THE DISSOCIATION CONSTANT OF ACETIC ACID FROM 0 TO 35° CENTIGRADE[1]
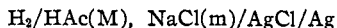
BY HERBERT S. HARNED AND RUSSELL W. EHLERS

Recently, Harned and Owen[1a] have shown that it is possible to determine the dissociation constants of weak acids from cells without liquid junctions of the type

$$H_2/HAc(M), NaCl(m)/AgCl/Ag$$

From the results of Harned and Robinson,[2] they computed the dissociation constant of acetic acid, and from their own data that of formic acid, both at 25°. The value obtained for the dissociation constant of acetic acid was 1.75×10^{-5}, which was considerably lower than the usually accepted value, but agrees with the value of 1.747×10^{-5} computed from conductance measurements as recently reported by MacInnes and Shedlovsky.[3] Since our value was determined from measurements which were not made for this purpose, we have redetermined this constant by a somewhat different method by employing the cell

$$H_2/HAc(m_1), NaAc(m_2), NaCl(m_3)/AgCl/Ag$$
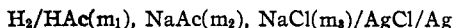
which is seen to contain an acetic acid–sodium acetate buffer mixture. To extend our knowledge of this subject, the dissociation constant has been evaluated at 0, 5, 10, 15, 20, 25, 30 and 35°.

Discussion of the Method

The electromotive force of the cell in question is given by the well-known equation

$$E = E_0 - \frac{RT}{F} \ln \gamma_H \gamma_{Cl}\, m_H m_{Cl} \tag{1}$$

The thermodynamic equation for the dissociation of acetic acid is

$$K = \frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}} \frac{m_H m_{Ac}}{m_{HAc}} \tag{2}$$

K is the dissociation constant of the acid, the "γ's" and "m's" represent the activity coefficients and molal concentrations of the ionic species denoted by subscripts, and E_0 is the normal electrode potential of the cell

$$H_2/HCl(m)/AgCl/Ag$$
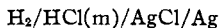
Upon eliminating m_H from equations (1) and (2), and rearranging terms, we obtain

[1] The present communication contains material which represents part of a Thesis to be presented by Russell W. Ehlers to the Graduate School of Yale University in partial fulfilment of the degree of Doctor of Philosophy, June, 1932.

[1a] Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

[2] Harned and Robinson, *ibid*, **50**, 3157 (1928).

[3] MacInnes and Shedlovsky *ibid.*, **53**, 2419 (1931).

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{HAc} m_{Cl}}{m_{Ac}} = -\frac{RT}{F} \ln \frac{\gamma_H \gamma_{Cl} \gamma_{HAc}}{\gamma_H \gamma_{Ac}} - \frac{RT}{F} \ln K \qquad (3)$$

This equation is extraordinarily easy to use if the values of E_0 are known at the desired temperatures. The first member on the right contains the logarithm of the ratio of two ionic activity coefficient products. This ratio equals unity at infinite dilution and varies little from unity at low ionic strengths. This is also true for γ_{HAc}. Further, the logarithm of such a quantity as this ratio is known to vary linearly with the ionic strength. Therefore, if the quantity on the left side of this equation be plotted against the ionic strength, μ, a curve which is very nearly straight should be obtained. The intercept at μ equals zero will be $-(RT/F) \ln K$, from which K may easily be computed.

A second method, and the one which we have employed, is as follows: Let the right-hand side of equation (3) equal $-(RT/F) \ln K'$: If K' be plotted against μ, its intercept at zero μ is K, since the activity coefficients become unity at infinite dilution. Indeed, in the present case, this method is as good as the first, since the plot of K' against μ has no greater curvature than the plot of log K' against μ at the lower concentrations.

The evaluation of the left-hand side of equation (3) is readily made. m_{Cl} is known, m_{HAc} equals $m_1 - m_H$, and m_{Ac} equals $m_2 + m_H$. If an approximate value of K be used, then m_H may be computed and m_{HAc} and m_{Ac} evaluated.[4] Thus, since all the terms on the left are capable of being known, K' and subsequently K may readily be evaluated.

Preparation of Solutions and Experimental Procedure

(1) **Materials.**—Sodium acetate was purified by three recrystallizations of a high grade analyzed salt from conductivity water. The solutions were never boiled, so that loss of acetic acid by evaporation from the hydrolyzed salt solution was avoided. The crystals were dried by suction.

