XXXVII.—*The Hydrogen-ion Concentration of Aqueous Iodine Solutions.*

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THE use of iodine solutions in the study of the dynamics of autocatalysed reactions of the keto–enol type has directed attention to the question of the hydrogen-ion concentration of such solutions. Apart from this particular application, the problem is of interest in that the p_H value of aqueous solutions which contain iodine and iodide cannot be determined directly by the usual methods. Their nature precludes the use of the hydrogen-electrode and indicator methods, and the measurement of electrical conductivity can only be applied to iodide-free solutions of iodine. It is possible that the glass-electrode method could be employed, but the results obtained with this in the case of other solutions appear to be somewhat erratic.

The object of this paper is to show how the p_H value may be derived indirectly from a consideration of the equilibria which are involved in the interaction of iodine, potassium iodide, and water. The equilibria in question for freshly prepared solutions* are

$$I_2 + H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{I} + HIO \quad . \quad . \quad . \quad . \quad (1)$$

$$H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{OH} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$I_2 + \overset{-}{I} \rightleftharpoons \overset{-}{I_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for which the respective constants at 25° are

$$K_1 = [\overset{+}{H}][\overset{-}{I}][HIO]/[I_2] = 6 \times 10^{-13} \quad . \quad . \quad . \quad (4)$$

$$K_w = [\overset{+}{H}][\overset{-}{OH}] = 10^{-14} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{and } K_2 = [I_2][\overset{-}{I}]/[\overset{-}{I_3}] = 1{\cdot}38 \times 10^{-3} \quad . \quad . \quad . \quad . \quad (6)$$

The constant K_1 is based on the determination by Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) of the electrical conductivity of a saturated solution of iodine in pure water; K_w is the ionic product for water; and K_2 is derived from experiments on the distribution of iodine between iodide solutions and a non-aqueous medium immiscible with water (compare Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). Although the reaction between the halogens and water is commonly referred to as a hydrolytic process, there is an obvious similarity between the production of hydrogen ions in this way and by the dissociation of an acid. The dissolved halogen behaves indeed like a weak acid, and the p_H value of iodine–iodide solutions is determined by the joint effect of the hydrion-producing processes which are represented by equations (1) and (2). The relative importance of the two reactions depends on the concentration of the free iodine in the solution, and this in turn depends on the concentration of the iodide.

In essence, the problem under consideration may be said to resemble very closely that which is involved in the determination of the hydrogen-ion concentration of a solution which contains two weak acids. If the concentrations of the two weak acids HA_1 and HA_2 are C_1 and C_2, and the corresponding ionisation constants are K' and K'', we have in accordance with the mass law

$$[\overset{-}{A_1}] = K'C_1/[\overset{+}{H}] \text{ and } [\overset{-}{A_2}] = K''C_2/[\overset{+}{H}]$$

$$\text{and since} \quad [\overset{+}{H}] = [\overset{-}{A_1}] + [\overset{-}{A_2}] = [K'C_1 + K''C_2]/[\overset{+}{H}]$$

we obtain $[\overset{+}{H}] = \sqrt{K'C_1 + K''C_2}$, which gives the hydrogen-ion concentration of the solution containing the two acids.

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* On keeping, iodic acid is formed (compare Sammet, *Z. physikal. Chem.*, 1905, **53**, 687), but the effect of this has not been considered in the calculations.

In applying a similar procedure to the determination of the hydrogen-ion concentration of iodine–iodide solutions, the total concentrations of the iodide and iodine will be denoted by a and b, respectively. If then x represents the molar concentration of the free iodine, the concentration of the tri-iodide ion is given by $(b - x)$ and that of the iodine ion by $(a - b + x)$. The equilibrium constant K_2 may then be written $K_2 = x(a - b + x)/(b - x)$, from which $2x = \sqrt{(K_2 + a - b)^2 + 4K_2b} - (K_2 + a - b)$, and this enables us to calculate the concentration of the free iodine in the solution.

Denoting the concentration of the hydrogen ion derived from the hydrolysis of iodine by $[\overset{+}{\mathrm{H}}]_1$, and that derived from the ionisation of water by $[\overset{+}{\mathrm{H}}]_2$, we obtain from equations (4) and (5)

$$[\overset{+}{\mathrm{H}}]_1 = [\mathrm{HIO}] = K_1[\mathrm{I}_2]/[\overset{-}{\mathrm{I}}][\overset{+}{\mathrm{H}}]$$

and
$$[\overset{+}{\mathrm{H}}]_2 = [\mathrm{O}\overset{-}{\mathrm{H}}] = K_w/[\overset{+}{\mathrm{H}}]$$

in which $[\overset{+}{\mathrm{H}}] = [\overset{+}{\mathrm{H}}]_1 + [\overset{+}{\mathrm{H}}]_2$ is the total concentration of the hydrogen ion. From the above we derive

$$[\overset{+}{\mathrm{H}}]_1/[\overset{+}{\mathrm{H}}]_2 = K_1[\mathrm{I}_2]/K_w[\overset{-}{\mathrm{I}}] = K_1x/K_w(a - b + x) \quad . \quad (7)$$

which gives the relative quantities of hydrogen ions resulting from the two proton-producing processes. Furthermore, we obtain

$$[\overset{+}{\mathrm{H}}]_1/[\overset{+}{\mathrm{H}}] = [K_1x/(a - b + x)]/[K_w + K_1x/(a - b + x)] \quad (8)$$

$$[\overset{+}{\mathrm{H}}]_2/[\overset{+}{\mathrm{H}}] = K_w/[K_w + K_1x/(a - b + x)] \quad . \quad . \quad (8a)$$

and
$$[\overset{+}{\mathrm{H}}] = \sqrt{K_w + K_1x/(a - b + x)} \quad . \quad . \quad . \quad . \quad (9)$$

