the cupric ammonium salts, the trichlorides, and the nitrogen esters formed by the reaction of benzyl chloride with the respective alkali salts at elevated temperature. The analogy is less exact for the diamides, the mercuric salts and the oxygen esters.

2. The existence of a trichloride and of an oxygen ester indicates that hydroxyl groups are present in the molecule of cyameluric acid.

3. The analogy with cyanuric compounds and the presence of hydroxyl groups substantiate the planar ring structure for cyameluric acid proposed by Pauling and Sturdivant.

4. Melam is probably dicyanurylimide and melem, cyameluryl triamide.

5. It is proposed that melon is a condensation product of cyameluryl triamide, and that the resulting very large molecules consist of planar cyameluryl rings joined through nitrogen atoms.

PASADENA, CALIF. RECEIVED NOVEMBER 6, 1939

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Ionization Constants of Weak Acids at 25° from Conductance Measurements. A Method of Extrapolating the Data[1]

BY BLAIR SAXTON[2] AND LAWRENCE S. DARKEN[3]

A large number of investigations[4-14] have been conducted in recent years on the determination of ionization constants of weak acids by the conductance method. At the lower concentrations the degree of ionization is determined accurately from conductance data alone by use of the additive law that the specific conductance of the weak acid is equal to the specific conductance of the hydrogen ion and the acid ion as determined from the conductance of the sodium or the potassium salt of the acid, sodium or potassium chloride and hydrochloric acid at the corresponding ionic concentration. The salts and hydrochloric acid are considered completely ionized. The degree of dissociation of the weak acid is set equal to Λ/Λ_e where Λ_e is the equivalent conductance of the theoretical completely dissociated acid at the same ionic concentration. Values of Λ/Λ_e are obtained by a method of successive approximations from the above-mentioned data. From the degree of dissociation of the acid a so-called mass law ionization constant is determined directly according to the relation

$$k = \alpha^2 c/(1 - \alpha) = c_i^2/c_u$$

where α is the degree of dissociation, c is the stoichiometric concentration of the weak acid, c_i is the ionic concentration, and c_u is the concentration of undissociated weak acid. At finite concentrations

$$K = y_{\pm}^2 k$$

where K is the thermodynamic ionization constant as usually written, and $y_{\pm}$ is the mean ionic activity coefficient. Several investigators[4-14] have shown that at extremely low concentrations the variation of k with concentration is in good agreement with that predicted by the Debye–Hückel[15] theory of interionic attraction which at low ionic concentrations reduces to this relation

$$\log y_{\pm} = -A\sqrt{c_i}$$

which combined with the previous equation gives

$$\log K = \log k - 2A\sqrt{c_i}$$

Unfortunately, the range over which this equation holds within an experimental error of one part in a thousand (to give a constant value of log K) is below an ionic concentration of about 0.003 (depending on the acid). Hence, extrapolating to obtain the limiting value of log K from a plot of log k *versus* $\sqrt{c_i}$ is not a convenient method in that it demands high accuracy at low concentrations. It will be shown that the true thermodynamic ionization constant may be determined

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(1) This paper contains material which represents part of the dissertation submitted by Lawrence S. Darken to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1933. Original manuscript received July 20, 1939.

(2) The experimental work and calculations herein reported were completed before the death of Professor Saxton.

(3) Present address: Research Laboratory, United States Steel Corporation, Kearny, New Jersey.

(4) MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

(5) Davies, *ibid.*, **54**, 1698 (1932).

(6) Saxton and Langer, *ibid.*, **55**, 3638 (1933).

(7) MacInnes, Shedlovsky, and Longsworth, *Chem. Rev.*, **13**, 29 (1933).

(8) Ives, *J. Chem. Soc.*, 731 (1933).

(9) Brockman and Kilpatrick, THIS JOURNAL, **56** 1483 (1934).

(10) Saxton and Meier, *ibid.*, **56**, 1918 (1934).

(11) Banks and Davies, *J. Chem. Soc.*, 73 (1938).

(12) Saxton and Waters, THIS JOURNAL, **59**, 1048 (1937).

