7. The interdependence of the rates of a base catalyzed reaction and the dissociation constants of the catalysts on passing to new media is discussed in the light of the Brönsted equation. Attention is called to a linear relation between the logarithms of the rate constants in the two media.

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[Contribution from the Department of Chemistry, Columbia University]

Dissociation Constants of Deutero Acids by E. m. f. Measurements

By C. K. Rule and Victor K. La Mer

Although the dissociation constants of weak acids are decreased by a factor of two- to four-fold on passing from H_2O to D_2O, there is disagreement regarding the underlying theory. One school holds that the ratio of the dissociation constants of the proto and deutero forms of an acid is a function of the strength of the acid; the second that the ratio is constant for acids of a given type; a third,[1] that the ratio is uniformly three regardless of type.

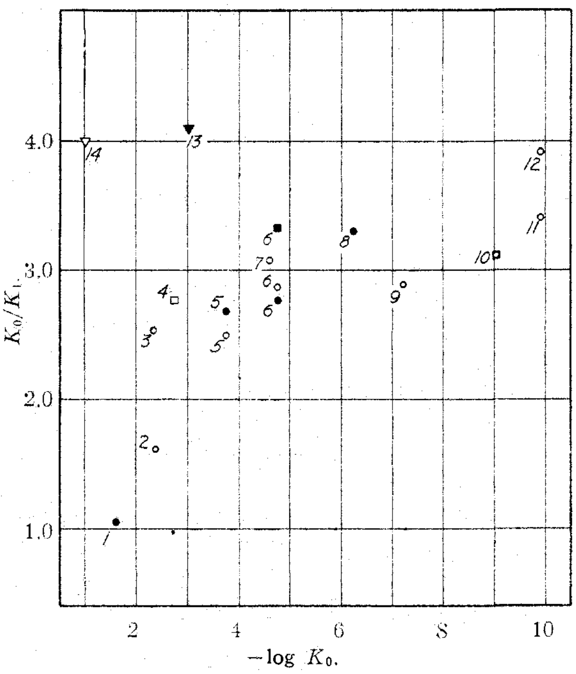

Fig. 1.—Dissociation constant ratios. Acids and references: 1 oxalic,[1a] 2 phosphoric (first),[3] 3 glycine,[3] 4 chloroacetic,[2] 5 formic,[1a,3] 6 acetic,[1a,4,23] 7 aniline hydrochloride,[3] 8 cacodylic,[1a] 9 phosphoric (second),[3] 10 ammonium chloride,[2] 11 glycine hydrochloride,[3] 12 trimethylamine hydrochloride,[3] 13 salicylic,[4] 14 picric.[1b] Methods of measurements: ● catalytic, ○ potentiometric with transference, □ conductimetric, ▽ distribution coefficient, ▼ potentiometric (approximate), ■ conductimetric and potentiometric without transference.

Lewis and Schutz[2] predicted that the ratio will depend on the strength of the acid—being larger the weaker the acid. They assumed that the potential field is unchanged by the substitution of a deuteron for a proton. Then the deutero acid will have a lower zero point energy and will be less dissociated, the difference increasing with decreasing strength of the acid. They mention that the difference in the extent of dissociation of the proto and deutero acids will depend also on the difference between their entropies of dissociation.

On the other hand, Schwarzenbach[3] concludes from measurements on cells with liquid–liquid junctions that the ratio is a function of the type of the acid, being smaller for carboxylic acids than for amine hydrochlorides.

A critical consideration of the data in the literature shows that there is little accurate work upon which to base a decision between these conflicting theories. These data are shown in Fig. 1. The ratios of the dissociation constants of the proto to those of the deutero acids are plotted against the logarithm of the dissociation constants of the proto acids. The differences of 15 and 20% between the ratios reported by different investigators for acetic acid are an indication of the inaccuracy of the data.

When accurate measurements are required, the uncertainty introduced by the presence of liquid–liquid junctions between H_2O and D_2O should be avoided in potentiometric studies. Korman and La Mer[4] have demonstrated the suitability of the quinhydrone electrode for measurements in H_2O–D_2O mixtures. We have accordingly reinvestigated their cells

[1] (a) Hornel and Butler, *J. Chem. Soc.*, 1361 (1936); (b) Gross and Wischin, *Trans. Faraday Soc.*, **32**, 879 (1936); (c) Drucker, *Trans. Faraday Soc.*, **33**, 660 (1937).

[2] Lewis and Schutz, This Journal, **56**, 1913 (1934). See also Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

[3] Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

[4] Korman and La Mer, This Journal, **58**, 1396 (1936).

$$\text{Ag–AgCl} \mid \text{HCl–DCl } (H_2O\text{–}D_2O)\ QQH_2\text{–}QQD_2 \mid \text{Pt} \quad \text{I}$$

$$\text{Ag–AgCl} \mid \text{HA–DA}(m_1),\ \text{MA}(m_2),\ \text{MCl}(m_3)\ (H_2O\text{–}D_2O)\ QQH_2\text{–}QQD_2 \mid \text{Pt} \quad \text{II}$$

at 25° and have extended the measurements to other acids and temperatures. QQH_2 and QQD_2 represent proto and deutero quinhydrone; HA and DA, the proto and deutero forms of a weak acid; MA, an alkali metal salt of the acid; MCl, an alkali metal chloride.