Sodium chloride was recrystallized twice from conductivity water.

Acetic acid was distilled four times, the first three from a 2% (2 g. per 100 g. of acetic acid) solution of chromic anhydride, in an all-glass still through an efficient fractionating column. The first and last quarters were always discarded.

(2) **Solutions.**—Water of specific conductance of 10^{-6} was used in the preparation of all solutions. Stock solutions of sodium acetate, sodium chloride, and acetic acid approximately 1 M were prepared and these were standardized as follows.

(a) The sodium chloride and hydrochloric acid solutions were analyzed by determining the chloride content by precipitation of silver chloride. Their molalities were known to within 1 part in 3000, or 0.03%.

(b) The sodium acetate solution was analyzed by evaporation of a 5-g. sample with sulfuric acid. This was carried out very slowly in a muffle furnace where the heat was distributed with sufficient uniformity so that any spattering was avoided. When

---

[4] As far as this correction is concerned, we have found that a change in K from 1.65×10^{-5} to 1.75×10^{-5} causes a change in K' of only one in the third decimal place. Since K may readily be estimated within their much narrower limits than the above, any error due to this correction is negligible.

the fumes of sulfur trioxide appeared, air saturated with ammonia was passed over, and the evaporation continued to the final stage. The quantity of sodium sulfate weighed was approximately 0.5 g. The analyses checked to within 0.05%.

(c) Acetic acid was standardized by titration against a carbonate-free sodium hydroxide solution whose strength was determined by titration against a very carefully analyzed hydrochloric acid solution. Weight burets were employed and vacuum corrections made when necessary. The values of the molalities represent the average of numerous determinations which agreed within 0.1% of the total acetic acid. The molality of the acetic acid was therefore known to at least 1 part in 1000, or 0.1%.

(3) **Experimental Procedure.**—The cells were of the customary kind for this purpose, and were arranged so that they could be filled in vacuum. The hydrogen electrodes were of platinum foil (1.5 × 3 cm.) and a deposit of platinum black formed by 0.5 ampere per electrode for three minutes was found very satisfactory. The silver-silver chloride electrodes were of the type (2) described by Harned.[5]

The solutions were prepared by weighing portions of the standardized solutions in weighed flasks. Appropriate amounts of water were added and the solutions boiled under reduced pressure. Hydrogen was then admitted into the flasks above the solutions. The loss in weight by boiling was assumed to be water. The cells were filled by employing vacuum technique.

For the preliminary measurements, the same solution and electrodes were used throughout the entire temperature range of from 0 to 35°. Sometimes thirty hours were necessary for these measurements and frequently cells containing solutions of the same concentration would barely agree within 0.1 mv., especially if the initial temperature was 0°. For this reason, the final results recorded were made in two series. The first was from 0 to 20° and the second from 15 to 35°. Duplicate cells checked within a few hundredths of a millivolt. All reported results of the electromotive forces of the cells containing the acetic acid are averages of six cells.

Ice was used to cool the thermostat to a temperature of 0.1 to 0.2°. The temperature was not changed until the readings were constant over a period of forty-five minutes. Two thermometers calibrated against a standard thermometer were placed at the ends of the thermostat. No variation in temperature was noticeable and the control was within ±0.01°. All electromotive forces are calculated for 1 atm. pressure of hydrogen.

Electromotive Forces of the Cells: $H_2/HCl(m)/AgCl/Ag$ **and the Evaluation of** E_0.—Table I contains the measurements of the cells containing the hydrochloric acid. The following procedure was adopted to compute E_0. The equation for the cells may be written

$$E + 2k \log m = E_0 - 2k \log \gamma \qquad (4)$$

where k equals $2.3026\ RT/NF$. The left side of this equation was first plotted on a large scale against $m^{1/2}$. The results at round concentrations read from this very sensitive family of graphs are given in Table II. The evaluation of E_0 at each temperature was made by the method suggested by Hitchcock.[6] In dilute solutions, $\log \gamma$ varies according to the law

$$\log \gamma = -0.5\ m^{1/2} + bm \qquad (5)$$

Combining with equation (4) and rearranging, we obtain

$$E + 2k \log m - km^{1/2} = E_0 - 2\ kbm \qquad (6)$$

[5] Harned, THIS JOURNAL, **51**, 416 (1929).

[6] Hitchcock, *ibid.,* **50**, 2076 (1928).