(13) Martin and Tartar, *ibid.*, **59**, 2972 (1937).

(14) Belcher, *ibid.*, **60**, 2744 (1938).

(15) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

conveniently and accurately by extrapolating to infinite dilution a plot of log $k - 2A\sqrt{c_i}$ *versus* c_u. Such a plot has been found to be linear up to a concentration of almost one molal.

Experimental

The conductance measurements were made with the apparatus and technique used in our earlier work[6,10] and the ionization constants were calculated by the method there described. Jena glass cells and a silica cell were used. The cell constants were determined by use of both 0.01 and 0.1 demal potassium chloride solutions and all conductivities here reported are based on Jones and Bradshaw's[16] determination of the conductivities of these solutions. In the case of formic acid, half of the measurements were made with bright electrodes while the remainder were made with platinized electrodes. In the latter case, special care was taken to remove carbon dioxide and oxygen by bubbling nitrogen through the solutions. These measurements were made a year apart on samples of acid which had been independently purified and analyzed.

Kahlbaum cyanoacetic acid was recrystallized several times from conductivity water. The results checked those obtained with acid recrystallized from an ether–chloroform mixture and then twice from conductivity water. Formic acid was freshly distilled and standardized just before each run. Eastman *n*-butyric acid was purified by partially crystallizing three times and discarding the unfrozen liquid. The stock solution of each acid was analyzed by titrating with sodium hydroxide solution which had been standardized with potassium acid phthalate certified by the Bureau of Standards. In each analysis the titration was finished with standard base one-tenth the concentration of that used for the major part of the titration. The results usually showed deviations of about 0.01% from the average.

Sodium salt solutions were made by adding the calculated quantity of pure sodium carbonate to the acid solution. Carbon dioxide was removed by treating with nitrogen. The potassium butyrate stock solution was prepared by neutralizing a butyric acid solution with the theoretical amount of potassium hydroxide solution (the same potassium hydroxide solution which had previously been used for conductance measurements and with which the titer of the acid was determined). To suppress hydrolysis about 0.25% excess acid was added. The cell concentration was based on the amount of alkali used.

Densities were determined with a pyknometer. The following equations express the results over the concentration range covered

Formic acid: $d = 0.99704 + 0.012089c - 0.000690c^{3/2}$
Cyanoacetic acid: $d = 0.99704 + 0.023m$
Sodium cyanoacetate: $d = 0.99704 + 0.057m$
Butyric acid: $d = 0.99704 + 0.00362m$
Potassium butyrate: $d = 0.99704 + 0.0496m$

Densities for sodium formate solutions were taken from the "International Critical Tables" (m = gram moles per kilogram; c = gram moles per 1000 cc.).

The equivalent conductances of the salts follow Shedlovsky's[17] extension of Onsager's[18] equation and are given by

$Na^+ + CNCH_2COO^-$:
$$\Lambda = 91.91 - 80.79\sqrt{c_i} + 76c_i(1 - 0.2276\sqrt{c_i})$$
$Na^+ + HCOO^-$:
$$\Lambda = 104.69 - 83.69\sqrt{c_i} + 86c_i(1 - 0.2276\sqrt{c_i})$$
$K^+ + C_3H_7COO^-$:
$$\Lambda = 105.39 - 83.76\sqrt{c_i} + 110c_i(1 - 0.2276\sqrt{c_i})$$

The experimental data are given in Table I. Combining these equations with the equation for $\Lambda_{(H^+)} - \Lambda_{(Na^+)}$ given in an earlier paper,[6] the equations for the sums of the equivalent conductances of the ions of the weak acids as functions of their ionic concentrations, c_i, become

$H^+ + CNCH_2COO^-$:
$$\Lambda_e = 391.71 - 148.98\sqrt{c_i} + 151c_i(1 - 0.2276\sqrt{c_i})$$
$H^+ + HCOO^-$:
$$\Lambda_e\ 404.50 - 151.88\sqrt{c_i} + 161c_i(1 - 0.2276\sqrt{c_i})$$
$H^+ + C_3H_7COO^-$:
$$\Lambda_e = 381.69 - 146.57\sqrt{c_i} + 180c_i(1 - 0.2276\sqrt{c_i})$$

The measured equivalent conductances of the acids and the thermodynamic ionization constants calculated with the aid of these equations are given in Table II.

