freed of water of hydration by drying at 170° for three hours. The silver salt, obtained by treatment of the sodium salt in aqueous solution with silver nitrate, separates directly without water of crystallization.

The reaction between the sodium salt (10 g.) and acetyl chloride (50 ml.) is completed by boiling the mixture for one hour. The sodium chloride is filtered off, the acetyl chloride is evaporated, and the residue (3.4 g.) is crystallized from ether. Similar treatment of the silver salt yields the same compound (mixed melting point) which forms yellow needles that melt at 77–78°.

*Anal.* Calcd. for $C_{14}H_{12}O_5$: C, 64.6; H, 4.6. Found: C, 64.7; H, 4.8.

Ethyl 3-acetoxyindone-2-carboxylate is readily hydrolyzed, even on exposure to atmospheric moisture, to 1,3-diketohydrindene.

**Benzoylation of Ethyl 1,3-Diketohydrindene-2-carboxylate.**—The reaction of the silver salt of the diketo ester with benzoyl chloride in benzene is completed by warming for one hour, and the product is crystallized from benzene and ether. In agreement with the description of Hantzsch and Gajewski,[3] the benzoate forms yellow crystals that melt at 146–148°.

The sodium salt of the diketo ester does not react with benzoyl chloride in boiling benzene. However, if the sodium salt (54 g.) is stirred with benzoyl chloride (60 g.) at 80° for five hours, a reaction takes place. Separated from the sodium chloride with ether and crystallized from benzene, the organic product forms large yellow prisms that melt at 140–141°.

*Anal.* Calcd. for $C_{14}H_{10}O_4$: C, 69.3; H, 4.1. Found: C, 69.4; H, 4.4.

The substance depresses the melting point of the benzoate. Treated with sodium ethoxide in alcohol it gives a red solution which becomes yellow on acidification. Benzoic acid may be sublimed from the tarry residue obtained by evaporating this solution.

## Summary

Bromination is suggested as a method for cleaving 2-acyl derivatives of 1,3-diketohydrindene. Some reactions of 2-benzoyl diketohydrindene and of ethyl 1,3-diketohydrindene-2-carboxylate are described.

MINNEAPOLIS, MINN. RECEIVED JUNE 8, 1936

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# Deuterium Exchange Equilibria in Solution and the Quinhydrone Electrode[1]

BY SAMUEL KORMAN AND VICTOR K. LA MER

## Introduction

For the elucidation of the isotopic influence of deuterium upon various phenomena in heavy water (deuterium oxide), it is important to know with some degree of precision the magnitude of the equilibrium constants of the exchange processes set up between the protons and deutons in the solvent and solute molecules. For example, the interpretation of acid and base catalysis in $D_2O$–$H_2O$ mixtures requires a knowledge of the distribution of deuterium and protium between the various substrate, catalyst (*e. g.*, $H_3O^+$ and $D_3O^+$) and solvent molecules.[2]

The measurement of the e. m. f. of galvanic cells involving $D_2O$ furnishes a precise means of determining these exchange constants. To exclude the experimental complications and the theoretical uncertainties inherent in galvanic cells with liquid junction potentials, we have restricted our investigation to cells without transference. The experimental difficulties attendant upon the use of the deuterium gas electrode with small quantities of solution make an appropriate substitute highly desirable.

We have found that the quinhydrone electrode[3] establishes equilibrium quickly and is particularly well adapted for the micro technique necessary for heavy water studies. To this end, the following cells were investigated

(I) Pt, $Q{\cdot}QH_2/HCl\ (0.01\ M)$ in $H_2O/AgCl$, Ag

(II) Pt, $\{Q{\cdot}QH_2 + Q{\cdot}QD_2\}/HCl\text{-}DCl\ (0.01\ M)$ in $H_2O\text{-}D_2O/AgCl$, Ag

(III) Pt, $Q{\cdot}QH_2/\{HA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in $H_2O/AgCl$, Ag

(IV) Pt, $Q{\cdot}QD_2/\{DA(m_1) + NaA(m_2) + NaCl(m_3)\}$ in $D_2O/AgCl$, Ag

where $Q{\cdot}QH_2$ and $Q{\cdot}QD_2$ represent light and heavy quinhydrone, and HA and DA are the light and heavy varieties of a weak acid.

For (I) and (II) the cell reactions may be written

(A) $2HCl\ (0.01\ M) + Q(H_2O) + 2Ag(s) = 2AgCl(s) + QH_2(H_2O);\ E_H$

(B) $2DCl\ (0.01\ M) + Q(D_2O) + 2Ag(s) = 2AgCl(s) + QD_2(D_2O);\ E_D$

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(1) From a thesis submitted by Samuel Korman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) Hamill and La Mer, *J. Chem. Phys.*, **4**, 294 (1936); **4**, 395 (1936); Urey and Teal, *Rev. Modern Phys.*, **7**, 34 (1935). For a discussion of the importance of exchange reactions see pp. 52, 59, 60.

(3) La Mer and Korman, THIS JOURNAL, **57**, 1510 (1935).

