

68. *The Kinetic and Thermodynamic Activity of Protons and Deuterons in Water-Deuterium Oxide Solutions.*

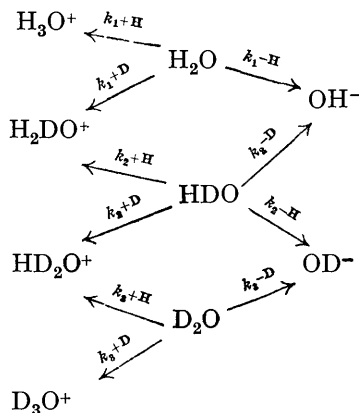
By W. J. C. ORR and J. A. V. BUTLER.

It has been pointed out (Pedersen, *J. Physical Chem.*, 1934, **38**, 581) that if the primary step in catalysis by acids is supposed to be the formation of a complex of hydrogen ion and the substrate, two cases arise: (1) the rate of formation of the complex is great compared with the rate of the reaction, so that its concentration will be that determined by the thermodynamic equilibrium $\text{H}^+ + \text{substrate} \rightleftharpoons \text{complex}$; (2) the rate of formation of the complex is small and becomes the rate-determining step of the reaction. In the former case the rate is determined by the concentration of the complex, which, depending on the thermodynamic equilibrium, will therefore be determined by the hydrogen-ion activity of the solution; in the latter, it will depend on the nature of the acids present in the solution. Hitherto the only means available of distinguishing the two cases has been to determine the catalytic activity of solutions containing acids other than H_3O^+ , in order to ascertain whether there is any catalytic action apart from that due to the activity of hydrogen ions. This can only be achieved with rapid reactions which permit of measurements at very low hydrogen-ion activities. An alternative test has, however, been suggested by Gross and co-workers (*Trans. Faraday Soc.*, 1936, **32**, 877). If the isotopic ratio of D : H is varied, in case (1) the change of the reaction rate will be proportional to the changes of the thermodynamic activity of the various hydrogen ions, but in case (2) this may fail.

Gross and his co-workers examined the dependence on the deuterium content of the solution of the rate of decomposition of diazoacetic ester and the hydrolysis of sucrose, obtaining the variation of the thermodynamic activity from the distribution of picric acid between water-deuterium oxide solutions and benzene. They found that the thermodynamic function agreed with the kinetic function in the diazoacetic ester reaction, but not with sucrose hydrolysis, and concluded that the former was of type (1), and the latter partly of type (2).

Hornel and Butler (J., 1936, 1361) recently determined the ratio of hydrolysis of acetal in hydrogen chloride solutions in water and in deuterium oxide, and showed that, by the use of buffers consisting of a weak acid and its salt, it was possible to determine the ratio of the dissociation constants of the acid in the two liquids. By the study of this reaction in solutions differing in deuterium content, it was thus possible (1) by using a strong acid at a constant concentration to determine the kinetic function of the rate on the isotopic composition of the water, (2) by similar measurements in formic acid-formate buffers to determine the variation of the dissociation constant of the acid, from which the thermodynamic function can be derived. Thus the same reaction serves to measure both the kinetic and the thermodynamic function.

Equilibrium in Water-Deuterium Oxide Mixtures, and the Activity of Protons and Deuterons.—In these solutions there are three neutral molecules, four positive ions, and two negative ions. All the possible equilibria between these species can be represented in terms of the following constants :



where $k_1^{+H} = \frac{[H_3O^+]}{\alpha_{H^+}[H_2O]}$, $k_1^{-H} = \frac{\alpha_{H^+}[OH^-]}{[H_2O]}$,
 $k_3^{+D} = \frac{[D_3O^+]}{\alpha_{D^+}[D_2O]}$, $k_3^{-D} = \frac{\alpha_{D^+}[OD^-]}{[D_2O]}$, etc. . . . (1)