TABLE I

$c \times 10^2$	Λ calculated	Λ observed
Potassium Butyrate		
0.114958	102.68	102.64
.19572	101.90	101.89
.21807	101.72	101.67
.34349	100.85	100.85
.39483	100.55	100.56
.51451	99.94	99.95
.62395	99.45	99.49
.72295	99.05	99.06
.86320	98.54	98.58
1.00045	98.07	98.09
1.2454	97.38	97.41
1.32332	97.17	97.17
1.5759	96.45	96.58
2.0437	95.59	95.45
2.3749	95.00	94.96
Sodium Formate		
$c \times 10^3$		
0.19505	103.52	103.43
.58885	102.72	102.63
1.2449	101.84	101.85
2.8045	100.50	100.50
4.1483	99.65	99.64
5.4916	98.95	98.96
6.5543	98.47	98.46
7.2663	98.17	98.17
8.9550	97.53	97.53
10.6180	96.96	96.96
Sodium Cyanoacetate		
0.010933	91.65	91.52
.033500	91.44	91.39
.19512	90.87	90.78
.30547	90.52	90.56
.41970	90.30	90.28
.52728	90.10	90.06
.60357	89.97	89.95
1.0364	89.39	89.39
1.9170	88.52	88.53
3.1400	87.61	87.59
4.6500	86.74	86.73
6.3959	85.92	85.92

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[16] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[17] Shedlovsky, *ibid.*, **54**, 1405 (1932).

[18] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927); *Trans. Faraday Soc.*, **23**, 341 (1927); *J. Phys. Chem.*, **36**, 2689 (1932).

TABLE II

CYANOACETIC ACID

$\times 10^3$	Λ	$K \times 10^3$	Series
0.3943	352.32	3.287	III
.9931	316.76	3.396	II
1.0169	314.82	3.340	I
1.1848	307.09	3.349	III
2.3848	266.74	3.356	III
2.9100	254.23	3.356	II
3.0217	251.82	3.356	I
3.8022	237.06	3.356	III
5.6930	210.97	3.352	III
5.7374	210.50	3.353	I
5.7749	210.08	3.352	II
7.6346	192.39	3.349	III
8.6832	184.42	3.347	II
8.7186	184.16	3.346	I
10.3136	173.96	3.342	III
12.1816	164.18	3.341	II
12.827	161.09	3.333	III
13.017	160.33	3.337	I
16.378	147.48	3.330	II
16.531	146.98	3.330	III
18.994	139.56	3.325	I

Formic Acid

$c \times 10^3$	Λ	$K \times 10^4$	Series
1.0739	137.52	1.831	V
6.8918	62.165	1.829	V
10.937	50.347	1.827	V
13.207	46.127	1.824	I
16.663	41.392	1.821	V
22.416	36.025	1.818	III
25.023	34.242	1.821	V
28.865	32.027	1.821	VI
31.738	30.605	1.818	III
35.982	28.868	1.820	V
36.929	28.500	1.817	III
41.611	26.946	1.818	II
45.085	25.939	1.817	III
48.852	24.957	1.814	V
67.463	21.445	1.818	VI
86.662	19.035	1.815	I
98.860	17.863	1.811	II
185.30	13.223	1.801	I
200.14	12.739	1.799	VI
207.15	12.528	1.797	II
361.80	9.5671	1.778	I
396.76	9.1487	1.774	VI
463.43	8.4756	1.763	II
546.81	7.8172	1.753	I
655.63	7.1437	1.738	II
734.04	6.7551	1.728	I
975.35	5.8535	1.695	VI
1141.50	5.3983	1.672	II
1227.2	5.1998	1.660	VI
1713.1	4.3530	1.590	VI
2015.9	3.9751	1.545	IV
2119.2	3.8670	1.532	VI
2549.3	3.4551	1.455	IV
3010.6	3.1335	1.399	IV
3694.0	2.7254	1.285	IV
4618.7	2.3257	1.157	IV
5690.5	1.9642	1.010	IV
6973.0	1.6194	0.8374	IV
8488.0	1.2949	.6552	IV
9555.0	1.1087	.5435	IV

