CV.—*Studies on Hypophosphorous Acid. Part I.
Its Ionisation Equilibria.*

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IN the course of some investigations on the velocity of various reductions by means of hypophosphorous acid, it was found that the reactions were catalysed by hydrogen ions; and as these reactions involved the production of mineral acids, such as hydrochloric and hydriodic acids, it was decided to investigate the ionisation of hypophosphorous acid in the presence of hydrochloric acid, in order to obtain data for more precise mathematical analysis of the reactions in question.

Although the catalysis of methyl acetate is in some respects an inferior method to those involving conductivity or hydrogen-ion potential methods for problems of this nature, yet it was chosen in this case as being more comparable with the catalytic reactions concerned. Moreover, one of the chief disadvantages of the method, namely, the slight uncertainty as to the effect of neutral molecules, has been overcome to a large extent by the method of calculating the results.

Many empirical formulæ have been advanced, from time to time, to connect the degree of ionisation of "strong" acids with the dilution in such a way as to give a constant analogous to that obtained for weak acids by Ostwald, but none of these is capable of predicting the equilibria which obtain when one of the ions is present in excess. It has been put forward as a working hypo-

thesis that, in a mixture of two strong electrolytes, each is ionised to the same degree as it would be if present alone in a solution having the same total ion concentration as the mixture. Arrhenius, for instance (*Zeitsch. physikal. Chem.*, 1888, **2**, 285; 1899, **31**, 218), used it in connexion with "neutral salt action," although it is often at variance with the requirements of the law of mass action; and Bray and Hunt, more recently (*J. Amer. Chem. Soc.*, 1911, **33**, 781), have found it to hold with considerable accuracy in the case of sodium chloride and hydrochloric acid mixtures.

When the values of the Ostwald function $\alpha^2/(1-\alpha)v$ were worked out for hypophosphorous acid, they were found to decrease arithmetically as the dilution v increased geometrically (over the range $v=8$ to $v=2048$). This connexion was expressed by the empirical formula

$$\alpha^2/(1-\alpha)v = 0.1015 - \frac{1}{3.5} \log v.$$

(All logarithms in this communication are to the base 10.)

In table I are shown under the various columns:

v = dilution.

λ = molecular conductivity.

α = degree of dissociation.

K_0 = the value of the Ostwald expression.

K_E = the value of the above empirical expression.

K = the value of $\alpha^2/(1-\alpha)v + \frac{1}{3.5} \log v$, which is practically a constant.

$[H^+]$ = the concentration of the hydrogen ions in the equilibria.

I = the total ionic concentration.

K_r = the value of van't Hoff's equation $\alpha^{1.5}/(1-\alpha)\sqrt{v} = K_r$.

TABLE I.

v .	λ .	α .	K_0 .	K_E .	K .	$[H]$.	I .	K_r .
1	—	—	—	0.1015	—	—	—	—
2	140	0.360	0.1012	0.0929	—	0.1800	0.360	0.238
4	172	0.442	0.0876	0.0843	—	0.1105	0.221	0.263
8	207	0.532	0.0757	0.0757	0.1015	0.0665	0.1330	0.293
16	245	0.630	0.0670	0.0671	0.1014	0.0394	0.0788	0.330
32	281	0.722	0.0587	0.0585	0.1017	0.02256	0.0451	0.391
64	312	0.802	0.0508	0.0499	0.1014	0.01255	0.0251	0.454
128	335	0.861	0.0417	0.0413	0.1019	0.00672	0.0134	—
256	352	0.905	0.0336	0.0327	0.1024	—	—	0.566
512	361	0.928	0.0234	0.0241	0.1008	—	—	—
1024	367	0.944	0.0154	0.0155	0.1014	—	—	—
2048	368.3	0.948	0.0082	0.0069	0.1028	—	—	—
α	389	—	—	—	—	—	—	—

Van't Hoff's expression obviously fails, and Rudolphi's is still less applicable. Concordant values cannot be obtained for the constant in Partington's equation. Kraus and Bray's expression, $\alpha^2/(1-\alpha)v = K + D(\alpha/v)^m$, applies over the same range as K_E when

$D=0.217$ and $m=0.10$, but this gives a negative value of $K=-0.090$.