Table I gives a series of numbers which have been calculated from the foregoing equations. It shows the variation in the hydrogen-ion concentration of a series of solutions which contain a fixed quantity of total iodine ($b = 0{\cdot}002$ mol. per litre) and variable quantities of potassium iodide. (The choice of this particular iodine concentration was determined by the circumstance that information in regard to these solutions was required for other purposes.) Col. 1 gives the molar concentration of potassium iodide; col. 2 the molar concentration of the free iodine; col. 3 the proportion of the total hydrogen-ion concentration which is due to hydrolysis of the iodine; col. 4 the total hydrogen-ion concentration of the solutions; and col. 5 the corresponding p_{H} value.

TABLE I.

p_H values of iodine–iodide solutions containing 0·002 mol. of iodine per litre.

a.	$x \times 10^3$.	$[\overset{+}{H}]_1/[\overset{+}{H}]$.	$[H] . 10^7$.	p_H.*
0·001	1·48	0·995	13·6	5·86
0·002	1·11	0·985	7·8	6·11
0·004	0·680	0·94	4·0	6·40
0·006	0·472	0·86	2·7	6·57
0·015	0·189	0·46	1·35	6·87
0·02	0·140	0·315	1·20	6·92
0·05	0·056	0·065	1·05	6·98

* According to Bray's conductivity measurements, the p_H value of an iodide-free saturated aqueous solution of iodine is 5·0.

From the above table it is apparent that the p_H value of solutions which contain a fixed amount of iodine increases with the concentration of the potassium iodide and approaches asymptotically to the limiting value $p_H = 7{\cdot}00$ when the iodide is present in large excess. This relation is directly connected with the circumstance that the concentration of the free iodine in the solution tends towards a zero limiting value.

Table II shows the variation of p_H for a series of solutions for which the ratio of iodine to iodide is constant whilst the absolute concentration is varied. The results show that the dilution of such a solution is associated with a diminution of the p_H value.

TABLE II.

p_H values of iodine solutions for which $[KI]/[I_2] = 2{\cdot}0$.

a.	$x . 10^3$.	$[\overset{+}{H}]_1/[\overset{+}{H}]$.	$[\overset{+}{H}] . 10^7$.	p_H.†
0·0004	0·158	0·965	5·2	6·28
0·004	0·68	0·94	4·0	6·40
0·01	0·94	0·90	3·25	6·47
0·05	1·25	0·74	1·95	6·71
0·20	1·23	0·43	1·32	6·88

† It may be shown that the p_H value of this series of solutions approximates with increasing dilution to a limiting value of $p_H = 6{\cdot}25$. This value assumes that $[\overset{-}{I}]$ is not affected by the hydrolysis of the free iodine. The ultimate limiting value is of course $p_H = 7{\cdot}00$.

It should be recognised that the p_H values recorded in the above tables are based on the number which has been recorded by Bray for the constant K_1 for the hydrolytic equilibrium and therefore refer only to freshly prepared solutions.

The method of procedure for the derivation of p_H remains the same if the iodine–iodide solutions contain small quantities of carbonic acid or other very weak acid. Denoting the concentration of such a weak acid HA by C and its ionisation constant by K_a, we have the following relations :

$$[\overset{+}{\mathrm{H}}] = [\mathrm{HIO}] + [\mathrm{O}\overset{-}{\mathrm{H}}] + [\overset{-}{\mathrm{A}}]$$

$$[\mathrm{HIO}] = K_1x/(a - b + x)[\overset{+}{\mathrm{H}}]$$

$$[\mathrm{O}\overset{-}{\mathrm{H}}] = K_w/[\overset{+}{\mathrm{H}}]$$

$$[\overset{-}{\mathrm{A}}] = K_aC/[\overset{+}{\mathrm{H}}]$$

whence $$[\overset{+}{\mathrm{H}}] = \sqrt{K_aC + K_w + K_1x/(a - b + x)} \quad . \quad . \quad (10)$$

If the product K_aC is of the same order of magnitude as $K_1x/(a + b - x)$, the p_{H} value of the solution will of necessity be determined jointly by the ionisation of the acid HA and the hydrolysis of the iodine.

Observations on the initial velocity of certain acid-catalysed reactions in iodine–iodide solutions have given results which suggest that the actual variations in p_{H} are in general agreement with the changes indicated by the data in the tables.

Summary.

The hydrogen-ion concentrations of aqueous solutions of iodine have been calculated.

For a fixed concentration of iodine, they fall with increase in the amount of iodide present.

For solutions with a fixed ratio $[\mathrm{KI}]/[\mathrm{I}_2]$, they increase with the dilution.

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