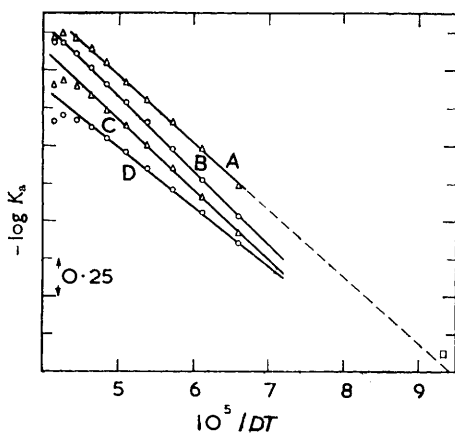
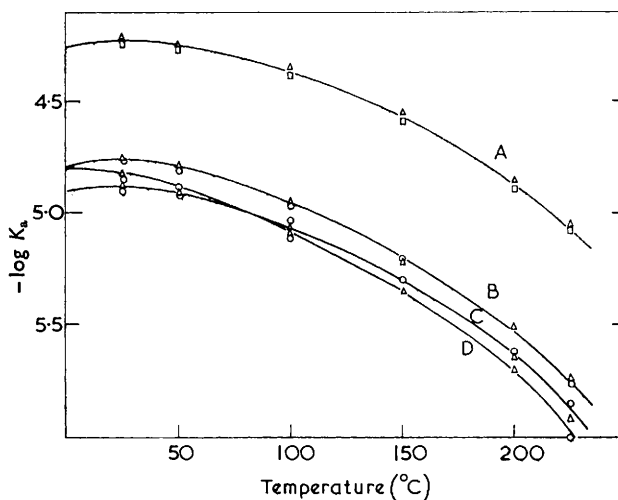


FIG. 5. Values of  $\log K_a$  vs.  $1/DT$  from  $0^\circ$  to  $225^\circ$ .  $\square$  Noyes's value at  $306^\circ$  for acetic acid. A, acetic acid; B, butyric acid; C, propionic acid; D, benzoic acid.

where  $K_c$  and  $K_e$  are the equilibrium constants corresponding to the chemical and electrical free-energy changes.

The heat change  $\Delta H_c$  corresponding to the chemical part of the ionization process is likely to show only a small variation with temperature (cf.,  $\Delta C_p^\circ$  is close to zero for iso-electric reactions<sup>21</sup>). Therefore  $\log K_c$  will vary in proportion to  $1/T$ . As a graph of  $\log K_a$  against  $1/T$  shows marked curvature (*i.e.*,  $\Delta H^\circ$  changes rapidly with temperature) the first term of eqn. (6) is not predominant. The controlling effect of the electrical

<sup>21</sup> Harned and Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd edn., Reinhold, New York, 1958.

term was shown by plotting  $\log K_a$  against  $1/DT$  for the four acids, with the result shown in Fig. 5. Above about 75–100° a straight line passed through the experimental results for each acid taken from the curves of Fig. 4 at 25° intervals. For acetic acid the line was extended to 306° where it passed through a value of  $\log K_a$  equal to  $-6.96$ , compared with Noyes's experimental value,<sup>1</sup> now allowing for activity coefficient corrections, of  $-6.88$ . A simple graph of  $\log K_a$  against  $1/DT$  therefore appears to be a useful extrapolation method, providing experimental values of  $K_a$  are obtained to temperatures about 100° above the temperature of maximum ionization of the weak electrolyte in water.

If the variations in  $\log K_c$  of equation (6) are neglected, the slopes of the lines in Fig. 5 can be equated to  $-Ne^2/9.150r$ , or on inserting numerical values for constants,  $-36250/r$  where  $r$  is in Å. Table 10 gives the derived values of  $r$  which should be interpreted as useful constants rather than as values of mean ionic radii, although they are of reasonable magnitude.

The predominance of the electrical term at high temperatures allows further observations to be made. For the second stage of ionization of a di- or tri-basic acid the decrease in  $\log K_a$  with increasing temperature will be twice, and for the third stage three times, that for the process producing univalent ions (the product of ion charges  $Z_+Z_-$  appears

TABLE 10.

Values of  $r$  derived from the straight-line gradients in Fig. 5.

Acid	Acetic	Propionic	n-Butyric	Benzoic
$r$ (Å)	0.818	0.787	0.743	0.916

in the numerator of the Born equation). For example Noyes's approximate results for sulphuric and phosphoric acids show that the rate of decrease of  $\log K_a$  for the ionization of hydrogen sulphate is rather more than twice that for the first stage of phosphoric acid, an acid of comparable strength at 25°. Di- or tri-basic salts such as sulphates, phosphates, and hydrogen phosphates will show extensive hydrolysis in water above 250–300°. At these temperatures the major ion components of aqueous solutions will become confined to univalent ions.

A linear relationship of  $\log K_a$  and  $1/DT$  can be investigated to show the trend of  $\Delta C_p^\circ$  with temperature. From the equation  $\log K_a = \log K_c - n/DT r$  where  $n$  is equal to 36,250, with  $\log K_c$  taken as constant,

$$\frac{\partial \log K_a}{\partial T} = \frac{n}{rDT^2} \left( 1 + T \frac{\partial \ln D}{\partial T} \right)$$

and 
$$\Delta H^\circ = \frac{4.575 n}{rD} \left( 1 + T \frac{\partial \ln D}{\partial T} \right) \quad (7)$$

Also 
$$\frac{\partial \Delta H^\circ}{\partial T} = \Delta C_p^\circ = \frac{4.575 n T}{Dr} \left[ \frac{\partial^2 \ln D}{\partial T^2} - \left( \frac{\partial \ln D}{\partial T} \right)^2 \right] \quad (8)$$

The product of eqn. (8) becomes increasingly negative at higher temperatures, and therefore  $\Delta C_p^\circ$  of ionization would also follow this trend.

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<sup>22</sup> Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 1955.