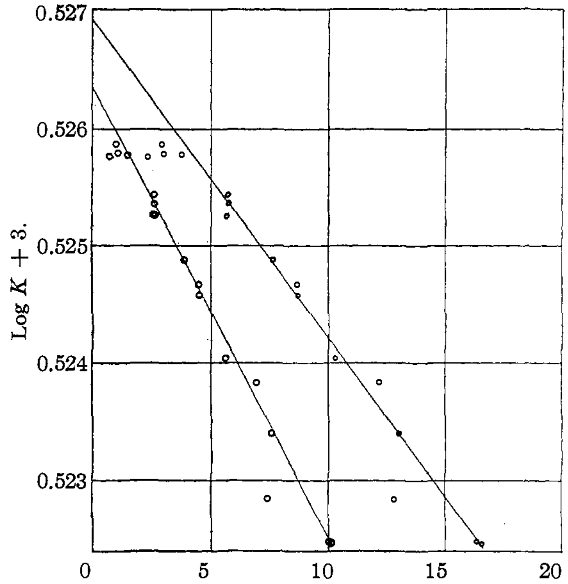
Butyric Acid

$c \times 10^3$	Λ	$K \times 10^5$	Series[a]
0.3344	73.806	1.5320	I
.67024	53.581	1.5307	II
1.4000	38.084	1.5204	I
2.6510	28.768	1.5204	II
3.5224	24.471	1.5111	I
5.9664	18.975	1.5104	I
6.2922	18.940	1.5141	II
8.8766	15.638	1.5082	I
14.412	12.335	1.5030	I
14.721	12.491	1.5040	II
20.740	10.305	1.4966	I
21.060	10.475	1.5003	II
30.612	8.4910	1.4865	I
32.012	8.4924	1.4843	II
44.014	7.0759	1.4727	I
48.041	6.9232	1.4678	II
60.446	6.0226	1.4556	I
67.480	5.6899	1.4470	II
78.623	5.2610	1.4369	I
93.044	4.8178	1.4212	II
99.738	4.6475	1.4157	I
116.72	4.2721	1.3956	III
123.53	4.1498	1.3919	I
125.54	4.1126	1.3889	II
160.79	3.5976	1.3545	II
161.89	3.5824	1.3492	III
200.32	3.1846	1.3166	II
241.70	2.8625	1.2786	II
253.84	2.7836	1.2666	III
399.15	2.1158	1.1413	III
518.69	1.78146	1.0473	III
605.69	1.59898	0.98268	III
735.98	1.38433	.89334	III
861.82	1.22183	.81362	III
1006.4	1.07096	.72937	III
1070.0	1.01352	.69443	III
1220.6	0.89517	.61786	III

[a] In run II the silica cell (cell constant 0.9776) was employed. Jena glass cells were used in runs I and III (cell constants 3.7265 and 4.5760, respectively).

Discussion

The values of the mass law constant, *k*, follow the theoretical slope of the limiting Debye–Hückel law up to an ionic concentration of approximately 0.003 demal. This concordance has been demonstrated conclusively by earlier investigations.[4–14] The increase of the experimental error at these lower concentrations where the limiting law of Debye and Hückel holds is quite pronounced; hence it would be highly desirable to employ a method of extrapolation which would make use of measured conductances at the higher concentrations where the error is much smaller. With this in view various methods of extrapolating were tried and it was found that the various extensions of the limiting law of Debye and Hückel did not account satisfactorily for the observed departures. These departures of K from constancy are such that log K is linear with the concentration of undissociated acid. It is also true that the plot of log K is essentially linear with the total concentration. It was hoped that the data on cyanoacetic acid, which is the most highly dissociated of the acids considered here, would show clearly whether log K is linear with c_u or with c. Although in the case of this acid the difference between c_u and c is pronounced, neither plot shows decided departure from linearity, but slight evidence is offered in favor of the plot against c_u. The extrapolation is shorter in the case log K *versus* c_u than in the case log K *versus* c. These plots are shown in Fig. 1.