Since the cells are without liquid–liquid junctions, the cell processes are unambiguous

$$\text{I}\quad Q(H_2O\text{–}D_2O) + 2(H^+ + D^+) + 2Cl^-\ (H_2O\text{–}D_2O) + 2Ag(s) \rightleftharpoons (QH_2\text{–}QD_2)\ (H_2O\text{–}D_2O) + 2AgCl(s)$$

$$\text{II}\quad Q(H_2O\text{–}D_2O) + 2(HA + DA)\ (m_1 \text{ in } H_2O\text{–}D_2O) + 2MCl(m_3 \text{ in } H_2O\text{–}D_2O) + 2Ag(s) \rightleftharpoons 2AgCl(s) + (QH_2\text{–}QD_2)(H_2O\text{–}D_2O) + 2MA(m_2 \text{ in } H_2O\text{–}D_2O)$$

Apparatus and Experimental Procedure

Accurate measurements with the silver–silver chloride electrode require the exclusion of oxygen and liberal washing with the cell solution.[5] A semi-micro cell, Fig. 2, was devised which avoided waste of solution, exposure to air, or contact of the solution with any surfaces except Pyrex which had been steamed. The relatively higher ratio of glass and electrode surfaces to the volume of solution in the micro as compared to the macro technique demands special care in cleaning apparatus and eliminating contact with foreign gases.

Solutions were made up in a 50-cc. flask fitted with a ground glass cap, stopcock and a small ground glass joint. The solvent was run directly from the pycnometer into the flask; solids were added contained in micro weighing bottles; liquid solutes were added from weight burets. The flask containing the solution was attached to the vacuum and nitrogen gas lines and air was removed from the solution by repeated evacuation and shaking followed by the admission of nitrogen. Account was taken of the loss of water by evaporation.

The cell with electrodes in place was connected to the vacuum line. The flask containing the solution was connected directly to the cell through a ground glass joint. Having evacuated the cell, small amounts of solution were admitted to wash the silver–silver chloride electrodes. The wash solution was kept in contact with the electrodes for some ten minutes, was drawn off into a trap, and the washing was either repeated or the entire cell filled. No difference was observed between the potentials of cells in which the electrodes were rinsed twice and those in which they were rinsed only once. Each solution of 16 cc. sufficed to fill two cells, allowing for rinsing.

A Leeds and Northrup type K-II potentiometer was used with two Bureau of Standards Weston cells. The thermostats were maintained at 5, 25 and 45 ± 0.02° as determined by a B. of S. platinum resistance thermometer. No hysteresis was observed when the cells were transferred back and forth from one thermostat to another. Distillation of solvent was prevented by filling the cells completely. The potentials of the duplicate silver–silver chloride electrodes against the duplicate quinhydrone electrodes were recorded every ten minutes. Equilibrium was assumed when the potentials remained constant within 0.1 millivolt for an hour. No drift of potential was observed in the use of the quinhydrone electrode at 45° except when the cell contained a buffered solution of dihydrogen phosphate.

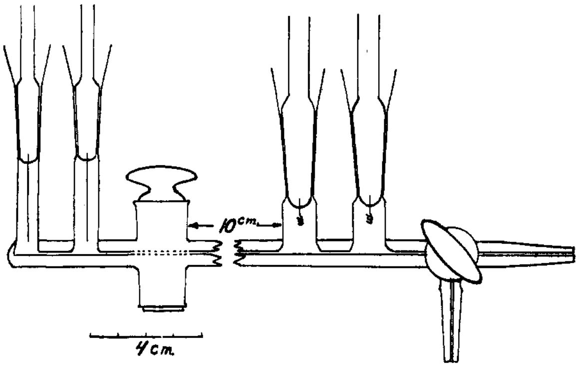

Fig. 2.

Purification of Materials.—Three preparations of quinhydrone were used—one made by the method of Biilman and Lund.[6] The others were Eastman, one of which was purified by recrystallization from conductivity water in an atmosphere of carbon dioxide. All gave the same potentials. Silver–silver chloride electrodes were made as described by Rule and La Mer,[7] the silver chlorate having been prepared from silver carbonate and chloric acid free from other halogens, and twice recrystallized.

Bureau of Standards benzoic acid was used. Sodium benzoate was recrystallized from alcohol and was neutral to phenolphthalein. Potassium dihydrogen phosphate was recrystallized three times and dried at 110°. Its loss of weight on ignition was 13.16% (theory 13.23%). When titrated against sodium hydroxide using phenolphthalein indicator, its molecular weight was found to be within 0.3% of the theoretical. $Na_2HPO_4 \cdot 2H_2O$ was a sample of special purity prepared for work with enzymes. It was exposed to the atmosphere until it had reached constant weight. Loss on ignition was 25.29% (theory 25.30%). Analysis for phosphate, by precipitation as $MgNH_4PO_46H_2O$ and weighing as $Mg_2P_2O_7$, showed 53.29% (theory 53.36%).

Sodium chloride was recrystallized by La Mer and Kamner.[8] Potassium chloride was recrystallized once. They were dried at 110°.

H_2O–D_2O mixtures were recovered from previous experiments. The quinhydrone was oxidized by alkaline potassium permanganate in a flask kept at 80° for thirty-six hours or until permanganate was no longer reduced. The water was distilled *in vacuo* and redistilled *in vacuo* from an alkaline solution. Its density and conductivity were determined in a combined pycnometer and conductivity cell whose volume was 16 cc. The water was forced through a glass tube directly from the pycnometer into the flask in which the solution was made up. Water having a specific conductivity greater than 2.10^{-6} ohm^{-1} was not used.

Constant boiling hydrochloric acid was prepared according to Bonner and Titus.[9]

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[5] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[6] Biilman and Lund, *Ann. chim.*, [9] **16**, 321 (1921).

[7] Rule and La Mer, THIS JOURNAL, **58**, 2339 (1936).

[8] La Mer and Kamner, *ibid.*, **57**, 2662 (1935).

[9] Bonner and Titus, *ibid.*, **52**, 633 (1930).

