moving through the solution, since the electric force driving them is proportional to the charge upon them.

It has also been shown that the ionization values for the salts involved in this investigation, most of which are of multivalent types, conform to the principle that at the same concentration the ionization is roughly the same for all salts having the same valence product and to the principle that the un-ionized fraction is greater, the greater the value of the valence product (see Fig. 2, page 753).

In conclusion, the authors wish to express their thanks to Professor A. A. Noyes for suggesting this research and for his valuable advice and assistance freely given throughout its progress.

BOSTON, April, 1909.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 41.]

THE RATE OF HYDRATION OF PYROPHOSPHORIC ACID IN AQUEOUS SOLUTION.

BY G. A. ABBOTT.

Received April 19, 1909.

It is well known that pyrophosphoric acid is unstable in aqueous solution, gradually changing through hydration into orthophosphoric acid. At the room temperature, in dilute solutions, the change is complete only after weeks, or even months, but the rate is enormously accelerated by rise of temperature. Thus, at 100°, in a 0.05 formular solution of pyrophosphoric acid, the hydration has been found to be practically complete after two hours. This hydration is attended by a marked decrease in the conductance of the solution; therefore the rate of the reaction may be easily determined by measuring the change of the conductance. By choosing a suitable temperature the velocity may be made to assume a value convenient for the measurements.

The measurements about to be described were made in one of the platinum-lined steel bombs used in this laboratory for investigating the conductance of aqueous solutions at high temperatures.[1] This apparatus proved admirably adapted to the work, for it enabled measurements to be made of the conductance of the acid solutions at temperatures up to 100°, without danger of contamination or change of concentration by evaporation.

A solution of pyrophosphoric acid containing 0.05 formular weights of $H_4P_2O_7$, prepared as described in the recent article of Abbott and Bray,[2] was put into the bomb, which was properly closed and then brought

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[1] See Carnegie Institution Publications, No. 63, p. 9 (1907). *Z. physik. Chem.*, **46**, 325 (1903).

[2] See preceding paper.

to the temperature of 18° in a cylindrical thermostat filled with pseudocumene. The specific conductance of this solution was found to be in good agreement with the value previously obtained by Abbott and Bray by measuring solutions of the acid in a glass conductance apparatus.

The bomb was next removed from the pseudocumene bath, which was then rapidly heated to 100°. When the temperature of the bath became constant, the cold bomb was placed in it (at 11.11 A.M.) and measurements of the conductance were made. It is probable that the bomb had assumed substantially the temperature of the bath within 8–10 minutes.

The following table contains the results. The columns headed $L \times 10^6$ give the specific conductance (L) in reciprocal ohms, multiplied by 10^6.

Table I.—Measurements at 100° with 0.05 Formular $H_4P_2O_7$.

Time.	$L \times 10^6$.	Time.	$L \times 10^6$.	Time.	$L \times 10^6$.
11.19	20, 530	11.44	13, 250	12.50	10, 500
11.21	19, 970	11.48	12, 730	1.00	10, 450
11.24	18, 430	11.52	12, 340	1.20	10, 370
11.26	17, 580	11.56	12, 030	1.40	10, 350
11.28	16, 840	12.00	11, 750	2.00	10, 340
11.30	16, 200	12.10	11, 240	2.20	10, 330
11.32	15, 590	12.20	10, 950	2.40	10, 330
11.35	14, 800	12.30	10, 750		———
11.40	13, 790	12.40	10, 590	Final value,	10, 330

In order to determine whether or not the hydration was complete, the temperature was increased to 128.2° and maintained there for one hour. The conductance was found to remain constant at this temperature. The bath was then cooled to 100° and the conductance was redetermined at this temperature and found to be identical with the final value above, showing that this corresponded to complete hydration.

The temperature was then lowered to 18° and the conductance again measured. At 18° the final specific conductance of the solution was found to be $9{,}651 \times 10^{-6}$, which is about 54.5 per cent. of the initial value. The value for the 0.1 formular orthophosphoric solution prepared directly was found by Abbott and Bray[1] to be 9650×10^{-6}, in complete agreement with the final value for the hydrated pyrophosphoric acid. Incidentally this agreement of the results with these two utterly independent samples of acid furnishes a strong indication of the purity of both of them.

The experiment was repeated using a solution of pyrophosphoric acid of nearly the same strength, containing namely 0.0502 formula weight of $H_4P_2O_7$ per liter. But the temperature of the bath was brought to 75° (instead of 100°) and kept there. The cold bomb was introduced into the bath at 11.15 A.M.