10^3 × Concentration—upper curve.
10^3 × Concentration of undissociated acid, lower curve.

Fig. 1.—Log K *versus* c (upper curve) and c_u (lower curve) for cyanoacetic acid at 25°.

The data on formic acid were extended up to the region of the constant boiling mixture of this acid with water in order to determine the upper limit to which the linearity of log K *versus* c_u prevails. Although at the higher concentrations the ionic concentrations and hence k and K calculated by this method are meaningless, they are included in Table II as formal functions resulting from the application of the method. The linearity persists up to a concentration of about 0.7 demal; the deviation amounting to less than 0.5% in the demal solution. The data on formic acid up to 1.2 demal are represented by the top curve in Fig. 3, the scale being such that the deviations mentioned above are not perceptible. The first set of experiments on formic acid in which bright electrodes were employed yielded a value of the ionization constant (1.825×10^{-4}) which differed considerably from that obtained by Harned and Embree[19] from e. m. f. measurements of cells with buffered solutions (1.767×10^{-4}) (a figure obtained by multiplying their published value by the density of water to convert from molality to demality). As their results check the previous results of Harned and Owen[20] obtained similarly with unbuffered solutions, it was deemed advisable to repeat the work. This was done about a year later using lightly platinized electrodes and taking care to exclude oxygen. The agreement with the previous year's results is satisfactory. The discrepancy between our value and that resulting from e. m. f. measurements seems inexplicable. Previous work on acetic[4] and chloroacetic[6] acids has shown satisfactory agreement between the two methods.

Our value for the ionization constant of butyric acid agrees well with that obtained from e. m. f. measurements by Harned and Sutherland.[21] The agreement with Belcher's[14] measurements by essentially the same method is not as good as might be anticipated, as may be seen from Fig. 2, where Belcher's experimental points would appear as a cluster near log $K = -5.177$–8 and $c_u = 0.000 - 0.005$. The 0.7% discrepancy in K_0 (the extrapolated value of K) is due in part (0.3%) to differences in the measured conductances of the acid, and in part (0.4%) to differences in the measured conductances of the salt, which are reflected in Λ_0 for butyric acid. The disparity in the results of the three investigators is shown in the following table

	Saxton and Darken	Belcher[14]	Harned and Sutherland[21] Measured	From smoothed curve
$K_0 \times 10^5$ (25°C.)	1.518	1.508	1.510	1.518
Λ_0	381.69	382.40		

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(19) Harned and Embree, THIS JOURNAL, **56**, 1042 (1934).

(20) Harned and Owen, *ibid.*, **52**, 5079 (1930).

(21) Harned and Sutherland, *ibid.*, **56**, 2039 (1934).

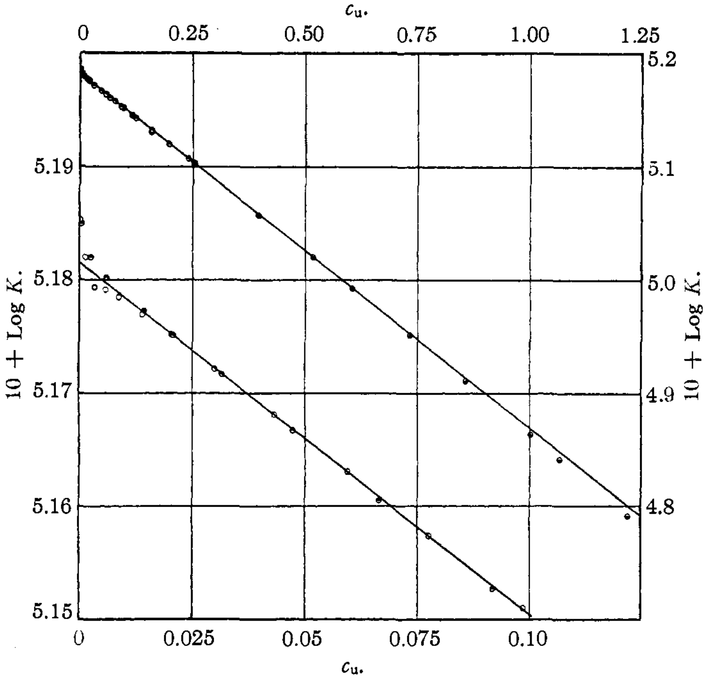

Fig. 2.—Log K *versus* c_u for butyric acid at 25°: concentration ranges, 0–0.1 (lower curve) and 0–1.25 (upper curve).

