#### MURRAY : THE HYDROLYSIS OF IODINE

## CXXIII.—The Hydrolysis of Iodine as Measured by the Iodine Electrode.

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To account for the hydrolysis of iodine in aqueous solution, it is convenient to postulate some degree of dissociation. The simplest case is the production of two oppositely charged ions from the diatomic iodine molecule. Hydrolysis follows from the reaction:

$$I' + H_2O = H' + HIO.$$

In solution there is, then, between the iodine and hypoiodous acid molecules and the ions H<sup>•</sup>, I<sup>•</sup>, I<sup>'</sup>, and I<sub>3</sub><sup>'</sup>, an equilibrium which is derivable from the mass-action laws :  $[I^{\bullet}][I^{\bullet}]/[I_2] = K_1$ ;  $[I^{\bullet}][I_3]/[I_3'] = K_2$ ;  $[I^{\bullet}][OH']/[HIO] = K_3$ . Hence under conditions where any hydrogen iodide formed is largely dissociated,

$$K_{1} = \frac{[I']^{2}}{[I_{2}]} \cdot \frac{1 + 1/K_{2} \cdot [I_{2}]}{1 + K_{w}/K_{3} \cdot 1/[H^{*}]} \quad . \quad . \quad (1)$$

The object of this investigation was to determine, so far as possible, the value of  $K_1$  by means of an iodine-iodide electrode. It was necessary that the solutions to be examined should be acid, in order to repress the formation of the iodate ion; and with the object of eliminating liquid junction potential differences, a mercurous sulphate electrode was adopted as a reference electrode. This made desirable a determination of the E.M.F. of this electrode against the hypothetical normal hydrogen electrode, or failing this, against the iodine electrode, for which accurate values have been recorded. The method adopted was to determine the normal electrolytic potential for the iodine electrode in N/10-potassium chloride against the N/10-calomel electrode, and then, employing concentrations of iodine and iodide of a similar order, measure the potential difference between the iodine electrode and the mercurous sulphate electrode.

The value of  $K_2$  has been determined with considerable accuracy at different temperatures, but it was thought advisable to redetermine it for solutions containing potassium chloride and sulphuric acid. To this end, solutions of iodine in carbon tetrachloride were shaken with solutions of potassium iodide in N/10-potassium chloride and in N/10-sulphuric acid until the distribution of iodine between the two layers was constant. Preliminary determinations gave the values 84·1 and 81·9 for the distribution coefficients of iodine at 25° between carbon tetrachloride and N/10-potassium chloride and N/10-sulphuric acid, respectively, over a range of 0.0006-0.00004 mol./litre in the aqueous layer. Both methods gave the same value for  $K_2$  at 25° within the limits of experimental error:  $0.001390 \pm 0.000002$ . This is higher by about 0.000010 than the accepted value for pure aqueous solutions.

To determine the normal potential of the iodine electrode, successive weighed quantities of pure dry potassium iodide were dissolved in N/10-potassium chloride, and the resulting solution was shaken with iodine several times sublimed. The amount of iodine taken up was controlled to a certain extent by the length of time for which the solution was shaken. The iodine solutions were filtered through glass wool into the electrode vessels, and a portion was removed and titrated against thiosulphate. The electrodes were of platinum foil very slightly coated with platinum black. Measurements were made after the E.M.F. had been constant for about an hour. The results are given in Table I: C is the concentration of the potassium iodide added, in mols./litre; A, the total concentration of iodine found by titration, *i.e.*,  $[I_2] + [I_3']$ , in mols./litre; a, the activity coefficient of the iodide ion interpolated from Lewis's results ("Thermodynamics," Lewis and Randall, 1923). The concentrations of free iodine and iodide ion are calculated from the tri-iodide equilibrium.

# TABLE I.

$\mathbf{r}$ $\mathbf{t}$ . $x$	$I_2 y \Lambda I +$	10-ROI	10-KU	$ng_2 O_2$ .	пу. тетр	. 20 .
$A  imes 10^4$ .	$C  imes 10^3$ .	$[I_2] = x.$	$[\mathbf{I'}] = y.$	a.	E.	$E^{o}$ .
5.707	6.764	0.0001032	0.006296	0.790	(a) 0.3039 (b) 0.3036	0.6207
4.304	6.764	0.0000767	0.006410	,,	(a) 0.2990	0.6201
4·373	2.073	0.0001891	0.001825	0.793	(a) 0.3433	0.6207
$2 \cdot 232$	2.073	0.0000931	0.001943	,,	$\begin{array}{c} (b) & 0.3430 \\ (a) & 0.3325 \\ (b) & 0.2221 \end{array}$	0.6203
					(0) 0.3321 Mean	0.6201 0.6204
			0.05011	г т з		

$$E^{0} = E' - \frac{0.05911}{2} \log \frac{[\mathbf{I}_{2}]}{a^{2}[\mathbf{I}']^{2}} \quad . \quad . \quad (2)$$

*E* is the actual *E.M.F.* found, referred to the *N*/10-calomel electrode. *E'* is the potential of the iodine electrode referred to the normal hydrogen electrode, *i.e.*, *E* increased by 0.3351 volt, the value adopted by Lewis as the difference between the two.  $E^0$  is the normal potential calculated from these results. Its mean value is 0.6204 volt. Lewis (*op. cit.*) quotes three determinations of this value, one recalculated from data given by Maitland (*Z. Elektrochem.*, 1906, 12, 263) and two by Lewis and Faragher (unpublished work) and Gerke (*J. Amer. Chem. Soc.*, 1922, 44, 1682). If these are made applicable to the free iodine electrode by adding 0.0849 volt, they become 0.6212, 0.6210, and 0.6202, respectively.