Subtracting (A) from (B)

$$\text{(C)}\quad 2\text{DCl}\ (0.01\ M) + \text{QH}_2(\text{H}_2\text{O}) + \text{Q}(\text{D}_2\text{O}) = 2\text{HCl}\ (0.01\ M) + \text{QD}_2(\text{D}_2\text{O}) + \text{Q}(\text{H}_2\text{O});\ (E_\text{D} - E_\text{H})$$

Measurements of the solubility of quinone in light and heavy water given below, permit (C) to be rewritten as

$$\text{(D)}\quad 2\text{DCl}\ (0.01\ M) + \text{QH}_2(\text{H}_2\text{O}) = 2\text{HCl}\ (0.01\ M) + \text{QD}_2(\text{D}_2\text{O});\ (E_\text{D} - E_\text{H})$$

Then

$$(1)\quad (E_\text{D} - E_\text{H}) = \frac{RT}{2F}\ln K,\ \text{where}\ K = \frac{(\text{QD}_2)\ (\text{HCl})^2}{(\text{QH}_2)\ (\text{DCl})^2}$$

From this fundamental exchange constant, by appropriate combination with values obtained from other sources, a number of important exchange equilibrium constants will be derived.

Furthermore, the data on cells (III) and (IV) can be used to obtain the ratio of dissociation constants of weak acids following the method of Harned and co-workers[4] who used the hydrogen electrode. To maintain precision using a micro method, we again substitute the quinhydrone electrode for the gas electrode. The cell reaction then becomes

$$\text{(E)}\quad 2\text{AgCl(s)} + \text{QH}_2 + 2\text{NaA}(m_2) = 2\text{Ag(s)} + 2\text{HA}(m_1) + 2\text{NaCl}(m_3) + \text{Q}$$

for which

$$(2)\quad E - E_0 = -(RT/F)\ \ln f_\text{H} f_\text{Cl} m_\text{H} m_\text{Cl}$$

where $E_0$ is the normal electrode potential of cell (I). Since

$$K_\text{HA} = f_\text{H} f_\text{A} m_\text{H} m_\text{A} / f_\text{HA} m_\text{HA}$$

we substitute for $m_\text{H}$ in equation (2) and rewrite the expression

$$(3)\quad E - E_0 + \frac{RT}{F}\ln\frac{m_\text{HA} m_\text{Cl}}{m_\text{A}} = -\frac{RT}{F}\ln\frac{f_\text{H} f_\text{Cl} f_\text{HA}}{f_\text{H} f_\text{A}} - \frac{RT}{F}\ln K_\text{HA}$$

and a similar expression involving $D_2O$, $QD_2$, etc., for the deutero acid. The logarithm of the ratio of the activity coefficient products is zero at infinite dilution and varies but little from zero at low ionic strengths. The extrapolation of the right side of equation (3) plotted against ionic strength is linear at temperatures over 15° for ordinary water.[4] Since the dielectric constants of $H_2O$ and $D_2O$ are almost identical,[5] the same extrapolation will be valid in heavy water. Thus the values of $K_\text{HA}$ and $K_\text{DA}$ may differ, but their ratio will certainly remain constant to a very good approximation in the dilute range ($\sim \mu = 0.05$). We thus have a method for obtaining the ratios of dissociation constants of weak acids in heavy and light water, which have proved to be valuable in the interpretation of acid catalyzed reactions in heavy water.[2]

## Experimental

**Materials.**—Quinhydrone,[6] constant boiling hydrochloric acid solution,[7] heavy water[8] and silver oxide[9] were prepared according to directions given previously. Acetic anhydride was purified by fractional distillation, while sodium acetate, sodium salicylate and sodium chloride were recrystallized from conductivity water. Salicylic acid was recrystallized from chloroform. Quinone was resublimed twice.

**Apparatus.**—The micro cell has been described by La Mer and Armbruster.[6] Their preliminary measurements established the reliability of the method as applied to the silver chloride electrode in heavy water, where the quantities of solution available for rinsing are severely limited. The vacuum technique for removing oxygen from the final cell solution, for rinsing the silver chloride electrodes. and for filling the cell, follows closely the method given by Harned and Wright.[10] The cell shown in Fig. 1 was of 4-cc. capacity. Space is provided for duplicate electrodes of each kind, and stopcocks arranged to separate the compartments for rinsing of the silver chloride electrodes.

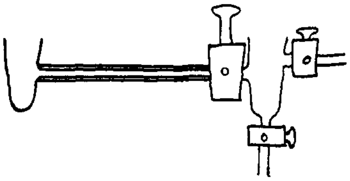

Fig. 1.—Diagram of cell.

**Electrodes.**—Reproducible quinhydrone electrodes were prepared by immersing several platinum spiral wires, carefully sealed in separate glass tubes filled with mercury contacts, in 0.01 *N* hydrochloric acid solution saturated with quinhydrone, and "short circuiting" them together for about a half hour.[11] They then agreed to within 0.03 millivolt. The electrodes were kept in cleaning solution[12] until another pair was required, whereupon they were rinsed thoroughly with distilled water.

The silver-silver chloride electrodes were the Type 2 described by Harned.[13] Several electrodes made simultaneously were washed repeatedly with distilled water, immersed in 0.01 *N* hydrochloric acid solution, and "shorted" together for twenty-four to thirty hours. They agreed to within 0.05 millivolt. The electrodes so prepared were protected against light.

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[4] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 2179 (1933).

[5] Lewis, Olson and Maroney, *ibid.*, **55**, 4731 (1933); Müller, *Physik. Z.*, **36**, 1009–11 (1935); P. Abadie and G. Champetier, *Compt. rend.*, **200**, 1387 (1935).

[6] La Mer and Armbruster, THIS JOURNAL, **57**, 1510 (1935).

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

[8] W. N. Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[9] Helferich and Klein, *Ann.*, **450**, 225 (1926).