The extrapolated values from the log K *versus* c_u plots shown in Figs. 1 and 2 and the top curve of Fig. 3 correspond to 3.360×10^{-3}, 1.825×10^{-4}, and 1.518×10^{-5} for the ionization constants of cyanoacetic, formic and butyric acids, respectively.

Plots of log K *versus* c_u are shown in Fig. 3. The results of all available precise conductance measurements on aqueous solutions of weak acids (at 25°) are here shown in such a manner that the proper relative slopes of the lines are maintained, although the coördinate scales vary by large factors. From top to bottom the acids represented are: formic, acetic,[4] propionic,[14] monochloroacetic,[6] cyanoacetic, lactic,[13] and benzoic.[10] In order to avoid confusion, points corresponding to extremely low concentrations have been omitted.

Interpretation of the linearity of the plot of log K against c_u is complicated by the number of assumptions made in the evaluation of log K. In the series of equations

$$\log K_0 = \frac{-\Delta F^\circ}{2.3026\ RT} = \log \frac{a_{\pm}^2}{a_u} = \log \frac{c_i^2}{c_u}\frac{\gamma_{\pm}^2}{\gamma_u} = \log k + 2A\sqrt{c_i} + Bc_u = \log K + Bc_u$$

the first three equalities result from definition, ΔF° being the free energy of formation of one mole of undissociated acid (HA) from one mole of positive ion (H^+) and one mole of negative ion (A^-) at infinite dilution in pure water. It will be noted that the use of the third equality requires a method of measuring c_i and c_u. In the construction of Table II it is assumed that c_i and c_u can be obtained validly from conductance data. The fourth equality involves definition of k, introduction of the Debye–Hückel limiting law and statement of the linear c_u effect, while the fifth is merely another definition. The constant "A" is calculated on the assumption that the dielectric constant of the solution is that of pure water.

The reasons that log K varies with the concentration may be grouped in three classes:

1. Improper interpretation of the conductance data. In the calculation of Λ_e the effect of the presence of undissociated acid on the equivalent conductance of the dissociated portion of the acid, due to changes in viscosity and dielectric constant, has been neglected. Reliable measurements of the viscosity and dielectric constant of weak acid–water solutions are at present unavailable.

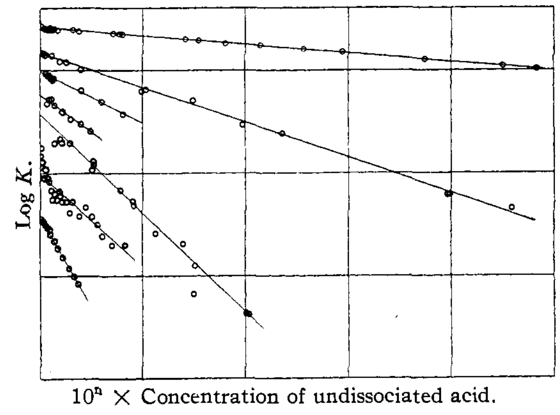

Fig. 3.—Log K *versus* c_u for aqueous solutions at 25° of: formic acid, acetic acid, propionic acid, chloroacetic acid, cyanoacetic acid, lactic acid, benzoic acid.

2. Errors introduced by use of the simplified form of the Debye–Hückel expression for the ionic activity coefficient. The authors have found that inclusion of extended terms in the Debye–Hückel relation does not improve the constancy of "K" but rather makes the deviations appear more complex. The error in the constant "A"

(caused by the assumption that the ion solvent is pure water, whereas it is really an aqueous solution of undissociated acid) is undoubtedly small.