Nitrogen gas was freed from oxygen by passage through a tower containing copper spirals bathed with a solution of ammonium hydroxide saturated with ammonium chloride.[10] Ammonia and water were removed subsequently by means of two absorption towers filled with sulfuric acid solutions, followed by two traps cooled to −78°.

Methods of Calculation

The ratio of the dissociation constants of hydroquinone in H_2O and D_2O can be calculated from the difference of the electromotive forces of cell I when H_2O is replaced by D_2O.[11] Silver and silver chloride are solids whose activities are unity by definition whether the electrode be immersed in H_2O or in D_2O.[12]

Hence, the standard electromotive force of cell I is

$$E_0^0 = \frac{RT}{2F} \ln \frac{(\mathrm{QH_2})_0}{(\mathrm{Q})_0(\mathrm{HCl})_0} \qquad (1)$$

when the solvent is H_2O, and is

$$E_1^0 = \frac{RT}{2F} \ln \frac{(\mathrm{QD_2})_1}{(\mathrm{Q})_1(\mathrm{DCl})_1} \qquad (2)$$

when the solvent is D_2O.[14]

Subtracting E_0^0 from E_1^0

$$E_1^0 - E_0^0 = \frac{RT}{2F} \ln \frac{(\mathrm{QD_2})_1(\mathrm{Q})_0(\mathrm{HCl})_0^2}{(\mathrm{QH_2})_0(\mathrm{Q})_1(\mathrm{DCl})_1^2} \qquad (3)$$

Introducing K_0 and K_1, the geometric mean of the first and second dissociation constants of hydroquinone and hydroquinone-d_2, respectively

$$E_1^0 - E_0^0 = \frac{RT}{2F} \ln \frac{(\mathrm{Q})_0(\mathrm{Cl}^-)_0^2(\mathrm{Q}^=)_1K_0^2}{(\mathrm{Q})_1(\mathrm{Cl}^-)_1^2(\mathrm{Q}^=)_0K_1^2} \qquad (4)$$

The relative free energies of chloride ions and of quinone ions in H_2O and in D_2O not being known, we must assume that the factor $(\mathrm{Q})_0(\mathrm{Cl}^-)_0^2(\mathrm{Q}^=)_1/(\mathrm{Q})_1(\mathrm{Cl}^-)_1^2(\mathrm{Q}^=)_0$ is unity. Eq. (4) becomes

$$E_1^0 - E_0^0 = \frac{RT}{F} \ln \frac{K_0}{K_1} \qquad (5)$$

Using this equation, the ratios of the dissociation constants of hydroquinone and hydroquinone-d_2 can be calculated from the difference of the standard electromotive forces of cell I when the solvent is D_2O and when it is H_2O.

On the other hand, the equilibrium constant, K_2, of the exchange reaction $\mathrm{QH_2} + 2\mathrm{DCl} \rightleftarrows \mathrm{QD_2} + 2\mathrm{HCl}$ can be calculated on the assumption that quinone has the same activity in D_2O as in H_2O. Equation (3) then reduces to

$$E_1^0 - E_0^0 = \frac{RT}{2F} \ln \frac{(\mathrm{QD_2})_1(\mathrm{HCl})_0^2}{(\mathrm{QH_2})_0(\mathrm{DCl})_1^2} = \frac{RT}{2F} \ln K_2 \qquad (6)$$

The dissociation constants of other acids in H_2O–D_2O mixtures can be determined from the e. m. f. of cell II following the methods of Harned and co-workers[15] and Korman and La Mer,[4] who first applied the method to deutero acids. The e. m. f. of cell II for an H_2O–D_2O mixture in which the mole fraction of deuterium is n, is[16]

$$E_n = E_n^0 - \frac{RT}{2F} \ln \frac{(\mathrm{QH_2} + \mathrm{QD_2})_n}{(\mathrm{Q})_n(\mathrm{H^+} + \mathrm{D^+})_n^2(\mathrm{Cl}^-)_n^2} \qquad (7)$$

For low ionic strengths where the salt effect of the quinhydrone electrode is negligible $(\mathrm{QH_2} + \mathrm{QD_2})_n = (\mathrm{Q})_n$ and

$$E_n = E_n^0 - \frac{RT}{F} \ln \frac{1}{(\mathrm{H^+} + \mathrm{D^+})_n(\mathrm{Cl}^-)_n} \qquad (8)$$

In this equation E_n is the e. m. f. of cell II and E_n^0 is the standard e. m. f. of cell I when the fraction of deuterium in the solvent is the same for both cells. Defining the dissociation constant of an acid in an H_2O–D_2O mixture as[17]

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[10] Van Brunt, This Journal, **36,** 1448 (1914).

[11] La Mer and Korman, *ibid.*, **57,** 1511 (1935).

[12] Drucker[1] has attempted to show, by measuring the cells

$\mathrm{Ag{-}AgCl}\ |^1\ \mathrm{DCl(D_2O)}\ |^2\ \mathrm{KCl(satd., H_2O)}\ |^3\ \mathrm{KCl(H_2O)}\ |\ \mathrm{HgCl{-}Hg}$ A

$\mathrm{Ag{-}AgCl}\ |^4\ \mathrm{HCl(H_2O)}\ |^5\ \mathrm{KCl(satd., H_2O)}\ |^6\ \mathrm{KCl(H_2O)}\ |\ \mathrm{HgCl{-}Hg}$ B

that the difference in the e. m. f. arises from the difference in the solubilities of silver chloride in H_2O and in D_2O. Brodsky[13] and Schwarzenbach[5] hold similar views.

This cannot be correct. It is well recognized that the silver–silver chloride electrode operates by virtue of the fact that the activities of silver and silver chloride in solution are independent of the solvent since they are in equilibrium with a solid phase of fixed activity. The magnitude of the solubility, so long as it does not change the ionic strength appreciably, cannot influence the electromotive force.