[10] Harned and Wright, THIS JOURNAL, **55**, 4849 (1933).

[11] L. E. Baker, Thesis, Columbia University, 1922.

[12] Morgan, Lammert and Campbell, THIS JOURNAL, **53**, 454 (1931).

[13] Harned, *ibid.*, **51**, 416 (1929); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

**Preparation of Cell Solutions.**—The limiting factor in the precision of the measurements is the accuracy with which the composition of the cell solution is known. In the preparation of the buffer solutions, the equivalent amounts of sodium chloride and the sodium salt of the weak acid were transferred from weighing bottles to a 50-cc. ground glass-stoppered flask containing the water sample.[14] The final concentration of the cell solution was corrected for the water lost in the evacuation process.

**Characteristics of the Micro Cell.**—Equilibrium was attained within from twenty to forty-five minutes at 25°, and was maintained to within 0.05 millivolt for two to four hours, followed by a slow drift to higher values, due probably to the formation of chlorohydroquinone. There is a definite lag in attainment of equilibrium when the temperature is raised, while equilibrium is reached almost immediately in proceeding from a higher to a lower temperature.

## Results and Precision of the Measurements

**Hydrochloric Acid Solutions.**—$E$ (0.01) in Table I is calculated on the basis of mols/55.3 mols $D_2O$–$H_2O$. Figure 2 is $E$ (0.01) plotted against $N_{D_2O} = 9.377\ \Delta S - 1.01\ (\Delta S)^2$, where $\Delta S$ is the excess specific gravity of the solvent over ordinary water. The fourth column gives the average deviation from the mean, and the fifth column gives the precision measure for each experiment. This takes into account the deviation of the mean, the weighing error and the difference in electrodes. It will be seen that the average $\delta$ for this set of results does not exceed 0.06 millivolt, while the average deviation does not exceed 0.03 millivolt, a result which is about twice as precise as has been obtained with the hydrogen gas electrode, and ten times as precise as has been obtained with the deuterium gas electrode.[15] The precision with the weak acid solutions is about the same, and corresponds to that reported by Harned and Ehlers.[4]

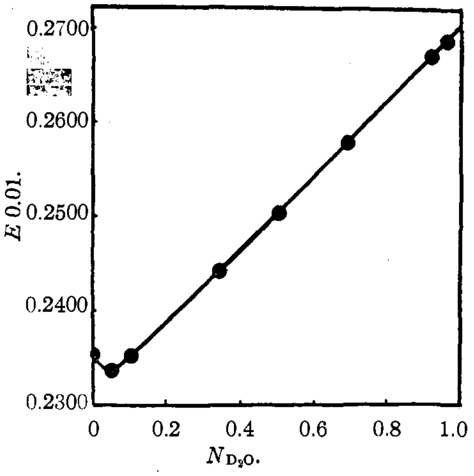

Fig. 2.—Quinhydrone electrode in heavy water.

TABLE I

DATA FOR CELLS (I) AND (II)

| $N_{D_2O}$ | Molality HCl ($M$/55.3 mols) | $-E_{\text{obsd.}}$ | A. d., mv. | $\delta$ mv. | $-E_{0.01}$ |
|---|---|---|---|---|---|
| 0.0 | 0.011182 | 0.24122 | 0.01 | 0.05 | 0.23548 |
| | .010855 | .23963 | .03 | .08 | .23541 |
| .0515 | .011263 | .23960 | .03 | .07 | .23349 |
| | .013103 | .24738 | .02 | .05 | .23350 |
| .1030[a] | .01010 | .23605 | | | .23555 |
| | .01010 | .23602 | | | .23552 |
| .3454 | .014100 | .26175 | .01 | .05 | .24409 |
| | .009139 | .23957 | .02 | .06 | .24419 |
| .5109 | .011913 | .25915 | .02 | .06 | .25016 |
| | .010762 | .25398 | .02 | .07 | .25021 |
| .6925 | .009528 | .25543 | .05 | .05 | .25770 |
| | .010470 | .26022 | .02 | .06 | .25766 |
| .9240 | .011524 | .27414 | .05 | .02 | .26685 |
| | .011022 | .27190 | .04 | .04 | .26690 |
| .9640 | .011870 | .27687 | .03 | .05 | .26807 |
| | .011878 | .27694 | .02 | .07 | .26812 |
| (1.0000) | | | | | ( .2700) |

[a] The results, for $N_{D_2O}$ = 0.1030, were obtained in 1934 by Dr. M. H. Armbruster in a preliminary investigation.

The curve in Fig. 2 has an unexpected but definite minimum at $N_{D_2O}$ = 0.05, corresponding qualitatively to the flat minimum at $N_{D_2O}$ = 0.6 for the cell Pt,$H_2$-$D_2$/HCl-DCl in $H_2O$-$D_2O$/AgCl,Ag, studied by Abel, Bratu and Redlich.[15] These data appeared during the progress of our investigation. No discussion or claim was given concerning the presence of a minimum in the curve for the gas electrode. The experimental difficulties inherent in the deuterium gas electrode prevented these authors from obtaining the precision which we have obtained with the quinhydrone electrode. They mention, however, that as a result of the large value of the constant for the exchange reaction (No. V, Table II below), the concentration of deuterium gas at the electrode was greater than they had supposed at the time the measurements were made. It is likely that their data for mixtures of $H_2O$ and $D_2O$ represent steady state values rather than true equilibrium values with the bulk of the solution since the exchange reaction occurs only on the platinum black at the surface of the electrode. This surface equilibrum will determine the e. m. f., but the e. m. f. will be disturbed depending upon the rate of convection and diffusion of acid and water from the bulk of the solution in $H_2O$–$D_2O$ mix-

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[14] For further details in the preparation of cell solutions, see W. N. Baker and V. K. La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[15] Abel, Bratu and Redlich, *Z. physik. Chem.*, **A173**, 353 (1935).