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HCl(m)/AgCl/Ag$

m	E_0'	E_5	E_{10}	E_{15}	E_{20}	m	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}
0.003215	0.50933	0.51196	0.51436	0.51662	0.51864	0.003215			0.52053	0.52224	0.52389
.003661	.50334	.50578	.50800	.51008	.51200	.003564	0.51150	0.51349	.51527	.51693	.51846
.005314	.48644	.48860	.49054	.49232	.49395	.004488	.50051	.50223	.50384	.50533	.50665
.005763	.48275	.48484	.48679	.48848	.49003	.004776			.50084	.50230	.50358
.007771	.46912	.47091	.47258	.47402	.47530	.005619	.48957	.49110	.49257	.49388	.49504
.008636	.46435	.46610	.46771	.46905	.47024	.006239	.48461	.48614	.48747	.48869	.48975
.008715	.46401	.46575	.46727	.46863	.46987	.007311	.47688	.47826	.47948	.48052	.48144
.011095	.45314	.45468	.45601	.45721	.45823	.008514					
.013049	.44586	.44725	.44843	.44947	.45039	.008636			.47135	.47226	.47304
.013407	.44466	.44596	.44719	.44811	.44899	.009138	.46635	.46757	.46860	.46949	.47024
.013981	.44273	.44411	.44522	.44620	.44704	.009436			.46711	.46795	.46868
.016457	.43544	.43667	.43766	.43850	.43921	.011195	.45672	.45775	.45861	.45934	.45991
.018369	.43055	.43170	.43260	.43335	.43394	.013500	.44776	.44868	.44938	.44998	.45038
.021028	.42425	.42526	.42607	.42676	.42726	.013407			.44974		
.025630	.41557	.41643	.41718	.41766	.41801	.01473	.44361	.44444	.44512	.44565	.44596
.034920	.40181	.40240	.40282	.40308	.40318	.01710	.43658	.43725	.43783	.43822	.43844
.041245	.39426	.39470	.39502	.39515	.39513	.02305	.42253	.42294	.42329	.42346	.42345
.04935	.38640	.38666	.38685	.38685	.38665	.02563			.41824	.41830	.41821
.05391	.38255	.38284	.38299	.38289	.38258	.04749	.38872	.38861	.38834	.38792	.38740
.06393	.37501	.37508	.37505	.37485	.37443	.05391			.38222	.38713	.38108
.07273	.36917	.36921	.36904	.36872	.36823	.06268	.37577	.37545	.37499	.37435	.37362
.08631	.36167	.36157	.36130	.36085	.36022	.09751			.36363	.35265	.35158
.09751	.35610	.35597	.35568	.35511	.35438	.12381			.34199	.34086	.33963
.12354	.34567	.34530	.34478	.34402	.34311	.005314	.34383	.34297	.49145	.49275	.49385
.009436	.46050	.46210	.46359	.46492	.46609						
.004776	.49142	.49360	.49564	.49754	.49930						

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HCl(m)/AgCl/Ag$ AT ROUND CONCENTRATIONS

m	E_0'	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}
0.005	0.48916	0.49138	0.49338	0.49521	0.44690	0.49844	0.49983	0.50109
.006	.48089	.48295	.48480	.48647	.48800	.48940	.49065	.49176
.007	.47390	.47584	.47756	.47910	.48050	.48178	.48289	.48389
.008	.46785	.46968	.47128	.47270	.47399	.47518	.47617	.47704
.009	.46254	.46426	.46576	.46708	.46828	.46937	.47026	.47103
.010	.45780	.45943	.46084	.46207	.46319	.46419	.46499	.46565
.02	.42669	.42776	.42862	.42925	.42978	.43022	.43049	.43058
.03	.40859	.40931	.40993	.41021	.41041	.41056	.41050	.41028
.04	.39577	.39624	.39668	.39673	.39673	.39666	.39638	.39595
.05	.38586	.38616	.38641	.38631	.38614	.38589	.38543	.38484
.06	.37777	.37793	.37802	.37780	.37749	.37709	.37648	.37578
.07	.37093	.37098	.37092	.37061	.37017	.36965	.36890	.36808
.08	.36497	.36495	.36479	.36438	.36382	.36320	.36285	.36143
.09	.35976	.35963	.35937	.35888	.35823	.35751	.35658	.35556
.1	.35507	.35487	.33451	.35394	.35321	.35240	.35140	.35031
E_0	.23627	.23386	.23126	.22847	.22550	.22239	.21918	.21591