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[1] See Table X of their article.

TABLE II.—MEASUREMENTS AT 75° WITH 0.0502 FORMULAR $H_4P_2O_7$.

Time.	$L \times 10^6$.	Time.	$L \times 10^6$.	Time.	$L \times 10^6$.
11.20	21,430	12.00	19,660	2.20	15,095
11.22	21,610	12.10	19,202	2.40	14,708
11.24	21,546	12.20	18,739	3.00	14,369
11.26	21,500	12.30	18,250	3.20	14,037
11.28	21,350	12.40	17,868	3.40	13,768
11.30	21,250	12.50	17,532	4.00	13,516
11.32	21,150	1.00	17,156	4.20	13,314
11.36	20,912	1.15	16,693	4.40	13,059
11.40	20,628	1.30	16,284	5.00	12,854
11.44	20,426	1.45	15,870		———
11.50	20,136	2.00	15,524	Final value,	10,553

Another series of measurements was made at 75° using a solution of pyrophosphoric acid of smaller concentration. The bomb was placed in the bath at 11.48 A.M.

TABLE III.—MEASUREMENTS AT 75° WITH 0.0125 FORMULAR $H_4P_2O_7$.

Time.	$L \times 10^6$.	Time.	$L \times 10^6$.	Time.	$L \times 10^6$.
11.50	6,750	12.56	6,356	4.20	5,439
11.52	6,766	1.00	6,338	4.40	5,380
11.54	6,722	1.05	6,291	5.00	5,329
11.56	6,752	1.10	6,262	5.20	5,288
11.58	6,747	1.15	6,232	5.40	5,233
12.00	6,738	1.20	6,207	6.00	5,180
12.02	6,720	1.25	6,170	6.20	5,136
12.04	6,715	1.30	6,143	6.40	5,098
12.06	6,705	1.40	6,084	7.00	5,063
12.08	6,696	1.50	6,034	7.20	5,026
12.10	6,675	2.00	5,996	7.40	4,997
12.12	6,666	2.10	5,939	8.00	4,965
12.16	6,616	2.20	5,894	8.30	4,919
12.20	6,586	2.30	5,843	9.00	4,880
12.24	6,565	2.40	5,797	9.30	4,842
12.28	6,539	2.50	5,757	10.00	4,805
12.30	6,520	3.00	5,716	10.30	4,776
12.32	6,504	3.10	5,710	11.00	4,755
12.36	6,477	3.20	5,640	12.00	4,719
12.40	6,455	3.30	5,604	12.30	4,699
12.44	6,406	3.40	5,573	1.00	4,679
12.48	6,394	3.50	5,538		———
12.52	6,377	4.00	5,502	Final value,	4,392

Before interpreting these results it was necessary to determine whether or not the conductance of either acid is appreciably affected by admixture with the other, and therefore whether the change in conductance can be assumed to be proportional to the change in hydration. The following measurements of the conductance at 18° of mixtures of ortho- and pyrophosphoric acids were made for this purpose:

TABLE IV.—MIXTURES OF PYRO- AND ORTHOPHOSPHORIC ACID AT 18°.

	Specific conductance (L) × 10^6.				
At. wts. P. per liter.	100% ortho. 0% pyro.	75% ortho. 25% pyro.	50% ortho. 50% pyro.	25% ortho. 75% pyro.	0% ortho. 100% pyro.
0.1	9650	11114	13500	18808	17690
0.05	6135	7376	7828	9734	9622
0.01	2030	2036	2222	2502	2691
0.005	....	1237	1274	1327	1393
0.001	....	304.9	310.9	313.9	....

When these values are plotted, the conductance composition graph is found to be a straight line.

In order to discover, if possible, the law governing the rate of hydration of the acid, the velocity constant (specific reaction rate) was calculated (1) on the assumption that the hydration is catalyzed by hydrogen ion, and is therefore proportional to the concentration of the hydrogen ion as well as to that of the unchanged pyrophosphoric acid, and (2), on the assumption that the rate is independent of the hydrogen ion concentration, and proportional only to the concentration of the pyrophosphoric acid.

Let C_0 be the concentration of pyrophosphoric acid at the start, and C its concentration at any time t; L_0, L_∞, and L, the specific conductance at the start, at the end, and at the time t; (H^+) the concentration of hydrogen ion; and k', k'', k_1, k_2 ... be various constants.