TABLE II

EXCHANGE EQUILIBRIA IN SOLUTION

| No. | Process | $E^0 = (0.059/n) \log K$ | $K$ | Observer |
|---|---|---|---|---|
| I | $2DCl + QH_2 = 2HCl + QD_2$ | 0.0345 | 14.64 | L. and K. |
| II | $QH_2 + D_2O = QD_2 + H_2O$ | | 0.96 | H. and L. |
| III | $2DCl + H_2O = 2HCl + D_2O$ | | 15.30 | I–II |
| IV | $2DCl + H_2(g) = 2HCl + D_2(g)$ | .0034 | 1.30 | A., B. and R. |
| V | $D_2(g) + H_2O = H_2(g) + D_2O$ | | 11.80 | III–IV |
| VI | $QH_2 + D_2(g) = QD_2 + H_2(g)$ | | 11.26 | I–IV |
| VII | $2H_2O + D_2(g) + 2NaOD = 2D_2O + H_2(g) + 2NaOH$ | .0431 | 28.58 | A., B. and R. |
| VIII | $H_2O + 2NaOD = D_2O + 2NaOH$ | | 2.42 | VII–V |
| IX | $HCl + NaOD = DCl + NaOH$ | | 0.40 | $^1/_2$ (VIII–III) |
| X | $2NaOD + H_2(g) = 2NaOH + D_2(g)$ | | .21 | VII–2V |
| XI | $D^+ + OD^- + H_2O = H^+ + OH^- + D_2O$ | .0233 | 6.13 | $^1/_2$(VII + IV) |

tures. The deuterium content of the gas phase was always greater than that determined by the exchange equilibrium set up on the surface of the electrode between the gaseous $H_2$–$D_2$ mixture and the HCl–DCl and the $H_2O$–$D_2O$. Since an excess of hydrogen in the cell solution occurred in all the intermediate mixtures which were used, Abel, Bratu and Redlich's measurements can be considered only as indicative of the presence and position of a minimum. Their value for pure $D_2O$ and the pure deuterium gas electrode obtained by short extrapolation, however, should not be affected appreciably by any disturbance of the equilibrium mixtures.

The substitution of the quinhydrone electrode results not only in greater precision, but in contrast to the two-phase gas electrode, the exchange equilibria in cell (II), since they occur entirely in the cell solution, are homogeneous. This circumstance establishes our measurements in mixtures as true equilibrium values. Our results show conclusively that the e. m. f. curve of the quinhydrone electrode, when plotted against the $D_2O$ content of the solvent, has a minimum value, which we may reasonably suppose will be true for the analogous deuterium electrode, although the position of the minima will be different.

## Exchange Equilibrium Constants

$K$ of equation (I) may now be evaluated, and may be combined with constants derived in a similar way from the data on the deuterium electrode,[15] and from the exchange reaction

$$\text{(F)}\quad QH_2 + D_2O = QD_2 + H_2O$$

studied by Hamill and La Mer.[16] Table II lists the values of the constants obtained in this way.

The value of the constant for No. V is in excellent agreement with the values which have been calculated from other data by use of the following equations[17]

$$\text{(G)}\quad H_2 + D_2 = 2HD;\ K_1 = (HD)^2/(H_2)(D_2) = 3.27$$

$$\text{(H)}\quad H_2O + D_2O = 2HDO;\quad K_2 = (HDO)^2/(H_2O)(D_2O) = 3.27$$

$$\text{(J)}\quad H_2O + HD(g) = HDO(l) + H_2(g);\ K_3'$$

$$\text{(L)}\quad H_2O(l) + D_2(g) = D_2O(l) + H_2(g);\quad K_4' = (D_2O)(H_2)/(H_2O)(D_2) = (K_3')^2K_1/K_2 = (K_3')^2$$

From Table II, $K_4' = 11.8$; therefore our value of $K_3' = (11.8)^{1/2} = 3.44$. The values of $K_3'$ obtained from other sources are as follows.

TABLE III

VALUES OF $K_3'$ AT 25°

| $K_3'$ | Catalyst | Observer |
|---|---|---|
| 3.8 | Pt black | Bonhoeffer and Rummel[18]<br>Horiuti and Polanyi[19] |
| 2.95 | Pd black | Farkas and Farkas[20] |
| 3.24 | B. coli | Farkas, Farkas and Yudkin[21] |
| 3.44 | (e. m. f.) | La Mer and Korman |
| Av. 3.36 | | |

The exchange constants listed in Table II may also be interpreted as ratios of dissociation constants. For example, process VI is the ratio for the dissociation equilibria

$$\text{(M)}\quad QH_2(s) = Q(s) + H_2(g);\quad K_{QH_2}$$

$$\text{(N)}\quad QD_2(s) = Q(s) + D_2(g)\quad K_{QD_2}$$

$K_{QH_2}$ has the value $10^{-23.65}$.[22] Since $K_{QH_2}/K_{QD_2} = 11.26$, then $K_{QD_2} = 10^{-24.70}$. Processes I and XI, Table II, can be treated as ratios of dissociation constants for weak acids. If we assume that the activity of the chloride ion is the same in both

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[16] Hamill and La Mer, unpublished results; for an outline of the experimental method, see Hamill and Freudenberg, THIS JOURNAL, **57**, 1427 (1935).