It was hoped that the value of α could be found mathematically from the known value of the total ion concentration, or, of course, from the hydrogen-ion concentration, which is one half of it. This hope has been partly fulfilled, but the formula cannot apply to solutions more concentrated than $v=8$, beyond which the empirical formula fails. Nevertheless, the value of α as found agrees with that demanded by the total ion hypothesis up to the highest concentrations studied, which are considerably beyond the limit mentioned above.

Obviously the empirical formula fails before $v=3600$, where it gives negative values.

The data on which the values of α in the table are based are Ostwald's conductivity measurements at 25° , but the molecular conductivity at infinite dilution is not given by him, and had to be obtained from a consideration of several values for the $\text{H}_2\text{PO}_2'$ ion combined with the value 347 for the hydrogen ion, which is the value now generally adopted (Kendall, T., 1912, **101**, 1283).

The data selected as being most consistent were:

(a) Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 191), from the sodium salt, finds the value for $\text{H}_2\text{PO}_2'$ at 25° to be 41.8.

(b) Bredig (*ibid.*) finds 105.3 for the barium salt, whence $\text{H}_2\text{PO}_2'=39.5$.

(c) Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 99), using old units, gives a value for hypophosphorous acid which by conversion becomes 389, and this is the value adopted.

Hypophosphorous acid is one of the few acids which show a maximum of equivalent conductivity with increasing temperature; it occurs at 55° for this acid. This has been investigated by Arrhenius (*loc. cit.*), who refers it to anomalous values for the heat of neutralisation, and, therefore, for the heat of ionisation, which is negative instead of positive, as is normally the case.

Although hypophosphorous acid is described in the literature as a weak acid (Arrhenius, *ibid.*, and Abegg's "Theory of Electrolytic Dissociation" in Ahrens' Sammlung), yet it appears to be a "strong" acid according to more recent convention, which regards as "intermediate" acids those having ionisation constants of 0.001 to 0.01.

EXPERIMENTAL.

The determinations of the velocity constants were carried out in a thermostat at $25 \pm 0.05^\circ$. The methyl acetate was freshly distilled and free from acid. The hypophosphorous acid was an old

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stock of Kahlbaum's chemically pure acid, which showed only a trace of oxidation to phosphorous acid, so that its titre was almost identical with either methyl-orange or phenolphthalein as indicator, but as the latter indicates the second hydrogen ion of phosphorous acid, the titre with this indicator was used in all cases where differences were involved, and the actual strength of the solution was based on its titre with methyl-orange as indicator.

Baryta solutions, prepared by diluting a $N/4$ -solution to one-half, one-fourth, or one-eighth of its strength, were used for titrations. Steamed and dried Jena-glass bottles of 500 c.c. capacity were employed. The required amount of water was run in by 100, 50, and 25 c.c. pipettes, and 10 c.c. were drawn out to allow for the subsequent addition of that volume of ester. The necessary volumes of $N/2$ - or $N/8$ -acids were added, and the volume before the addition of the ester was 390 c.c. in each case. The general procedure was as in routine methods. Thus all experiments were strictly comparative.

Several titrations were carried out between fifty and seventy minutes after mixing, and were then adjusted to that for sixty minutes by making use of the velocity found for the early stages; the mean of these was used as zero time. In the stronger acid solutions, the final value was attained in ten days, and was employed in the equation $kt = \log x_{\infty} - \log(x_{\infty} - x)$. This equation is only strictly applicable in the early stages of the reaction, since it fails to take into account the reverse reaction between alcohol and acid. The more accurate velocity equation is $dx/dt = k'(a - x) - k''x^2$, where a represents the whole amount of ester (which is of the order of 5 per cent. greater than x_{∞}), and where k' , like k , embodies the large and practically constant value of the molecular concentration of water. Hence, remembering that $k'(a - x_{\infty}) = k''x_{\infty}^2$, one obtains the integrated expression

$$k't \frac{2a - x_{\infty}}{x_{\infty}} = \log \frac{x(a - x_{\infty}) + ax_{\infty}}{a(x_{\infty} - x)} = \log \left[\frac{x_{\infty}}{x_{\infty} - x} + \frac{x(a - x_{\infty})}{a(x_{\infty} - x)} \right].$$

From this it can be shown that the measurements should not extend beyond the first third of the reaction, in order that the change in the ratio k/k' may not exceed one-third per cent., and thus be within the experimental error. Within the prescribed limits, k/k' is equal to 1.055, and the relative error caused by using the simpler formula may be ignored.