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The mercurous sulphate required for the electrode was prepared electrolytically. The N/10-sulphuric acid (10 litres) was standardised with sodium carbonate, and the same solution was used throughout. As a check on the preparation, the mean value of the E.M.F. of the mercurous sulphate electrode measured against the hydrogen electrode in N/10-sulphuric acid was determined and found to be E = 0.7550 volt. The value obtained by Lewis and Lacey (J. Amer. Chem. Soc., 1914, **36**, 804) is E = 0.7546 volt.

The iodine solutions were prepared as before, but the potassium iodide was dissolved in N/10-sulphuric acid. The results are given in Table II. TABLE II.

Pt. $xI_2 y $	KI + N/	10-H <sub>2</sub> SO <sub>4</sub>  2	$V/10-H_2SO_2$	$_{1} \mathrm{Hg}_{2}\mathrm{SO} $	4. Hg. Ter	np. 25°
$A  imes 10^4$ .	$C   imes  10^3$ .	$[\mathbf{I}_2] = x.$	$[\mathbf{I'}] = y.$	a.	E.	$E^{\prime\prime}.$
38.52	29.13	0.0001990	0.02333	0.772	(a) 0.0688	0.6829
					(b) 0.0686	0.6827
<b>4·9</b> 93	3.163	0.0001645	0.002828	,,	(a) 0.0171	0.6829
0 -00	0.005	0.000000	0.000451		(b) 0.0165	0.6823
2.729	2.625	0.000088	0.002451	,,	(a) 0.0198	0.6827
1.920	2.401	0.0000476	0.009999		(0) 0.0201	0.6833
1.209	2.401	0.0000410	0.002022	,,	(b) 0.0284	0.6835
					Mean	0.6829
			0.05011	ET 1	7	

$$(E'' + E) = E^{0} + \frac{0.05911}{2} \log \frac{[I_2]}{a^2[I']^2} \quad . \quad . \quad (3)$$

*E* is the actual *E.M.F.* measured. *E''* is the potential of the mercurous sulphate electrode prepared with N/10-sulphuric acid, calculated from *E* and referred to the normal hydrogen electrode. The mean value is E'' = 0.6829 volt. The value calculated from (isohydric) data recorded by Noyes and Stewart (*J. Amer. Chem. Soc.*, 1910, **32**, 1133), taking their mean value for the hydrogen-ion concentration in 0.05M-acid—0.0585, is 0.6820 volt.

The value of the potential of the iodine electrode in acid solution was now measured. Pure powdered iodine which had been sublimed several times was shaken with successive quantities of N/10-sulphuric acid, the solution filtered through glass wool into the electrode vessel, and a portion removed and titrated. To obtain reproducible results, it was found necessary to wash the electrodes very thoroughly if they had been previously used in potassium iodide solutions. By combining equations (1) and (2) there is obtained the expression,

$$\log K_1 \left( 1 + \frac{K_w}{K_3} \cdot \frac{1}{[\mathbf{H}]} \right) = \frac{2}{0.05911} (E^0 - E'' - E) + \log \frac{1}{a^2} (1 + 1/K_2 \cdot [\mathbf{I}_2]),$$

which may be written

$$\log B = \frac{2}{0.05911} (E_x - E) + \log (1 + 1/K_2 \cdot [I_2]) \quad . \tag{4}$$

where  $B = K_1 \left( 1 + \frac{K_w}{K_3} \cdot \frac{1}{[\mathbf{H}^*]} \right)$  and  $E_x = -0.0559$ . The values of a used in calculating the electrode potentials were obtained by interpolation from Lewis's values for the activity coefficient. They have been employed to facilitate comparison with his experimental work, but reference to equations (3) and (4) will show that, if measurements are made in such a solution that we may give to a the value assigned to it in obtaining E'', then the calculated concentration of the iodide ion, and hence of the quantity B, is independent of the value given to a. In calculating B on the basis of the mass action laws, we make the assumption, which appears to be approximately true, that the iodide ion is completely dissociated in N/10-sulphuric acid. The results are given in Table III.

### TABLE III.

$\mathbf{Pt.}$	$xI_2 yKI +$	N/10-H <sub>2</sub> SO	$_{4} N/10-{ m H}_{2}{ m S}0$	$\mathrm{O_4 Hg_2SO_4}$ . Hg	•
$A \times 10^5$ .	E.	$B \times 10^8$ .	$A~ imes~10^5.$	E. E	$3 \times 10^{\circ}$ .
81.57	(a) $0.1880$	0.89	9.06	(a) 0.1818	0.97
	(b) 0·1872	0.95		(b) 0.1818	0.97
27.19	(a) 0·1849	0.84	4.08	(a) 0.1793	1.14
	(b) 0.1843	0.89		(b) 0.1795	1.12
	• •			Mean	0.97

A constant value for B is obtained, except in the most dilute solution. Now by combining the equations  $[I'][I']/[I_2] = K_1$  and  $[I'][OH']/[HIO] = K_3$  we find,

 $K_1 K_w / K_3 = [\text{HIO}][\text{H'}][\text{I'}] / [\text{I}_2],$ 

the value of which is  $3 \times 10^{-13}$  (Bray, J. Amer. Chem. Soc., 1910, **32**, 932).  $K_1 K_w / K_3 \cdot 1 / [\text{H}^{\circ}]$ , therefore, is of the order  $10^{-12}$ , and ignoring it compared with the value of  $K_1$ , we can write,

 $K_1 = 0.97 \times 10^{-8}$  at 25°.

By substituting Bray's value in the expression above, we obtain in addition,

$$K_3 = 3.2 \times 10^{-10}$$
 at 25°.

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