The difference of e. m. f. between cells A and B arises in fact from the liquid–liquid junction potentials 2 and 5.

[13] Brodsky, *Trans. Faraday Soc.*, **33,** 1180 (1937).

[14] In this paper symbols in parentheses represent activities. The symbol E^0 represents the standard electromotive force of cell 1. The subscript 0 is used when the solvent is H_2O; and the subscript n when the solvent is an H_2O–D_2O mixture in which the mole fraction of deuterium is n.

[15] Harned and Owen, This Journal, **52,** 5079 (1930); Harned and Ehlers, *ibid.*, **54,** 1350 (1932); **55,** 652 (1933).

[16] $(\mathrm{H^+} + \mathrm{D^+})$ in these equations means the sum of the activities of all the hydrogen and deuterium ions whether hydrated or not.

[17] That it is permissible thermodynamically to write the sums $(\mathrm{QH_2} + \mathrm{QD_2})_n$ and $(\mathrm{H^+} + \mathrm{D^+})_n$ in defining cell processes and dissociation constants in H_2O–D_2O mixtures can be shown as follows. When the quinhydrone electrode is used in an H_2O–D_2O mixture there will be two oxidation–reduction systems; one is composed of quinone and hydroquinone

$$E_\mathrm{a} = E_\mathrm{a}^0 - \frac{RT}{2F} \ln \frac{(\mathrm{QH_2})_n}{(\mathrm{Q})_n(\mathrm{H^+})_n^2}$$

and the other of quinone and hydroquinone-d_2

$$E_\mathrm{b} = E_\mathrm{b}^0 - \frac{RT}{2F} \ln \frac{(\mathrm{QD_2})_n}{(\mathrm{Q})_n(\mathrm{D^+})_n^2}$$

At equilibrium the potentials of the two systems are equal. Introducing into equation (7) the fraction, α, of hydroquinone-d_2 and the fraction, β, of deuterium ion and omitting the chloride ion we obtain either

$$E_n = E_n^0 - \frac{RT}{2F} \ln \frac{(\mathrm{QH_2} + \mathrm{QD_2})_n(1 - \alpha)}{(\mathrm{Q})(\mathrm{H^+} + \mathrm{D^+})_n^2(1 - \beta^2)}$$

or

$$E_n = E_n^0 - \frac{RT}{2F} \ln \frac{(\mathrm{QH_2} + \mathrm{QD_2})_n\,(\alpha)}{(\mathrm{Q})(\mathrm{H^+} + \mathrm{D^+})_n^2\,(\beta)^2}$$

Hence the normal potential of the quinhydrone electrode as defined

$$K_n = \frac{(H^+ + D^+)(A^-)}{(HA + DA)}$$

we substitute for $(H^+ + D^+)$ in equation (8)

$$E_n = E_n^0 = \frac{RT}{F} \ln \frac{(A^-)_n}{(HA + DA)(Cl^-)_n K_n}$$

simplifying

$$\log K_n = \frac{E_n - E_n^0}{2.3RT/F} - \log \frac{(HA + DA)_n(Cl^-)_n}{(A^-)_n}$$

Introducing the activity coefficients and the molal concentrations m_1, m_2 and m_3 of the acid, of its ion and of the chloride ion, respectively

$$\log K_n = \frac{E_n - E_n^0}{2.3RT/F} - \log \frac{m_1 m_3}{m_2} - \log \frac{f_1 f_3}{f_2} \quad (9)$$

In the case of acids whose anions have unit charge, the last term is the ratio of the activity coefficients of two univalent ions and, being sensibly unity, can be neglected. The error introduced will be particularly small when the ratio of the dissociation constants in H_2O and in D_2O is considered.

In the case of the dissociation of dihydrogen phosphate, the anion formed is a divalent ion and the last term in equation (9) becomes appreciable, requiring extrapolation of the data to infinite dilution. We set

$$\log f_1 f_3/f_2 = 2A\sqrt{\mu} + B\mu$$

where A is the theoretical constant of the Debye–Hückel limiting law and B is an empirical constant. Replacing the last term in equation (9) by these functions and transferring the term B to the left-hand side

$$\log K_n + B\mu = \frac{E_n - E_n^0}{2.3RT/F} - 2A\sqrt{\mu} - \log \frac{m_1 m_3}{m_2} \quad (10)$$

The data of Nims[18] on this system indicate that a plot of the right-hand side of equation (10) against the ionic strength, μ, gives a straight line at least to an ionic strength of 0.17. The intercept at zero ionic strength gives the logarithm of the thermodynamic ionization constant.

Experimental Results

In Table I are the observed potentials E_n^m for cell I, and the normal potentials, E_n^0.

TABLE I

ELECTROMOTIVE FORCE OF CELL I

Each recorded potential is the mean of measurements with two cells filled with the same solution. Each cell contained duplicate quinhydrone and duplicate silver–silver chloride electrodes.