In tables IIA and IIB, under the heading k , are shown the constants obtained; they are in all cases the mean of several values agreeing usually within 1 per cent., so that the error in k does not exceed one-half per cent., and is generally much less.

In each case, a formula enclosed in square brackets indicates the molecular concentration of the molecule or ion in question.

α represents the degree of dissociation of the acid concerned in table IIA, and of the hypophosphorous acid in IIB.

α_s and K_s are the values of α and K in solutions of hypophosphorous acid alone which have the same hydrogen-ion (or total ion) concentration as the mixed solution to which they relate. Both were taken from curves plotted from the data in table I. K_s (found) is calculated from the experimental results by a formula which is developed later.

The values of $k \times 10^6/[H^+]$ in the case of hydrochloric acid are obviously affected by the undissociated molecules, which possess about double the catalytic activity of the hydrogen ions (Snethlage, *Zeitsch. Elektrochem.*, 1902, **18**, 539, and Dawson, T., 1913, **103**, 2139). Lundén (*Zeitsch. physikal. Chem.*, 1904, **49**, 189) puts the activity of the hydrogen ions of hydrochloric acid in ester-catalyses equal to $[H^+]\{1 + 0.34[H^+]\}$, and application of this formula gives the more consistent values under its heading.

The undissociated hypophosphorous acid molecules have a much smaller effect, but may account for the high value for its strongest

TABLE IIA.

$[H_3PO_2]$	$[HCl]$	$k \times 10^6$	α	$[H^+]$	$k \times 10^6/[H^+]$	$\frac{k \times 10^6}{[H^+]\{1 + 0.34[H^+]\}}$	
—	0.125	350	0.914	0.1143	3060	2950	Mean 2930
—	0.0625	174	0.934	0.0584	2990	2920	
—	0.03125	87.1	0.950	0.0297	2930	2910	
—	0.01563	44.5	0.963	0.01505	2960	2940	
0.125	—	199.0	0.532	0.0665	(2990)	Mean 2925	
0.0625	—	115.0	0.630	0.0394	2920		
0.03125	—	66.0	0.722	0.02255	2925		
0.01563	—	36.7	0.802	0.01225	2925		

TABLE IIB.

$[H_3PO_2]$	$[HCl]$	$k \times 10^6$	Due to H_3PO_2	$[H_2PO_2']$	$[H^+]$	α (found)	α_s	K_s (found)	K_s
0.125	0.01563	228	183.5	0.0626	0.0776	0.501	0.503	0.0784	0.0790
0.125	0.03125	262	175.1	0.0598	0.0895	0.478	0.477	—	—
0.125	0.0625	337	163	0.0556	0.1150	0.445	0.436	—	—
0.125	0.125	490	140	0.0478	0.1625	0.382	0.377	—	—
0.0625	0.01563	151	106.5	0.03635	0.0514	0.582	0.580	0.0714	0.0710
0.0625	0.03125	187	99.9	0.0341	0.0638	0.546	0.541	0.0749	0.0750
0.0625	0.0625	266	92	0.0314	0.0898	0.502	0.476	—	—
0.0625	0.125	422	72	0.0246	0.1389	0.393	0.400	—	—
0.03125	0.01563	104	59.5	0.0203	0.03535	0.650	0.648	0.0654	0.0652
0.03125	0.03125	140.6	53.5	0.01825	0.0479	0.584	0.592	0.0700	0.0698
0.03125	0.0625	220	46.0	0.0157	0.0741	0.502	0.510	—	—
0.03125	0.125	389	39.0	0.0133	0.1276	0.426	0.416	—	—
0.01563	0.01563	76.6	32.1	0.01095	0.0260	0.701	0.698	0.0609	0.0608
0.01563	0.03125	117.0	29.9	0.01025	0.0400	0.656	0.626	0.0668	0.0672
0.01563	0.0625	200	26	0.00887	0.0673	0.568	0.528	0.0753	0.0762
0.01563	0.125	370	20	0.00683	0.1211	0.437	0.426	—	—

solution, where they constitute nearly half of the acid. As the acid does not give a definite affinity constant, the formula of Taylor (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, Nos. 34, 35, 37) cannot be applied to estimate this effect, but indicates that it is very small.