The symbols in square brackets represent the activities of the various species. The proton and deuteron activities are indefinite and may be defined by putting

$$k_1^{+H} = 1, k_3^{+D} = 1; \text{ i.e. } \alpha_{H^+} = \frac{[H_3O^+]}{[H_2O]}, \alpha_{D^+} = \frac{[D_3O^+]}{[D_2O]}$$

The various accessible equilibria between the species are obtained by combining two of these constants. There are a number of inter-relations between the constants. Thus, writing

$$\frac{[HOD]^2}{[H_2O][D_2O]} = K \quad (2)$$

and $\frac{\alpha_{H^+}^2[D_2O]}{\alpha_{D^+}^2[H_2O]} = L \quad (3)$

we have

$$\frac{k_1^{+D}}{k_2^{+H}} = \frac{k_1^{-H}}{k_2^{-D}} = \sqrt{\frac{K}{L}}$$

$$\frac{k_2^{+D}}{k_3^{+H}} = \frac{k_2^{-H}}{k_3^{-D}} = \sqrt{\frac{L}{K}} \quad (4)$$

The total concentration of the isotopic hydrogen ions in the solution is

$$\begin{aligned} \Sigma H_3O^+ &= H_3O^+ + H_2DO^+ + HD_2O^+ + D_3O^+ \\ &= (\alpha_{H^+}/f^+)\{[H_2O] + k_2^{+H}[HDO] + k_3^{+H}[D_2O] + (\alpha_{D^+}/\alpha_{H^+})[D_2O]\} \end{aligned}$$

where f^+ is the activity coefficient of the hydrogen ions. Thus we obtain by (3)

$$\alpha_{H^+} = \Sigma H_3O^+ \cdot f^+ [H_2O]^{1/2} / Q'(n)$$

where

$$Q'(n) = [H_2O]^{3/2} + [HOD][H_2O]^{1/2}k_2^{+H} + [D_2O][H_2O]^{1/2}k_3^{+H} + [D_2O]^{3/2}/\sqrt{L} \quad (5)$$

Similarly, it can be shown that

$$\alpha_{D^+} = \Sigma H_3O^+ \cdot f^+ [D_2O]^{1/2} / Q(n)$$

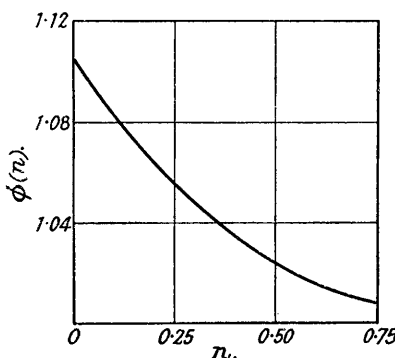
where

$$Q(n) = Q'(n)\sqrt{L}$$

Now when $K = 4$, it has been shown that $[H_2O] = (1 - n)^2$, $[D_2O] = n^2$, $[HOD] = 2n(1 - n)$, where n is the fraction D/(H + D). The best value of K at about 20° appears to be 3.27 (Topley and Eyring, *J. Chem. Physics*, 1934, 2, 220), and no simple expressions for $[H_2O]$, etc., can then be obtained, but the deviations from the values for $K = 4$ can be calculated and expressed by a function $\phi(n)$, such that

$$[H_2O] = (1 - n)^2\phi^2(1 - n); [D_2O] = n^2\phi^2(n) \quad (6)$$

FIG. 1.



Value of $\phi(n)$ when $K = 3.27$.

The values of $\phi(n)$ for $K = 3.27$ are shown in Fig. 1. Then

$$\begin{aligned} \alpha_{H^+} &= \Sigma H_3O^+ \cdot f^+ \cdot (1 - n)\phi(1 - n) / Q'(n) \\ \alpha_{D^+} &= \Sigma H_3O^+ \cdot f^+ \cdot n\phi(n) / Q(n) \end{aligned} \quad (7)$$