$n = \frac{\Delta S}{0.1079}$	Moles of HCl per liter of solvent	25° E_n^m	25° E_n^0	45° E_n^m	45° E_n^0
0	0.03049	0.2897	0.4772	0.2756	0.4759
0	.02097	.2714	.4770	.2564	.4760
0	.011225	.2408	.4769	.2237	.4758
0.048	.02765	.2865	.4787	.2725	.4778
.048	.02482	.2809	.4783	.2665	.4774
.056	.02096	.2732	.4788	.2582	.4778
.056	.02034	.2714	.4785	.2562	.4774
.096	.01644	.2627	.4802	.2470	.4793
.096	.02094	.2744	.4801	.2594	.4791
.252	.02463	.2874	.4852	.2728	.4841
.252	.02169	.2810	.4850	.2660	.4839
.511	.02149	.2900	.4944		
.547	.01958	.2865	.4955		
.764	.01807	.2910	.5039	.2755	.5028
.775	.01869	.2937	.5052	.2782	.5038
.987	.02797	.3214	.5130		
		5°			
.252	.02169	.2988	.4879		
.511	.02149	.3080	.4976		

Unpublished data of Noonan and La Mer employing the cell Pt D_2/ DCl / AgCl–Ag indicate that the interionic activity coefficients of HCl and DCl do not differ appreciably. The molal potential of cell I was therefore calculated from the observed potentials, E_n^m, by subtracting the e. m. f. of the cell

$$H_2/HCl\ (m=1)/AgCl–Ag–AgCl/HCl\ (m)/H_2$$

The e. m. f. of this cell was calculated from the data of Harned and Ehlers.[19]

The differences of the molal potentials for cell I when the solvent is an H_2O–D_2O mixture and when it is H_2O are plotted in Fig. 3 against the mole fraction, n, of deuterium in the solvent. A number of measurements were made in the neighborhood of 5% D_2O, where evidence for a minimum had been reported previously.[4] No minimum was found, the differences being an almost linear function of the fraction of deuterium in the solvent. The least squares equation of the curve, obtained from the data at 25°, is

$$E_n = E_0 + 0.02975n + 0.00985n^2 - 0.00301n^3 \quad (11)$$

The same equation fits the data equally well at 45 and at 5°, though additional data are desirable at the latter temperature. The temperature coefficient of the e. m. f. is consequently the same in H_2O, in D_2O and in their mixtures at

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by equation (7) differs from the normal potential E_a^0 only by the factor

$$\frac{RT}{2F} \ln \frac{(1 - \alpha)}{(1 - \beta)^2}$$

and from the potential E_b^0 by the factor

$$\frac{RT}{2F} \ln \frac{\alpha^2}{\beta}$$

These factors are constants for an H_2O–D_2O mixture containing a fixed fraction of deuterium.

[18] Nims, THIS JOURNAL, **55**, 1946 (1933).

[19] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

temperatures between 5 and 45°. The average deviation of the data from equation (11) is 0.2 mv.

Using equations (5) and (6), the exchange constant, K_2, and the ratios of the dissociation constants of hydroquinone and hydroquinone-d_2 were calculated and are shown in Table II.

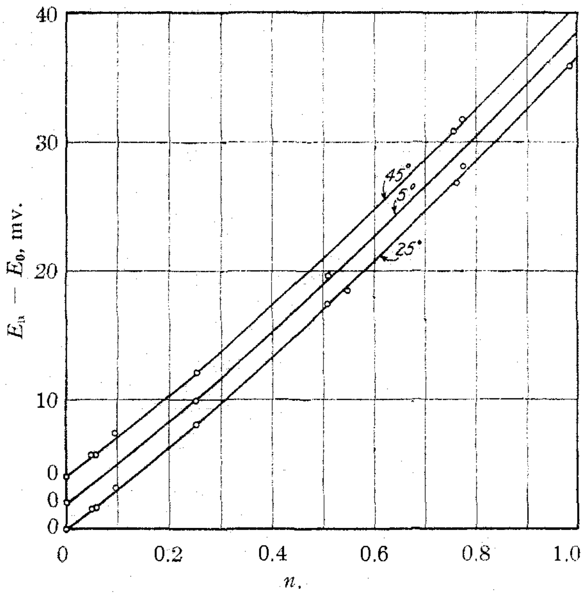

Fig. 3.—The molal potential of cell I as a function of the mole fraction of deuterium in the solvent. The curves for 5 and 45° have been displaced upward by 4 and 8 millivolts, respectively.

TABLE II

Temp., °C.	5	25	45
K_2	19.1	15.6	13.0
K_0/K_1	4.61	4.16	3.80

Since the temperature coefficient of the electromotive force is zero, the difference between the free energies of dissociation of hydroquinone and of hydroquinone-d_2 is the same as the difference in the heats of dissociation. The difference in the entropies is zero within 0.4 entropy unit.

In Table III are the data on the composition of the benzoic acid buffer solutions used in cell II, the e. m. f. data and the dissociation constants calculated from equation (9). The ratios K_n/K_0 are plotted in Fig. 4 against the mole fraction of deuterium in the solvent. K_n is the dissociation constant in an H_2O–D_2O mixture and K_0 is the dissociation constant in H_2O. The short extrapolation to D_2O was made using the equation

$$\frac{K_n}{K_0} = \frac{\left((H_2O) + M(HDO) + N(D_2O) + \frac{\sqrt{(D_2O)^3}}{\sqrt{(H_2O)^3}}\frac{1}{\sqrt{L}}\right)\sqrt{(H_2O)}\sqrt{L}}{\left(\sqrt{(H_2O)}\sqrt{L} + \frac{K_0}{K_1} - (D_2O)\right)\left((H_2O) + (HDO) + (D_2O)\right)} \quad (12)$$

This is analogous to the equation employed by Gross, Steiner and Suess[20] and Orr and Butler.[21]

The significance of the constants L, M and N is shown by the equations

$$\sqrt{L} = \frac{(H_3O^+)}{(D_3O^+)}\frac{\sqrt{[D_2O]^3}}{\sqrt{[H_2O]^3}}$$
$$\frac{1}{M} = \frac{(H_3O^+)}{(H_2DO^+)}\frac{[HDO]}{[H_2O]}$$
$$\frac{1}{N} = \frac{(H_3O^+)}{(HD_2O^+)}\frac{[D_2O]}{[H_2O]}$$

In these equations, symbols in brackets represent moles per liter and symbols in parentheses represent activities.