[17] A. Farkas, "Light and Heavy Hydrogen," Cambridge Univ. Press, Cambridge, England, 1935, p. 182 ff.

[18] Bonhoeffer and Rummel, *Naturwiss.*, **22**, 45 (1934).

[19] Horiuti and Polanyi, *Nature*, **132**, 819 (1933); **133**, 142 (1934); **134**, 377 (1934).

[20] Farkas and Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934).

[21] Farkas, Farkas and Yudkin, *Proc. Roy. Soc.* (London), **B115**, 373 (1934).

[22] V. K. La Mer and L. E. Baker, THIS JOURNAL, **44**, 1954 (1922).

TABLE IV

DISSOCIATION CONSTANTS OF ACETIC AND SALICYLIC ACIDS

($\mu \cong 0.05$)

| $t$, °C. | $-E_{\text{obsd.}}$ | $-E_0$ | Molality acid | Molality Na salt | Molality NaCl | $K$ |
|---|---|---|---|---|---|---|
| | | | Salicylic Acid | | | |
| | | | $N_{D_2O} = 0$ | | | |
| 25.0 | 0.17189 | 0.47745 | 0.008304 | 0.021811 | 0.019379 | $0.98 \times 10^{-3}$ |
| | .17222 | | .008321 | .021855 | .019416 | 0.96 |
| | .18381 | | .010504 | .019770 | .021610 | 1.01 |
| | | | $N_{D_2O} = 0.917$ | | | |
| 25.0 | 0.17095 | 0.50885 | 0.008748 | 0.023766 | 0.020657 | 0.26 |
| | .16871 | | .008664 | .021751 | .021002 | 0.214 |
| | | | $K_{HA}/K_{DA} = 4.09$ | | | |
| | | | Acetic Acid | | | |
| | | | $N_{D_2O} = 0$ | | | |
| 12.5 | 0.07773 | 0.47906 | 0.008682 | 0.035988 | 0.0189991 | $1.79 \times 10^{-5}$ |
| 25.0 | .05945 | .47745 | .008682 | .035988 | .0189991 | 1.85 |
| 37.5 | .04020 | .47679 | .008682 | .035988 | .0189991 | 1.80 |
| 12.5 | .09425 | | .017179 | .036280 | .019488 | 1.74 |
| 25.0 | .07658 | | .017179 | .036280 | .019488 | 1.79 |
| 37.5 | .05807 | | .017179 | .036280 | .019488 | 1.73 |
| 12.5 | .08365 | | .010568 | .035661 | .019864 | 1.77 |
| 25.0 | .06507 | | .010568 | .035661 | .019864 | 1.80 |
| 37.5 | .04585 | | .010568 | .035661 | .019864 | 1.71 |
| | | | $N_{D_2O} = 0.917$ | | | |
| 12.5 | 0.11661 | 0.51046 | 0.027605 | 0.043260 | 0.023060 | 0.754 |
| 25.0 | .09242 | .50885 | .027605 | .043260 | .023060 | .613 |
| 37.5 | .07520 | .50819 | .027605 | .043260 | .023060 | .634 |
| 12.5 | .11301 | | .025765 | .043571 | .021463 | .756 |
| 25.0 | .08856 | | .025765 | .043571 | .021463 | .611 |
| 37.5 | .07125 | | .025765 | .043571 | .021463 | .634 |

| $t$, °C. | $K_{HA}/K_{DA}$ |
|---|---|
| 12.5 | 2.34 |
| 25.0 | 2.96 |
| 37.5 | 2.75 |

waters, No. I may be considered as the difference of the dibasic acid dissociations

$$\text{(O)}\quad QH_2 = Q^{=} + 2H^+ \text{ (in } H_2O); \quad K_H$$

$$\text{(P)}\quad QD_2 = Q^{=} + 2D^+ \text{ (in } D_2O); \quad K_D$$

where $K_H$, the average dissociation constant, equals $(K'K'')^{1/2} = [(1.75 \times 10^{-10})\ (4 \times 10^{-12})]^{1/2} = 2.64 \times 10^{-11}$ for ordinary water.[23] Log $(K_H/K_D) = 0.0345/0.05911 = 0.5837$, or $(K_H/K_D) = 3.84$. No. XI is the ratio of the acid dissociations

$$\text{(Q)}\quad H_2O = H^+ + OH^-; \quad K_w(H_2O)$$

$$\text{(R)}\quad D_2O = D^+ + OD^-; \quad K_w(D_2O)$$

and equals 6.13 at 25°.

**Salicylic and Acetic Acid Solutions.**—The data for cells (III) and (IV) for salicylic and acetic acids are given in Table IV, with the ratios $K_{HA}/K_{DA}$. To obtain this ratio for acetic acid at 12.5 and 37.5°, we employ the equation of Harned and Wright[10]

$$\text{(4)}\quad E_0 = -0.47745 + (91.02 \times 10^{-6})(\ - 25) - (3.008 \times 10^{-6})(t - 25)^2$$

In the absence of a similar equation for the corresponding heavy water cell, we have assumed that the coefficients for the temperature terms are the same for both waters. The $E_0$ values are given in Table IV. Figure 3 shows $R$ log $(K_{HAc}/K_{DAc})$ plotted against $(1/T)$. The slope of the curve is a measure of the difference $(\Delta H_H - \Delta H_D)$ of the heats of dissociation between proto- and deutero-acetic acids. From these preliminary measurements, there appears to be a maximum in the curve. The indication that this quantity changes sign, as a function of temperature, suggests that the temperature coefficient of the dissociation constant of deutero-acetic acid be subjected to a more detailed investigation to eliminate the assump-

[23] S. E. Sheppard, *Trans. Am. Electrochem. Soc.*, Preprint 39 (1921); La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923).

tion of equality of the temperature coefficients of the DCl and HCl cells.