Dissociation of Weak Acids in Isotopic Water Mixtures.—For the dissociation of a weak acid, HA, we need the additional constants

$$K_0 = [A^-]\alpha_{H^+} / [HA], K_1 = [A^-]\alpha_{D^+} / [AD]$$

Then

$$[AH] / [AD] = K_1\alpha_{H^+} / K_0\alpha_{D^+} = K_1[H_2O]^{1/2}\sqrt{L} / K_0[D_2O]^{1/2}$$

and

$$\alpha_{H^+} = K_0 \left(\frac{[AH] + [AD]}{[A^-]} \right) \left\{ \frac{K_1\sqrt{L}[H_2O]^{1/2}}{K_1\sqrt{L}[H_2O]^{1/2} + K_0[D_2O]^{1/2}} \right\} \quad (8)$$

Introducing the value of α_{H^+} given in (5), and defining the dissociation constant in water containing a fraction n of deuterium as

$$K_n = \Sigma H_3O^+ \cdot f^+ [A^-] / \Sigma [HA]$$

we obtain

$$K_n = K_0 Q'(n) \{ K_1\sqrt{L} / (K_1\sqrt{L}[H_2O]^{1/2} + K_0[D_2O]^{1/2}) \} \quad (9)$$

and

$$Q'(n) = K_n / K_0 \{ (1 - n)\phi(1 - n) + K_0 Q'(1) / K_1 \cdot n\phi(n) \} \quad (10)$$

Rates of Reactions Catalysed by Hydrogen Ions.—On the assumption that the rate is proportional to the proton and deuteron activities, we may write $\kappa_n = \theta_1\alpha_{H^+} + \theta_2\alpha_{D^+}$, where κ_n is the velocity constant in water of deuterium content n . By (7), we have

$$\kappa_n = \Sigma H_3O^+ \cdot f^+ / Q'(n) \cdot \{ \theta_1 \cdot (1 - n)\phi(1 - n) + \theta_2 \cdot n\phi(n) / \sqrt{L} \} \quad (11)$$

The rates in water and deuterium oxide respectively are

$$\kappa_0 = \theta_1 \Sigma H_3O^+ \cdot f^+; \quad \kappa_1 = \theta_2 \Sigma H_3O^+ \cdot f^+;$$

so that, writing $\zeta_n = \kappa_n / \kappa_0$ for the ratio of the rate in a given solution to that in water at the same concentration of hydrogen ions, we have

$$\zeta_n = 1 / Q'(n) \{ (1 - n)\phi(1 - n) + \kappa_1 / \kappa_0 \cdot Q'(1) n\phi(n) \} \quad (12)$$

Similarly, in the presence of a weak acid and its salt,

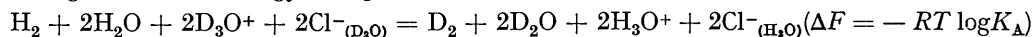
$$\kappa_n = \theta_1\alpha_{H^+} + \theta_2\alpha_{D^+} = K_n / Q'(n) \{ \theta_1 \cdot (1 - n)\phi(1 - n) + \theta_2 \cdot n\phi(n) / \sqrt{L} \} \Sigma AH / [A^-] \quad (13)$$

Comparing solutions in which $\Sigma AH / [A^-]$ is kept constant, with solutions of the strong acid in which ΣH_3O^+ is kept constant, we obtain, on the assumption that the activity coefficients do not vary with the composition of the water,

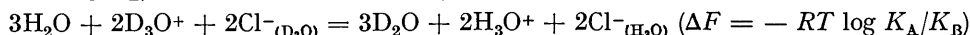
$$\kappa_n / \kappa_0 = (K_n / K_0) \zeta_{n(HCl)} \quad (14)$$

from which the relative dissociation constants can be obtained.