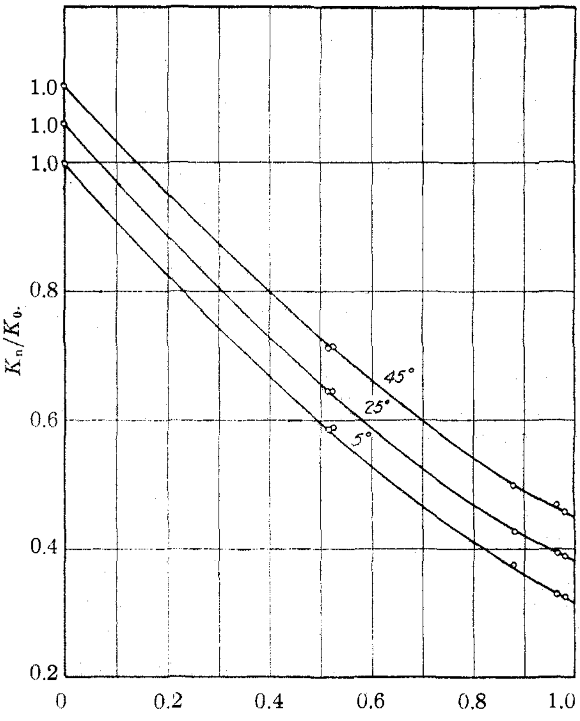

Fig. 4.—Dissociation constant ratios for benzoic acid as a function of the mole fraction of deuterium in the solvent. The curves for 25 and 45° have been displaced upward by 0.06 and 0.12 unit, respectively.

L can be calculated from the equation[3]

$$\log L = \frac{2F\Delta E}{2.3RT} + \log K_3$$

K_3 is the equilibrium constant of the reaction $D_2 + H_2O \rightleftarrows H_2 + D_2O$, calculated from the data of Farkas and Farkas for the equilibrium

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(20) Gross, Steiner and Suess, *Trans. Faraday Soc.*, **32**, 883 (1936).

(21) Orr and Butler, *J. Chem. Soc.*, 330 (1937).

TABLE III

COMPOSITION OF SOLUTIONS, E. M. F. DATA AND DISSOCIATION CONSTANTS FOR BENZOIC ACIDS

Figures in parentheses show the number of cells from which the e. m. f. data were obtained. The average of the data is recorded as E_n.

$n = \frac{\Delta S}{0.1079}$	Grams solute per liter solvent Benzoic acid	Sodium benzoate	NaCl	25° E_n^0	E_n	$K_n\ 10^5$	45° E_n^0	E_n	$K_n\ 10^5$	5° E_n^0	E_n	$K_n\ 10^5$
0.9787	0.04375	0.03771	0.04530	0.5128	0.1585	1.99 (2)	0.5116	0.1339	2.00 (1)	0.5158	0.1832	1.83 (1)
.9651	.02518	.02247	.07109	.5122	.1753	2.03 (2)	.5111	.1522	2.07 (1)	.5152	.1987	1.85 (1)
.8799	.02891	.04166	.1040	.5087	.1546	2.23 (3)	.5077	.1302	2.24 (4)	.5117	.1805	2.13 (3)
.5242	.01434	.02447	.07087	.4949	.1555	3.55 (1)	.4938	.1315$_5$	3.53 (1)	.4979	.1798	3.33 (1)
.5145	.01801	.01854	.05938	.4945	.1635	3.56 (1)	.4934	.1400	3.52 (1)	.4975	.1871	3.32 (1)
0	.02382	.02026	.03242	.4770	.1493	6.16 (1)	.4759	.1254	5.95 (1)	.4800	.1733	5.94 (1)
0	.01782	.02351	.05937	.4770	.1540	6.15 (1)	.4759	.1307$_5$	6.01 (1)	.4800	.1773	5.72 (1)
0	.04117	.04565	.01184	.4770	.1602	6.02 (3)	.4759	.1372	5.88 (2)	.4800	.1833	5.65 (2)
Weighted average for H_2O						6.09			5.93			5.68

$H_2O + HD \rightleftharpoons HDO + H_2$, of Urey and Rittenberg for the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$, and of Topley and Eyring for the equilibrium $H_2O + D_2O \rightleftharpoons 2HDO$[22]. ΔE is the difference between the e. m. f. of the cell $H_2 \mid HCl \mid AgClAg$ when the solvent is D_2O and when it is H_2O. We are indebted to Mr. Evan C. Noonan for permission to use his data for ΔE before publication. The constants ΔE, K_3, and L are given in Table IV.

TABLE IV

CONSTANTS FOR EQUATION (12)

Temp., ° C.	5	25	45
ΔE	0.0041	0.0042	0.0049
K_3	11.6	8.70	6.45
L	16.3	12.04	9.21
M	0.97	1.04	1.12
N	1.03	1.15	1.28

The constants M and N were obtained by fitting equation (12) to the data for the dissociation constant ratios for hydroquinone in H_2O–D_2O mixtures calculated by means of equations (5) and (11) (see Fig. 5). The constants M and N are given in Table IV and at 25° agree closely with the values 1.05 and 1.10 obtained by Orr and Butler.[21]

The ratios K_0/K_1 for benzoic acid, obtained by the extrapolation in Fig. 4, together with the differences of heats, entropies, and free energies of dissociation are shown in Table V.

TABLE V

DIFFERENCE OF MOLAL HEATS, FREE ENERGIES, AND ENTROPIES OF DISSOCIATION FOR BENZOIC ACID

°C.	K_0/K_1	$R \ln K_0/K_1$	H_1-H_0 cal.	F_1-F_0 cal.	S_1-S_0 cal./deg.
5	3.16	2.29	−9	636	−2.3
25	3.13	2.27	175	676	−1.7
45	3.04	2.21	379	703	−1.0

Subscript 1 refers to benzoic acid-*d*; subscript 0 to protobenzoic acid.