The left side of equation (6) was plotted against m. The graphs have only a very slight curvature and may easily be extrapolated to zero m. The ordinate reading gives E_0. The values thus obtained at the eight temperatures are given in the bottom row of Table II. The same procedure was adopted at 25° using 0.5065 instead of 0.5 for the universal constant of the Debye and Hückel theory. This was found to make no appreciable difference in the value of E_0 obtained since the slope, $2\,kb$, varied simultaneously. From these results and by this method we believe that E_0 has been evaluated within ± 0.02 mv. Perhaps a different cell technique would give somewhat different values, but since we have employed the same procedure for the cells containing the acetic acid as for the cells under consideration, such a discrepancy would make no error in our final values of the dissociation constant. The value of 0.22239 at 25° agrees very well with that of Roberts[7] who obtained 0.22240 from his electromotive force measurements.

Measurements of the Cells $H_2/HAc(m_1)$, $NaAc(m_2)$, $NaCl(m_3)/AgCl/Ag$ and the Evaluation of the Dissociation Constant of Acetic Acid.—In Table III, measurements are given of the cells containing the acetic acid–sodium acetate buffer solutions and sodium chloride. From these results and the values obtained for E_0, the values of K' computed by equation (3) are given in the second part of Table III at the ionic strengths designated. In Fig. 1 these values are plotted against the ionic strength. The plots have a definite curvature, but straighten out at the lower concentrations so that the extrapolation may be readily and accurately made. The

7 Roberts, THIS JOURNAL, **52**, 3877 (1930).

TABLE III
ELECTROMOTIVE FORCES OF THE CELLS: $H_2/HAc(m_1)$, $NaAc(m_2)$, $NaCl(m_3)/AgCl/Ag$

m_1	m_2	m_3	E_0'	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}
0.004779	0.004599	0.004896	0.61995	0.62392	0.62789	0.63183	0.63580	0.63959	0.64335	0.64722
.012035	.011582	.012426	.59826	.60183	.60538	.60890	.61241	.61583	.61922	.62264
.021006	.020216	.021516	.58528	.58855	.59186	.59508	.59840	.60154	.60470	.60792
.04922	.04737	.05042	.56545	.56833	.57128	.57413	.57699	.57977	.58257	.58529
.08101	.07796	.08297	.55388	.55667	.55928	.56189	.56456	.56712	.56964	.57213
.09056	.08716	.09276	.55128	.55397	.55661	.55912	.56171	.56423	.56672	.56917

VALUES OF K' AND EXTRAPOLATED VALUES OF THE DISSOCIATION CONSTANT, K

$\mu = m_2 + m_3 + m_H$	$t = 0°$	$5°$	$10°$	$K' \times 10^5$ $15°$	$20°$	$25°$	$30°$	$35°$
0.00951	1.647	1.693	1.724	1.743	1.748	1.752	1.756	1.747
.02403	1.637	1.683	1.714	1.736	1.744	1.747	1.749	1.743
.04175	1.627	1.675	1.707	1.733	1.738	1.743	1.745	1.736
.09781	1.610	1.660	1.692	1.718	1.728	1.734	1.736	1.735
.16095	1.600	1.641	1.681	1.708	1.718	1.724	1.730	1.731
.17994	1.598	1.643	1.678	1.709	1.720	1.726	1.731	1.731
$K \times 10^5$	1.653	1.699	1.727	1.743	1.751	1.754	1.755	1.750