Comparison of $Q'(n)$ from Kinetic and Thermodynamic Data.—In order to determine $Q'(n)$ from ζ_n , it is necessary to know $Q'(1) = 1 / \sqrt{L}$. By (1) and (3), $L = [H_3O^+]^2 [D_2O]^3 / [D_3O^+]^2 [H_2O]^3$, *i.e.*, the equilibrium constant of the reaction $2D_3O^+ + 3H_2O = 2H_3O^+ + 3D_2O$. Abel, Bratu, and Redlich (*Z. physikal. Chem.*, 1935, *A*, **173**, 360) have determined ΔE , the difference of the e.m.f. of the cells $H_2 | HCl, H_2O, AgCl | Ag$ and $D_2 | DCl, D_2O, AgCl | Ag$. This gives the free-energy change of the reaction



Combining this with the free-energy change of the reaction $H_2 + D_2O = D_2 + H_2O$ ($-RT \log K_B$), we obtain the free-energy change of



This differs from $RT \log L$ by the difference of free energy of the chloride ions in deuterium oxide and in water. That such a difference exists is indicated by the different solubilities of salts in the two solvents, but sufficient data for evaluating this term have not been obtained. We have therefore identified L with K_A / K_B . Taking $K_A = 1.3$ from Abel, Bratu, and Redlich, and $K_B = 1/3.33^2$, we find that $L = 14.4$, $Q'(1) = 0.263$. Korman and La Mer's similar measurements (*J. Amer. Chem. Soc.*, 1936, **58**, 1396), with the quinhydrone in place of the hydrogen electrode, give, on the same assumption, $L = 15.3$, $Q'(1) = 0.256$. We shall adopt the value $Q'(1) = 0.26$ for *ca.* 15°. Table I shows the velocity constants of the hydrolysis of acetal in 0.001348*N*-HCl-DCl solutions, with ζ_n and $Q'(n)$ calculated by (12), and Table II gives the velocity constants in half-neutralised solutions of formic acid, with the relative dissociation constants of formic acid given by (14) and $Q'(n)$ calculated by (10).

TABLE I.

*Hydrolysis of acetal in 0.001348*N*-HCl-DCl solutions.*

n	0.0	0.124	0.241	0.309	0.633	0.713	0.848	0.985	1.000
$10^9 \kappa$	27.0	29.0	32.2	33.8	46.3	49.9	56.0	71.4	*
ζ_n	1.00	1.074	1.19	1.25	1.715	1.85	2.08	2.51	2.64
$Q'(n)$	1.00	0.90	0.79	0.73	0.48	0.43	0.36	0.28	0.26

TABLE II.

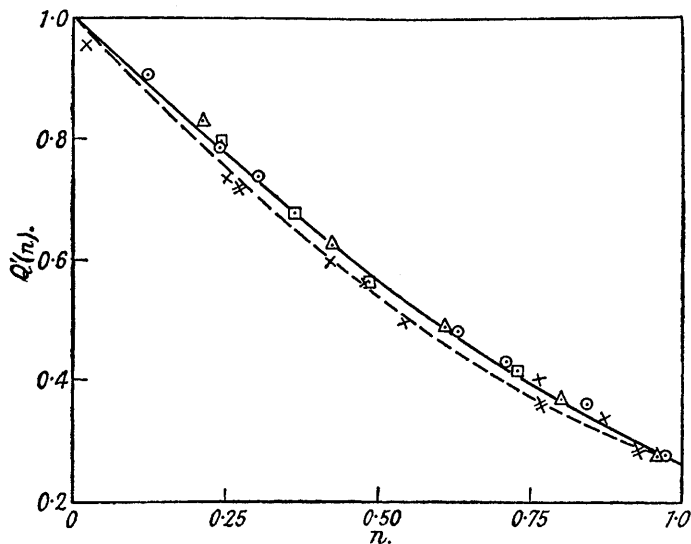
Relative dissociation constants of formic acid in H_2O - D_2O solutions (ionic strength = 0.01).

n	0.0	0.214	0.427	0.611	0.799	0.970	1.00
$10^9 \kappa$	4.42	4.43	4.16	4.13	3.92	4.07	—
K_n / K_0	1.00	0.863	0.678	0.556	0.437	0.350	0.340 *
$Q'(n)$	1.00	0.83	0.62	0.49	0.36	0.27	0.26

* Extrapolated.