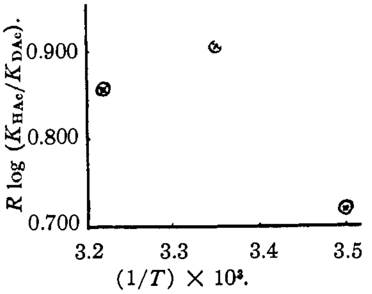

Fig. 3.—Dissociation constant of HAc and DAc.

**The Solubility of Quinone, Hydroquinone and Deuteroquinone in $H_2O$ and $D_2O$.**—The errors in the determination of solubility in heavy water by ordinary analytical methods, *viz.*, titration, become greatly magnified when the quantity of solvent is severely limited, so it is scarcely feasible when dilution with ordinary water is undesirable. Furthermore, distillation of the solvent and weighing of the residue is not permissible with volatile substances like quinone.

Although the Zeiss interferometer has long been used for the accurate determination of the concentration of dilute solutions encountered in precision cryoscopic work, the capabilities of the instrument apparently have never been exploited for the precise determination of solubility on small samples. We present some illustrative data necessary for the interpretation of the e. m. f. results upon the quinhydrone electrode in heavy water.

**The Method.**—A Zeiss–Löwe–Haber portable liquid interferometer was employed. The description of this instrument and the principle upon which its use in determining concentrations of binary mixtures is based is given by Adams.[24]

Deuteroquinone was prepared by dissolving an excess of hydroquinone in 92% $D_2O$ and separating by a vacuum distillation. The dry sample was kept in a vacuum desiccator.

About 5 g. of heavy water is weighed into a glass-stoppered 25-cc. flask and a quantity of solute just insufficient for saturation is added. About 0.15 cc. of the solution is sufficient for a reading in the interferometer when a special 10-mm. cell containing a 9-mm. glass block, producing a film of solution 1 mm. thick, is employed. Pure solvent is placed in the comparison chamber. For solutions more colored than saturated benzoquinone, 1 mm. is about the maximum thickness which will pass sufficient light.

If desired the aliquot may be returned to the flask with a micro-pipet. In any case the flask and solution remaining are reweighed, a small but accurately weighed additional quantity of solute dissolved and a new reading made with the interferometer. Finally, when a saturated solution has been produced, a considerable excess of solute is added. The solution is momentarily heated several degrees above 25°, and returned to the thermostat with constant swirling. Aliquots are removed at convenient (ten-minute) intervals, until an almost constant reading with the interferometer is obtained indicating an equilibrium state. The solution is then momentarily cooled below 25° and the procedure is repeated at convenient intervals. The average of the asymptotes of the two converging time–concentration curves is taken as the interferometer reading for the saturated solution. Obviously these observations can be repeated very readily upon the same sample if satisfactory results are not obtained at first.

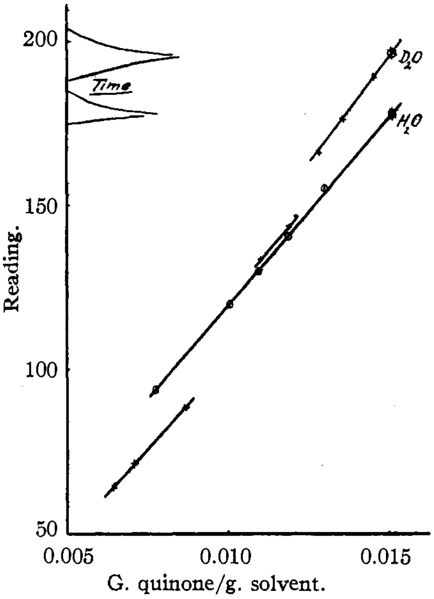

Fig. 4.—Solubility of quinone in $H_2O$ and $D_2O$.

The tables and figures show that the interferometer readings are linearly proportional to the concentration at least near the saturation point, and that the intersection of the time–concentration asymptotes and the concentration calibration curve yield a value for the concentration of the saturated solution which is precise to about 0.1 mg. per g. of solvent. For a 5-g. sample this

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[24] L. H. Adams, THIS JOURNAL, **37**, 1181 (1915).

is approximately the error produced by evaporation during transfer of solute. Figure 4 shows the curves for quinone in light and heavy water; Fig. 5 those for hydroquinone in $H_2O$ and for deuteroquinone in 99.8% $D_2O$.