3. Deviation of the activity coefficient of undissociated acid (γ_u) from unity. The determination of the activity coefficient of the undissociated portions of weak acids in a binary system, weak acid–water, according to the various possible experimental methods has not been investigated to any great extent. The activity coefficients of acetic acid from freezing-point lowerings show a rather pronounced maximum about 0.1 molal at 0°.[22,23] The effect in this region is complicated by the presence of a relatively large concentration of ions. Since the conductance data of MacInnes and Shedlovsky[4] on acetic acid (Fig. 3, second curve from top, covering the range up to 0.23 demal) show no such abnormality, it would seem either that conditions at 25° are significantly different from those at 0°, or that the interpretation of the freezing point measurements is erroneous, or that there is some compensating factor involved in the conductance data so that the maximum does not appear. Above 0.5 molal, freezing point data indicate an almost linear relationship between the activity coefficient of the undissociated portion of the acid and the molality (or any other common concentration function) for formic, acetic, propionic, and butyric acids.[21,22] Values of d log γ_u/dm at one molal obtained from freezing point measurements are compared in Table III with values of d log K/dc_u from conductance measurements at 25°, as shown in Fig. 3. Activity coefficients of weak acids in water from distribution experiments are not available at the present time, since the activity coefficients of these acids in solvents other than water are not known. The seemingly direct determination of activity coefficients from vapor pressure measurements is complicated by the polymerization of vapor acid molecules. In the case of acetic acid the extent of this polymerization has been investigated and the activity coefficients of undissociated acid in the aqueous phase, corrections being made for dimerization in the vapor phase, are tabulated in Landolt–Börnstein.[24] A plot of the log of these activity coefficients against the molality has a slope of about −0.12 at 1 molal. This compares favorably with d log K/dc_u read from the curve for acetic acid in Fig. 3 (−0.14). Similar data for formic acid are not available except at 80°, at which temperature the data in Landolt–Börnstein[24] yield a value for d log γ_u/dm of −0.007, which is considerably lower than d log K/dc_u read from the curve for formic acid in Fig. 3 (−0.035).

TABLE III

Acid	−d log γ_u/dm[19] (freezing point)	−Δ log γ_u/dm[20] (freezing point, m = 0.2–0.5)	−d log γ_u/dm (vapor pressure)	−d log K/d c_u (conductance) 25°C.
Formic	0.01	..	0.007 (at 80°)	0.035
Acetic	.029	0.12	0.12 (at 25°)	.14
Propionic	.051	..	..	.20
Butyric	.094	..	..	.31

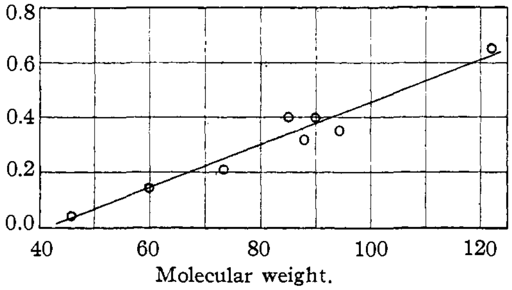

Fig. 4.—Slopes of (log K *versus* c_u) *versus* molecular weights of acids.

Hildebrand[25] has presented an equation relating the activity coefficient of one component of a "regular" binary solution to the mole fraction. At lower concentrations it reduces to the simple expression log $\gamma_2 = \alpha N_2$, in which the constant "α" is a function of the partial molal volumes and energies of vaporization of the two components. Since the ion concentrations are quite small at the higher concentrations of acids treated in this paper, the variation of activity coefficient of undissociated acid with concentration might be determined approximately from Hildebrand's equation by considering the solution to consist of two non-electrolytes, water and undissociated acid, forming "regular" solution. Unfortunately, "α" cannot be evaluated in the cases under consideration because of the polymerization of water and other departures from "regularity" as well as the uncertainty of the data available. However, it is interesting to observe that "α" and "B" have the same sign, and that, since the partial molal volumes are roughly in inverse order

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(22) Van Rysselberghe, *J. Phys. Chem.*, **39**, 415 (1935).