At 25° the heat of dissociation of benzoic acid-*d* is 175 cal. greater than that of protobenzoic acid and the entropy of dissociation is −1.7 calories per degree less.

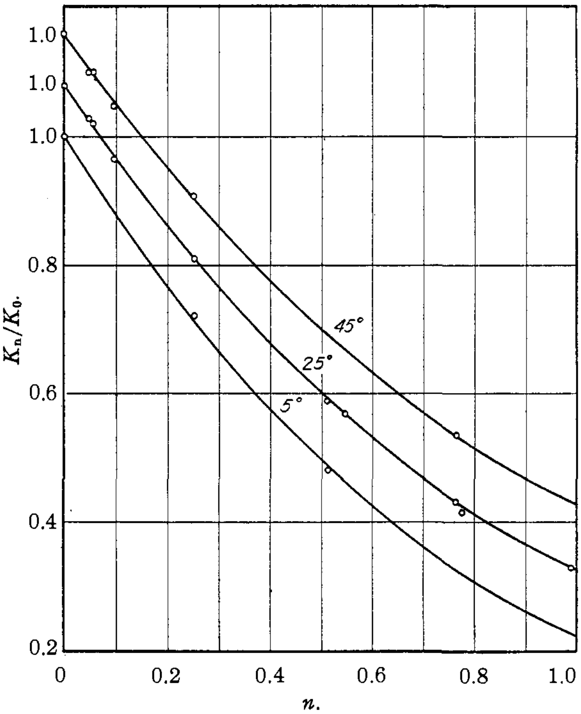

Fig. 5.—Dissociation constant ratios for hydroquinone as a function of the mole fraction of deuterium in the solvent. The curves for 25 and 45° have been displaced upward by 0.08 and 0.16 unit, respectively.

The composition of the phosphate buffer solutions used in cell II in the determination of the dissociation constant of $H_2PO_4^-$ at 25° and the e. m. f. data are given in Table VI. In Fig. 6 the dissociation constant data were extrapolated to infinite dilution employing equation (10). The extrapolated values are given in Table VII.

Equation (12) was employed in making the extrapolation to pure D_2O. The ratio K_0/K_1 is 3.62.

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[22] Farkas and Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934); Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933); Topley and Eyring, *ibid.*, **2**, 217 (1934).

TABLE VI

COMPOSITION OF PHOSPHATE BUFFER SOLUTIONS AND E. M. F. DATA

Each recorded potential is the mean of measurements with two cells filled with the same solution. The figure in parentheses in column (4) represents moles of NaCl instead of KCl.

	Moles of solute per liter						
$n = \frac{\Delta S}{0.1079}$	KH_2PO_4	Na_2HPO_4 $2H_2O$	KCl	μ	E_n^0	E_n	$-(\log K + B\mu)$
0	0.03671	0.01686	(0.03877)	0.1261	0.4770	0.0035	7.290
0	.01096	.01038	.01994	.06204	.4770	− .0357	7.242
0	.01051	.005967	.02145	.04987	.4770	− .0216	7.232
0	.001964	.001390	.004561	.01069	.4770	− .0697	7.155
0	.002908	.001304	.004749	.01157	.4770	− .0585	7.186
0	.008896	.003196	.008688	.02718	.4770	− .0345	7.199
0.9089	.01403	.01065	.01339	.05937	.5099	− .0365	7.734
.9069	.002699	.01755	.03192	.1116	.5099	− .0070	7.773
.9042	.02026	.01488	.01701	.08196	.5098	− .0280	7.751
.9854	.01897	.01524	.02045	.08521	.5137	− .0253	7.807

TABLE VII

DISSOCIATION CONSTANT RATIOS FOR $H_2PO_4^-$, 25°

n	$\log K_n$	$K_n\ 10^8$	K_n/K_0	K_0/K_1
0.000	$\bar{8}.810$	6.46	1	1
.9063	$\bar{8}.309$	2.04	0.316	
.9854	$\bar{8}.255$	1.80	0.279	
(1.000)	$\bar{8}.250$	1.78	0.276	3.62

Discussion

In Fig. 7 the ratios K_0/K_1 for benzoic acid, hydroquinone, and $H_2PO_4^-$ are plotted against log K_0. The length of the lines in the figure shows the estimated probable error of the dissociation constant ratio. In view of the fact that the dissociation constants of the proto and of the deutero acids were determined by exactly the same method, any constant errors of the method tend to cancel when their ratios are considered. The average deviation of the ratio should therefore be a fair measure of the probable error.

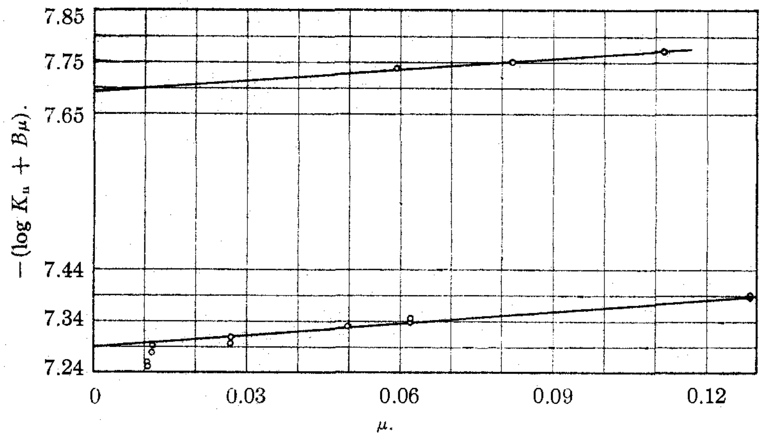

Fig. 6.—The secondary dissociation of phosphoric acid in H_2O–D_2O mixtures at 25° as a function of ionic strength. The lower curve refers to data obtained with H_2O. The upper curve refers to data obtained with 90.6% D_2O.