Discussion of Results.

In order to avoid the difficulty due to the uncertainty as to the effect of undissociated hydrochloric acid molecules, in each case the value for the appropriate concentration of hydrochloric acid (as shown in table IIA) is subtracted from the constant obtained, and the remainder is attributed to the hydrogen ions derived from the hypophosphorous acid. If this remainder is divided by 2930, the mean value of $k \times 10^6 \div [H^+]$, one obtains the concentration of the corresponding hydrogen and H_2PO_2' ions. (The experimental error is considerably magnified by this subtraction, and especially so in those cases where the hydrochloric acid ions are considerably in excess of those of the hypophosphorous acid.) The total hydrogen-ion concentration is obtained by adding that due to the hydrochloric acid alone. One assumes implicitly that the ionisation of the hydrochloric acid is not depressed, and, although this cannot be rigidly true, a comparison of the ionisation values of the two acids shows that the effect on the stronger acid would be negligible compared with that on the weaker acid. Moreover, as the molecules of the hydrochloric acid possess a catalytic activity, the total activity of the hydrochloric acid would be slightly increased, and so tend to lead to slightly high values for α .

The values for the ionisation of hydrochloric acid were selected from a mass of discordant data which vary by 3 per cent. or more in the literature on the subject, but the recent careful determinations by Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781) were used, by interpolation, as they agree well with the means of all others and also with those of Goodwin and Haskell (*Physical Rev.*, 1904, **19**, 369), which, however, were carried out at 18°.

It is clearly seen that α for hypophosphorous acid in any mixture approximates closely to α_s , the degree of ionisation it would have if present alone in the same concentration of hydrogen ions.

If we consider one mole of hypophosphorous acid in v litres of water, which also contain h equivalents of extraneous hydrogen ions, we have $\frac{\alpha(\alpha+h)}{(1-\alpha)v} = K_1$, and, considering a solution of one mole alone at a dilution v_1 , such that the concentration of hydrogen ions is the same as in the first solution, α_1 being its degree

of ionisation, we have $\frac{a_1^2}{(1-a_1)v_1} = 0.1015 - \frac{1}{3.5} \log v_1 = K_s$, but $a_1 = a$, as already found, and, since the hydrogen-ion concentrations are equal, $\frac{a+h}{v} = \frac{a_1}{v_1}$. Therefore $v_1 = v \frac{a}{a+h}$ and

$$K_1 = \frac{a(a+h)}{(1-a)v} = \frac{a_1^2}{(1-a_1)v_1} = K_s =$$

$$0.1015 - \frac{1}{3.5} \log \frac{va}{a+h} = 0.1015 - \frac{1}{3.5} \log \frac{a}{[H^+]}$$

This formula enables us to derive from the experimentally determined a a value of K_s which is seen to agree well with that found from a graph for a hypophosphorous acid solution having the same hydrogen-ion concentration, when this does not exceed that of a $N/8$ -solution (that is, 0.0665).

K_1 is not shown, as it is very susceptible to experimental error.

Attempts have been made, so far unsuccessfully (except possibly for phosphorous acid), to apply an analogous formula to other fairly strong acids, and also to seek for a theoretical significance.

Conclusions.

1. The hypothesis that, in a mixture of two electrolytes, each is ionised to the same extent as it would be if present alone in a solution having the same concentration of ions, has been found to apply to hypophosphorous acid in presence of hydrochloric acid.

2. The empirical formula $a^2/(1-a)v = 0.1015 - \frac{1}{3.5} \log_{10} v$ holds for hypophosphorous acid in dilutions down to $v=8$.

3. In virtue of these two facts, the ionisation equilibria of hypophosphorous acid in the presence of extraneous hydrogen ions is represented in dilute solutions by

$$[H^+][H_2PO_2']/[H_3PO_2] = 0.1015 - \frac{1}{3.5} \log_{10} a/[H^+].$$

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