(23) Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932.

(24) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Erg. III, Springer, Berlin, 1936.

(25) Hildebrand, "Solubility," Reinhold Publishing Corp., 330 West 42nd St., New York, N. Y., 1936.

of molecular weight for the acids considered, it would be expected on the basis of Hildebrand's equation that the "B" 's would be in the order of the molecular weights. This is in accordance with experimental finding, shown graphically in Fig. 4.

Summary

A method of extrapolating ionization constants determined by the conductance method has been suggested. The method consists of plotting the logarithm of the ionization constant, which includes the ion activity coefficient calculated by the Debye–Hückel limiting law, against the concentration of undissociated electrolyte. The validity of the method is based mainly on empirical evidence which indicates the linearity of such a plot up to high concentrations in the case of the organic acids considered.

The thermodynamic ionization constants of cyanoacetic, formic, and butyric acids in aqueous solution at 25° have been measured by the conductance method and found to be

Cyanoacetic acid	3.360×10^{-3}
Formic acid	1.825×10^{-4}
Butyric acid	1.518×10^{-5}

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Polarographic Study of the Reduction of Chromate Ion at the Dropping Mercury Electrode

BY JAMES J. LINGANE AND I. M. KOLTHOFF

The purpose of this study was to investigate the reduction of chromate ions at the dropping mercury electrode by means of the polarographic technique.[1] The only previous study of the reduction of chromate at the dropping electrode is found in a recent paper of Thanheiser and Willems,[2] which appeared after the present investigation was begun. These authors studied the reduction of chromate only in sodium hydroxide medium, with particular reference to the polarographic determination of chromium in steel. We have investigated the reduction of chromate in unbuffered solutions and in the presence of buffers, as well as in strongly alkaline medium, and have discovered several new and interesting phenomena.

Experimental

The current–voltage curves (polarograms) were obtained and photographically recorded by means of a standard Heyrovsky polarograph.[1] Most of the polarograms were obtained by using an external saturated calomel electrode as anode, rather than the customary stationary pool of mercury on the bottom of the cell, in order to minimize contact of the chromate solutions with mercury. The H-cell and dropping electrode arrangement described by Lingane and Laitinen[3] was used. The cell was kept in a water thermostat at 25 ± 0.1°, and air was displaced from the solutions with nitrogen. Reagent grade chemicals and conductivity water were used in preparing all solutions.

In most of the experiments the pressure on the dropping mercury, hereinafter designated by h, was maintained at 72.0 ± 0.2 cm. of mercury. The amount of mercury flowing from the dropping electrode per sec. under a pressure of 72 cm. designated by m, was determined by the method already described.[1,4] Two different capillaries were used, for which the values of m were, respectively, 1.54 and 1.58 mg. sec.$^{-1}$ at $h = 72$ cm.

The drop time, in dilute potassium chloride solution with the dropping electrode disconnected from the polarizing e. m. f., was 4.2 ± 0.1 sec. The drop time occasionally became erratic, especially in neutral or slightly acid chromate solutions. This probably was caused by the wetting of the interior of the capillary by the chromate solution when the mercury thread retracts momentarily into the lumen after each mercury drop falls. This erratic behavior was eliminated by dipping the tip of the capillary into concentrated nitric acid, and then washing with water, while the mercury was issuing from the tip. The erratic dropping also could be eliminated by simply polarizing the dropping electrode cathodically for a few seconds at a potential of about −1.5 v.

The current-recording galvanometer of the polarograph was calibrated carefully by the method already described.[4]

Reduction of Chromate in Alkaline Medium.— In unbuffered solutions of potassium chromate, with potassium chloride as the supporting electrolyte, the c. v. curve of chromate consists of several waves as shown by curve 1 in Fig. 1.

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(1) For a review of the polarographic method, see I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1–94 (1939).

(2) G. Thanheiser and J. Willems, *Mitt. Kaiser Wilhelm Inst. Eisenforsch. (Düsseldorf)*, **21**, 65 (1939).

(3) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal., Ed.*, **11**, 504 (1939).

(4) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).