Fig. 2 shows that the $Q'(n)$ values obtained from the two sets of data are in excellent agreement with each other, proving that in this reaction the catalytic function is determined by the thermodynamic activity of the ions. Brønsted and Wynne-Jones's conclusion (*Trans. Faraday Soc.*, 1929, 25, 39) that this reaction is a case of specific hydrogen-ion catalysis is thus confirmed by this method. The figure also shows the values of $Q'(n)$ derived from other data. La Mer and Chittum (*J. Amer. Chem. Soc.*, 1936, 58, 1642) have determined the dissociation constants of acetic acid at 25° in water–deuterium oxide mixtures by the direct conductivity method. The values calculated therefrom are somewhat lower than those given above. Gross's figures for the diazoacetic ester decomposition show excellent agreement with those of the acetal reaction, but his thermodynamic values, obtained from the distribution of picric acid, are on the whole distinctly lower.

FIG. 2.



$Q'(n)$ obtained by various methods: \odot from hydrolysis of acetal in HCl–DCl solutions; \triangle from relative dissociation constants of formic acid; \square from diazoacetic ester decomposition (Gross); \neq from dissociation constants of acetic acid (La Mer and Chittum); \times from picric acid distribution coefficients (Gross).

The broken line in Fig. 2 shows the calculated value of $Q'(n)$ by (5) and (6) when $k_2^{+H} = 1$, $k_3^{+H} = 1$. This does not differ greatly from the experimental points, but better agreement is obtained with the values $k_2^{+H} = 1.05$, $k_3^{+H} = 1.10$, shown by the full line.

EXPERIMENTAL.

The reaction rates were determined by following the refractive index change in the reaction by a Hilger–Rayleigh interferometer, fitted with a water-jacketed chamber maintained at $15^\circ \pm 0.1^\circ$. The hydrogen chloride solutions were prepared from 0.001348*N*-deuterium chloride solution, made by adding *N*-hydrochloric acid to 99.9% deuterium oxide and an aqueous solution of hydrogen chloride of the same concentration. The intermediate solutions were prepared by mixing these solutions in various proportions by weight, and the deuterium content was calculated by assuming a linear variation in density between water and deuterium oxide and equality of their molar volumes. *N*/50-Formic acid solutions in both solvents were made from A.R. formic acid, and exactly half-neutralised by standard carbon dioxide-free sodium hydroxide and the intermediate solutions prepared by mixing in various proportions. The acetal had been freshly distilled from sodium carbonate and was free from acid. The deuterium oxide had been distilled and was neutral.

1 c.c. of the appropriate solution and 1 c.c. of the corresponding aqueous solution were placed in the compartments of the interferometer cell and left for 1 hour until temperature equilibrium was attained. The reading then taken checked the accuracy of the buffers and that of the deuterium content determination, since both with the formic acid and with the hydrogen chloride

solutions there was a linear relation between the interferometer reading and the deuterium content. 0.025 G. of acetal at 15° was now injected into the reading solution by means of a calibrated syringe, and thorough mixing obtained by shaking the whole water jacket and its contents. Satisfactory readings were obtained in 2—5 mins. after addition of acetal, and no spurious drift due to evaporation or other cause was observed in experiments lasting up to 24 hours. The velocity constants were obtained by plotting $\log(r_{\infty} - r_t)$, where r = interferometer reading, against t , and excellent linearity was obtained, repeated experiments giving values of κ agreeing within 2%.

SUMMARY.

1. The rates of hydrolysis of acetal in $\text{H}_2\text{O}(\text{HCl})\text{--D}_2\text{O}(\text{DCl})$ mixtures have been determined, and this reaction has also been employed to determine the relative dissociation constants of formic acid in water–deuterium oxide solutions.

2. The possible equilibria between the three isotopic water molecules and the various isotopic ions have been formulated, and the function $Q'(n)$, which expresses the variation of the thermodynamic activity of protons (or deuterons) with the composition of the water, has been determined from the dissociation constants.

3. The rates of hydrolysis of acetal in solutions of hydrogen chloride and deuterium chloride give rise to the same function, and are therefore determined by the thermodynamic proton and deutron activities of the solution.

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