

THE IONIZATION OF THE SUCCESSIVE HYDROGENS OF ORTHO-PHOSPHORIC ACID.

GEORGE A. ABBOTT.

The dissociation relations of polybasic acids are at present imperfectly understood. Owing to the natural complexity of the compounds and the experimental difficulties due to hydrolysis, hydration, and possibly association in solution, few investigators have attempted to determine the dissociation constants of the different hydrogens of these acids; but the recent development of physico-chemical methods of investigating the nature of dissolved substances has made the solution of such problems appear entirely practicable. Therefore an extended investigation was undertaken, at the suggestion of Prof. A. A. Noyes, in the hope that an exhaustive study of the dissociation relations of the phosphoric acids might contribute toward a better understanding of their chemical behavior in inorganic reactions. This investigation was conducted in the Research Laboratory of Physical Chemistry of the Mass. Inst. of Technology.

In this paper I shall attempt to present briefly only a few results, in the hope that they may prove sufficiently interesting to justify their presentation. The method of measuring hydrolysis described in the previous paper gives us at once a reliable means of determining the dissociation constants of weak acids. When both acid and base are weak (slightly dissociated), the following relation holds:

$$\frac{h^2}{(1-h)^2} = \frac{K_w}{K_A K_B}$$

in which h denotes the degree of hydrolysis of the salt, and K_w , K_A and K_B are the dissociation constants of water, the acid and the base, respectively. They are defined by the following expressions of the Mass Action Law:

$$K_w = C_H \times C_{OH^-}$$

$$K_A = \frac{C_H \times C_{A^-}}{C_{HA}}$$

$$K_B = \frac{C_B \times C_{OH^-}}{C_{BOH}}$$

The dissociation constants of the successive hydrogens of Orthophosphoric Acid will be designated K_1 , K_2 and K_3 . They are defined by the Mass Action equations:

$$K_1 = \frac{H \times H_2\bar{P}O_4}{H_3\bar{P}O_4}$$

$$K_2 = \frac{H \times HPO_4^{\equiv}}{H_2\bar{P}O_4}$$

$$K_3 = \frac{H \times PO_4^{\equiv}}{HPO_4^{\equiv}}$$

They will be considered in inverse order.

K_3 may be determined by substituting the value of h , obtained by the partition method, in the hydrolysis equation.

$$h = .95.$$

$$K_w = 8 \times 10^{-15} \text{ (mols. per litre).}$$

$$K_B = 1.72 \times 10^{-7}.$$

$$\frac{(.95)^2}{(1 - .95)^2} = \frac{50 \times 10^{-16}}{(K_3)(1.72 \times 10^{-7})} \text{ whence,}$$

$$K_3 = 6.48 \times 10^{-13} \text{ (mols. per litre).}$$

K_3 was also determined by an utterly independent method based upon the measurement of the increase of electrical conductivity produced on adding to solutions of Na_2HPO_4 , varying amounts of ammonia. Time will not permit a description of the method and calculations which are somewhat complicated, but the values obtained at different concentrations agreed remarkably well with the above value.

In like manner K_2 may be calculated from the hydrolysis of $NaNH_4HPO_4$. The value obtained by substitution in the above equation is $K_2 = 3.9 \times 10^{-7}$, but this calculation fails to take into account the influence of the unionized substances in the solution.

The correction involves merely the application of the Mass Action Law, and the principle that, in a mixture of salts with a common ion each salt has the same degree of ionization as if it were present alone at a concentration equal to the sum of the concentration of the two salts. However, the algebra involved is not particularly entertaining, and it will perhaps be sufficient to give the mean corrected value of $K_2 = 2.09 \times 10^{-7}$. It is then seen that the correction is large. The value of K_3 , when corrected for the influence of unionized substances becomes $K_3 = 5.55 \times 10^{-13}$.

The hydrolysis of the salt $NH_4H_2PO_4$ is too small to be measured by the

partition method, for the ionization of the first hydrogen of Orthophosphoric Acid is fairly large. It does not accurately obey the Mass Action Law: hence K_1 has no definite meaning. However, the degree of dissociation was determined from the values of the electrical conductivity of the acid and its salts, and other known data, and the following values were obtained, at 18°C:

<i>Cone. Mols. per Litre.</i>	<i>Degree of Ionization.</i>
0.1	0.286
0.05	.364
0.01	.602
0.002	.839
0.0002	.965

Ostwald's Dilution Law requires that

$$\frac{C^2}{1-r} = K_1$$

wherein C represents the concentration and r the degree of ionization. Substituting the values of r we obtain, for the values of K_1 at the different concentrations:

<i>Concentration.</i>	<i>K.</i>
0.1	0.0114
.05	.0104
.01	.0091
.002	.0087
.0002	.0053

and it is seen that the deviation from the law is marked.

A comparison of the ionization constants of phosphoric acid with those of some other acids is interesting.

	$K \times 10^{10}$
Acetic Acid, $C_2H_3O_2 - H$	180,000.
Carbonic, $HCO_3 - H$	3,040.
Hydrosulphuric, $HS - H$	570.
Boric, $H_2BO_3 - H$	17.
*Phenol, $C_6H_5O - H$	1.3
Phosphoric Acid, $K_1 = H_2PO_4 - H$	100,000,000. (Approx.).
“ “ $K_2 = HPO_4 - H$	2,090.
“ “ $K_3 = PO_4 - H$	0.00555

*These values are taken from Walker, "Zeit Phys. Chem." 52, 137, 1900.

The first hydrogen of ortho phosphoric acid behaves in a manner analogous to that of the strong acids; the second to that of a weak acid intermediate between carbonic and hydrosulphuric; while the third is even weaker than phenol. This accounts for the well-known behavior of the acid toward indicators.