For benzoic acid, the average deviation of the data from the curve in Fig. 4 is 1%. For $H_2PO_4^-$, the necessity of extrapolating first to infinite dilution and afterward to pure D_2O increases the uncertainty of the result and 2% is a better estimate. For hydroquinone the assumptions underlying equation (5) introduce an error which cannot be estimated. On the basis of the average deviation of the e. m. f. data (0.2 mv.), the average deviation for the ratio K_0/K_1 is 1.6%.

The ratios for acetic acid (from the closely agreeing conductance and e. m. f. data of La Mer and Chittum[23] and of Korman and La Mer[4]) and for chloroacetic acid (from the conductance data of Lewis and Schutz[2]) are also plotted in Fig. 7. The data for acetic acid fit a curve similar to that for benzoic acid with an average deviation of about 1%. The precision of the data for chloroacetic acid cannot be estimated, for Lewis and Schutz do not report the exact fraction of deuterium in their H_2O–D_2O mixture. The dissociation constant for chloroacetic acid-*d*, is being redetermined in this Laboratory by Mr. James Yates.

The curve in Fig. 7 passes through or very near all the points and is consistent with an extrapolated ratio equal to unity at log K_0 = 1.75, or K_0 = 55, the dissociation constant of H_3O^+. The ratio decreases as the strength of the acid increases; for acids approaching the strength of H_3O^+, the dissociation constants may be the same in H_2O and in D_2O.

It should be noted that of all the data in the literature on the dissociation constants of deutero

[23] La Mer and Chittum, THIS JOURNAL, 58, 1642 (1936).

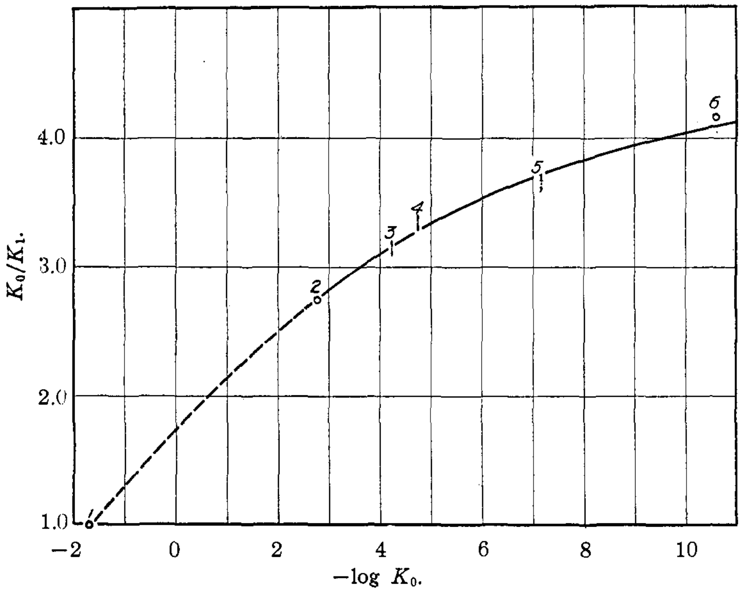

Fig. 7.—Ratios of dissociation constants for proto and deutero acids from conductimetric and potentiometric measurements.

	Acid	K_0	K_0/K_1	Reference
(1)	H_3O^+	55.5	(1)	
(2)	Chloroacetic	$1.72_6 \times 10^{-3}$	2.74	2
(3)	Benzoic	6.09×10^{-5}	3.13	This paper
(4)	Acetic	1.84×10^{-5}	3.33	23, 4
(5)	$H_2PO_4^-$	6.46×10^{-8}	3.62	This paper
(6)	Hydroquinone[a]	2.66×10^{-11}	4.16	This paper

[a] K_0 is the geometric mean of the first and second dissociation constants.[24]

acids, these are the only ones which have been obtained by modern conductimetric methods or by potentiometric methods employing cells without liquid–liquid junctions between H_2O and D_2O. We have pointed out the difficulty of interpreting the cell reactions and therefore the dissociation constant data obtained from cells with liquid junctions.

Summary

The cell Pt | QQH_2–QQD_2 HCl–DCl(H_2O–D_2O) | AgCl–Ag was reinvestigated at 25° and the measurements were extended to 5 and 45°. No minimum was found at 5% deuterium, the e. m. f. being an almost linear function of the deuterium content of the solvent. The temperature coefficient of the e. m. f. is the same in H_2O and in D_2O. The cell

Pt | QQH_2–QQD_2 Benzoic acid, Sodium benzoate (H_2O–D_2O), Sodium chloride | AgCl–Ag

was studied at 5, 25 and 45°. The heat of dissociation for benzoic acid d_1 is 175 calories greater than for protobenzoic acid at 25°. The difference in the entropies of dissociation is 1.7 calories per degree. The cell

Pt | QQH_2–QQD_2 KH_2PO_4, $Na_2HPO_4 2H_2O$ (H_2O–D_2O), KCl | AgCl–Ag

was studied at 25°.

The ratio of the dissociation constants for the deutero acid referred to, the proto acid for hydroquinone, $H_2PO_4^-$ and benzoic acid are compared with the ratios for acetic and chloroacetic acids as determined by other investigators using both thermodynamic and conductivity methods. The ratios decrease as the strength of the acid increases and may become unity for acids as strong as H_3O^+.

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(24) Sheppard, *Trans. Am. Electrochem. Soc.*, **39**, 429 (1921).