values of K thus determined at zero μ are given in the last row of the second part of Table III.   The results are of a very high order of accuracy since nearly all points lie within two in the third decimal place from the curves.   The maximum deviation which occurs at 0.1μ of the $5°$ series lies seven in the third decimal place from the curve.   This corresponds to an inconsistency of less than 0.1 mv.   Since at the lower concentrations the $35°$ graph lies very near that at $20°$, it has been shown on a separate part of the figure.   As previously mentioned, the maximum estimated error in analysis occurs with the acetic acid solutions and amounts to $\pm0.05\%$.   This causes an error in K of ±0.001.
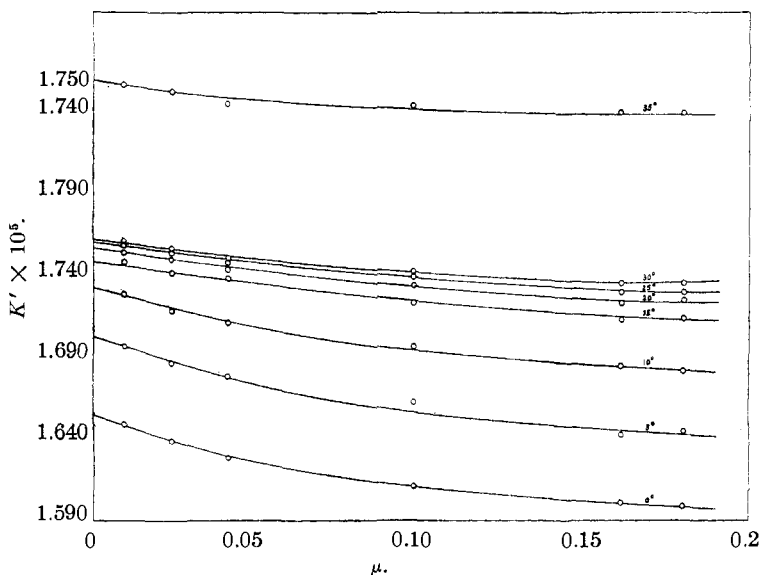

Fig. 1.—Plots of K' against μ employed in the determination of the dissociation constants.

In Fig. 2 the values of K are plotted against the temperature.   The results are very consistent since all points fall on the smooth curve to within one or two in the third decimal place.   Further, a maximum is apparent at $30°$.

The result we obtain at $25°$ is 1.754×10^{-5}, which agrees with the value of 1.75×10^{-5} obtained from somewhat different electromotive force measurements by Harned and Owen.   Harned and Murphy[8] found that K varied very little between 20 and $30°$, and assumed the value of 1.75×10^{-5}.   Our results show a slight variation of four in the third decimal place through this temperature range.   The result obtained by the electromotive force methods agrees very well with that of MacInnes and Shed-

[8] Harned and Murphy, THIS JOURNAL. **53**, 8 (1931)

lovsky, who obtained 1.747×10^{-5} by very careful conductance measurements. As a result of this agreement, we can say with certainty that K at 25° is known to the second decimal place and is 1.75×10^{-5}. Further, we have every reason to believe that the results at the other temperatures are as accurate as those at 25°.
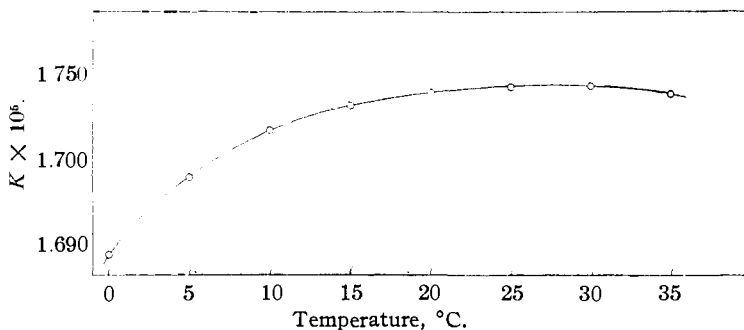

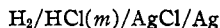Fig. 2.—The dissociation constant of acetic acid as a function of the temperature.

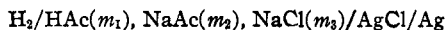## Summary

1. Measurements of the cells

$$H_2/HCl(m)/AgCl/Ag$$

at low concentrations of hydrochloric acid have been made at five-degree intervals through a temperature range of 0 to 35°. From these, values of E_0 of equation (1) have been evaluated at all temperatures in question.

2. Measurements of the cells

$$H_2/HAc(m_1), NaAc(m_2), NaCl(m_3)/AgCl/Ag$$

have been made at the same temperatures. From these measurements, the dissociation constant of acetic acid has been computed at 0, 5, 10, 15, 20, 25, 30 and 35°. The value of 1.754×10^{-5} at 25° agrees well with 1.75×10^{-5} obtained by Harned and Owen, and also compares favorably with 1.747×10^{-5} obtained by MacInnes and Shedlovsky from conductance measurements.

STERLING CHEMISTRY LABORATORY
NEW HAVEN, CONNECTICUT