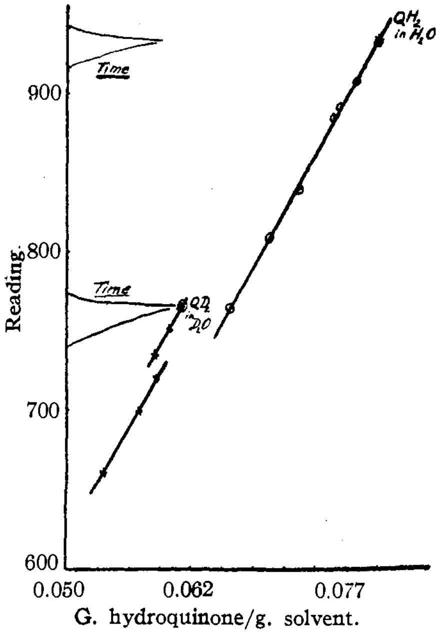

Fig. 5.—Solubility of hydroquinone in $H_2O$ and $D_2O$.

TABLE V

SOLUBILITY OF QUINONE IN $H_2O$ AND 99.8% $D_2O$

| G. Q/g. $H_2O$ | Reading, corr. | $10^7$ concn./reading | G. Q/g. $D_2O$ | Reading, corr. | $10^8$ concn./reading |
|---|---|---|---|---|---|
| 0.00774 | 94.0 | 823 | 0.00646 | 64.2 | .. |
| .01003 | 120.0 | 836 | .00707 | 71.9 | .. |
| .01099 | 130.0 | 845 | .00865 | 88.4 | .. |
| .01189 | 141.0 | 844 | .01103 | 133.3 | 8275 |
| .01298 | 155.7 | 834 | .01191 | 143.9 | 8278 |
| | | | .01282 | 166.3 | 7710 |
| | | | .01353 | 176.4 | 7664 |
| Av. for satd. soln. | | | .01451 | 189.7 | 7646 |
| .0151 | 178.5 | | .0151 | 196.5 | Av. s. soln. |

TABLE VI

SOLUBILITY OF HYDROQUINONE IN $H_2O$ AND DEUTEROQUINONE IN 99.8% $D_2O$

| G. $QH_2$/g. $H_2O$ | Reading, corr. | $10^8$ concn./reading | G. $QD_2$/g. $D_2O$ | Reading, corr. | $10^8$ concn./reading |
|---|---|---|---|---|---|
| 0.06583 | 765.3 | 8601 | 0.05336 | 661.7 | 8064 |
| .06592 | 765.4 | 8613 | .05696 | 699.9 | 8139 |
| .06959 | 809.1 | 8597 | .05861 | 721.0 | 8128 |
| .07261 | 840.0 | 8644 | .05861 | 735.8 | 7965 |
| .07589 | 885.2 | 8573 | .05991 | 752.1 | 7967 |
| .07649 | 892.1 | 8574 | | | |
| .07793 | 908.9 | 8574 | Av. for satd. soln. | | |
| .0802 | 934.0 | Av. satd. soln. | .0611 | 765.9 | |

TABLE VII

SOLUBILITY OF QUINONE, HYDROQUINONE AND DEUTEROQUINONE AT 25°

| | G./g. $H_2O$ | G./g. $D_2O$ | Mole/mole $H_2O$ | Mole/mole $D_2O$ | Mole ratio of soly. $H_2O$/$D_2O$ |
|---|---|---|---|---|---|
| Quinone | 0.0151 | 0.0151 | 0.0025 | 0.0028 | 0.900 |
| Hydroquinone | .0802 | .... | .0131 | .... | .... |
| Deuteroquinone | .... | .0611 | .... | .0109 | 1.204 |

**Dissociation Constants of Weak Acids in $H_2O$–$D_2O$ Mixtures.**—The preliminary experiments with acetic and salicylic acids in 91.7% $D_2O$ have established the feasibility of the microtechnique and the quinhydrone electrode in heavy water, as a method for determining dissociation constants of light and heavy acid mixtures. To extrapolate the dissociation constant obtained in $H_2O$–$D_2O$ mixtures to pure $D_2O$, we define a constant for weak acid solutions in $H_2O$–$D_2O$ mixtures by summing the various activities stoichiometrically[25]

$$K_{\mathrm{H,D}} \equiv \frac{[(\mathrm{H}^+) + (\mathrm{D}^+)]\,(\mathrm{A}^-)}{[(\mathrm{HA}) + (\mathrm{DA})]}$$

The fractions of deuterium ion and undissociated deutero-acid are

$$F_{\mathrm{D}^+} \equiv \frac{(\mathrm{D}^+)}{(\mathrm{H}^+) + (\mathrm{D}^+)};\quad F_{\mathrm{DA}} \equiv \frac{(\mathrm{DA})}{(\mathrm{HA}) + (\mathrm{DA})}$$

Then

$$K_{\mathrm{H,D}} = \frac{[(\mathrm{D}^+)/F_{\mathrm{D}^+}]\,(\mathrm{A}^-)}{[(\mathrm{DA})/F_{\mathrm{DA}}]} = K_{\mathrm{DA}}\,\frac{F_{\mathrm{DA}}}{F_{\mathrm{D}^+}}$$

To evaluate the fractions at various values of $N_{\mathrm{D_2O}}$, we utilize the constants for the exchange equilibria

$$\text{(S)}\quad \mathrm{HA} + \mathrm{HDO} = \mathrm{DA} + \mathrm{H_2O};\quad K = \frac{K_{\mathrm{HA}}}{K_{\mathrm{DA}}} \times \frac{1}{7.1}$$

$$\text{(T)}\quad \mathrm{D}^+ + \mathrm{H_2O} = \mathrm{H}^+ + \mathrm{HDO};\quad K = (15.3 \times 3.27)^{1/2} = 7.1$$

By so doing, we take account of the essential exchanges which must be postulated for $H_2O$–$D_2O$, HA–DA mixtures. Then

$$\text{(5)}\qquad \frac{K_{\mathrm{H,D}}}{K_{\mathrm{HA}}} = \frac{K_{\mathrm{DA}}}{K_{\mathrm{HA}}}\left[\frac{1 + 7.1\,\dfrac{(\mathrm{H_2O})}{(\mathrm{HDO})}}{1 + 7.1\,\dfrac{K_{\mathrm{DA}}(\mathrm{H_2O})}{K_{\mathrm{HA}}(\mathrm{HDO})}}\right]$$

The water ratios may be calculated from the equilibrium

$$\text{(U)}\quad \mathrm{H_2O} + \mathrm{D_2O} = 2\mathrm{HDO};\quad K = 3.27$$

If, then, we stipulate a value for $K_{\mathrm{HA}}/K_{\mathrm{DA}}$, we may determine the behavior of the constant $K_{\mathrm{H,D}}$ over the range of $H_2O$–$D_2O$ concentrations. The values for $K_{\mathrm{H,D}}/K_{\mathrm{HA}}$ given in equation (5) are

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(25) Abel, Bratu and Redlich (ref. 15) have employed a similar definition for the ion product of water in mixtures.

plotted in Fig. 6 as a function of $K_{DA}/K_{HA}$. It will be noted that the extrapolation is practically linear above 90% $D_2O$ for most ratios. Since measurements must frequently be made in $D_2O$ concentrations less than 100%, a reasonably accurate value for pure $D_2O$ should be obtained by a method of successive approximations. Thus $K_{HA}/K_{H,D} = 2.96$ for acetic acid in 92% $D_2O$ becomes $K_{HA}/K_{DA} = 3.3$ for pure $D_2O$. Since for most acids so far investigated this ratio lies between 3 and 6, the above method justifies our belief that extrapolations of $K_{H,D}$ from measurements over 90% $D_2O$ are fairly reliable.

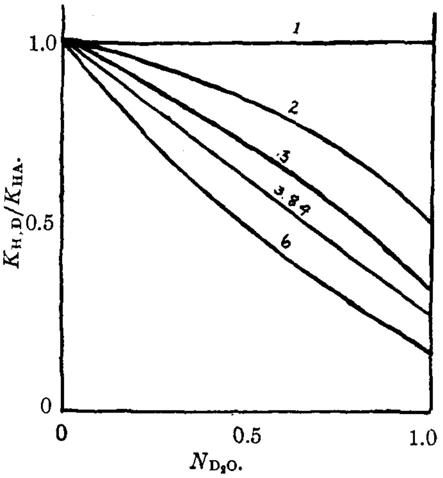

Fig. 6.—Dissociation constant, ratios in $H_2O$–$D_2O$ mixtures.

Halpern[26] has predicted that $K_{HA}/K_{DA}$, the ratio of the dissociation constants of a weak acid in pure $H_2O$ and pure $D_2O$, should increase as $K_H$ decreases. Our studies upon hydroquinone and acetic acid, together with the ratio of the water constants, indicate that this prediction is probably correct. The somewhat anomalous ratio for salicylic acid will serve to indicate that certain conditions must be satisfied before a rigorous comparison of weak acids can be attempted. The constitution of the anion must not be affected by the change of solvent medium for $H_2O$ to $D_2O$. A complicating factor may be introduced by the exchange of protium and deuterium atoms at points in the acid molecule other than those corresponding to the measured ionization. Thus, the exchange which occurs in the hydroxyl group of the salicylate ion may effectively alter the character of the ion, depending upon the isotopic composition of the medium.

## Summary

The free energy changes for a number of important deuterium exchange reactions in aqueous solution have been investigated, using the quinhydrone, silver chloride–silver electrodes and a semi-microtechnique on hydrochloric acid and weak acid buffer systems. The dissociation constants of the weak acids salicylic, acetic, hydroquinone and water in light and 92% heavy water have been measured. With the exception of salicylic acid, the ratio of these dissociation constants in light and heavy water decreases as the constant increases. An equation has been developed which affords a controlled extrapolation of this ratio to 100% $D_2O$ from a single measurement above 90% $D_2O$.

The quinhydrone electrode yields reliable results of greater precision than have been obtained with the deuterium gas electrode. The superiority of the quinhydrone electrode is due not only to the simplicity of manipulation, but to the fact that the equilibrium between the proto- and deutero-forms of quinhydrone, of water and of acid is established promptly in a homogeneous solution. With the gas electrode the exchange reactions are established only at the surface of the electrode, which equilibrium can be disturbed by convection and diffusion from the bulk of the solution, if the gas has been generated by the complete decomposition of a portion of the water employed.

The temperature coefficients of the e. m. f. indicate that the difference in the heats of ionization of the proto- and deutero-acetic acids may change sign in the neighborhood of 25°.

The solubilities of quinone, hydroquinone and deuteroquinone in small quantities of light and heavy water, necessary for the interpretation of the e. m. f. data, have been determined precisely by an interferometer method. Hydroquinone is 20% more soluble on a mole ratio basis than deuteroquinone at 25°, whereas quinone suffers no change in solubility.

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(26) Halpern, *J. Chem. Phys.*, **3**, 456 (1935). Halpern's treatment can have the status only of an approximate theory, since he consciously omits a detailed consideration of the specific contributions of moments of inertia, mass ratios and interaction effects, leaving the contribution of the vibrational frequencies of the proton and deuton bonds as the only significant factor in determining the ratio.