We have then for the expression (1) of the first of the foregoing assumptions, (2) of the proportionality between decrease in conductance and decrease in concentration of pyro acid, and (3) of the proportionality between hydrogen-ion concentration and specific conductance,[1] the following three equations:

$$dC/dt = k'C(H^+)$$

$$C/C_0 = (L - L_\infty)/(L_0 - L_\infty), \text{ or } dC/C_0 = dL/(L_0 - L_\infty)$$

$$(H^+) = k''L.$$

Combining these equations, we get

$$dL/L(L - L_\infty) = -k'k''dt.$$

On integrating and letting $k'k'' = 2.303\,k_1$ this yields the definite integral:

$$k_1 = \frac{1}{L_\infty(t_2 - t_1)} \log_{10}\left\{\frac{L_2}{L_1} \cdot \frac{L_1 - L_\infty}{L_2 - L_\infty}\right\}. \qquad (1)$$

Under the second of the above assumptions we have the two equations:

$$-dC/dt = k'''C$$

$$C/C_0 = (L - L_\infty)/(L_0 - L_\infty) \text{ or } dC = C_0\, dL/(L_0 - L_\infty).$$

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[1] Since the limiting equivalent conductances of $H^+H_3P_2O_7^-$ and $H^+H_2PO_4^-$ at 18° differ by only 1.8 per cent., it is almost certain that the error introduced by this assumption is insignificant.

From their combination follows:

$$-dL/(L-L_\infty) = k'''dt.$$

Integrating, and letting $k''' = 2.303\ k_2$, we get:

$$k_2 = 1/(t_2-t_1)\ \log_{10}\ (L_1-L_\infty)/(L_2-L_\infty). \qquad (2)$$

In Table V are given several values of the quantities k_1 and k_2, calculated by means of equations (1) and (2) from data chosen at random from the experimental results:

TABLE V.—CALCULATED VALUES OF THE SPECIFIC REACTION RATES.

Temp.	Conc.	Time.	$L-L_\infty$.	$k_1 \times 10$.	$k_2 \times 10^3$.
100°	0.05	[11.17][1]	[12200][1]	....	....
		11.21	9640	13.2	25.2
		11.24	8100	13.4	23.7
		11.28	6510	13.6	22.5
		11.30	5870	15.3	23.6
		11.35	4470	14.7	20.6
		11.44	2920	15.8	20.3
		11.52	2010	15.6	18.9
		12.00	1420	15.9	17.9
		12.20	620	17.5	18.7
		12.50	170	17.9	18.6
		1.40	20		
			Mean,	15.3[2]	
75°	0.0502	[11.20][1]	[11300][1]	....	....
		11.30	10697	1.21	2.38
		12.30	7697	1.25	2.22
		1.00	6603	1.26	2.03
		2.20	4543	1.29	1.89
		3.00	3816	1.32	1.83
		4.00	2963	1.39*	1.83
		5.00	2299		
			Mean,	1.27[2]	2.22**

[1] The initial values of time and of $L-L_\infty$, which are enclosed within brackets, were obtained as follows: In each of the three experiments several different initial times were considered and the corresponding value of L_0-L_∞ calculated by means of the formula for the monomolecular reaction (Equation 2) and the first values of $L-L_\infty$ and of k_2 given in this table. The times assumed for heating the bomb to the temperature of the experiment (*i. e.*, the intervals between the time at which the bomb was placed in the thermostat and the initial times chosen), and the values of the ratio between the initial and final conductances (L_0/L_∞) at the different temperatures were then compared. The following values were considered the most probable:

	Time for heating to		Ratio L_0/L_∞ at		
Concen.	75°.	100°.	18°.	75°.	100°.
0.0125	5 min.	.....	1.41	1.55	....
0.050	5 min.	6 min.	1.83	2.08	2.18

[2] Since the values of k_1 at 75° and 100° contain different proportionality factors (the ratio of H^+ ion concentration to specific conductance) these mean values, 1.27 and 17.3, are not directly comparable, they cannot, for example be used in determining the change of its rate with the temperature.

TABLE V. (*Continued*).

Temp.	Conc.	Time.	$I-I_{\infty}$.	$k_1 \times 10$.	$k_2 \times 10^3$.
75°	0.0125	[11.53][1]	[2400][1]	....	....
		12.00	2346		
		12.30	2128	2.13*	1.41
		1.30	1751	2.23	1.41
		2.30	1451	2.28	1.36
		3.30	1212	2.28	1.30
		5.00	937	2.28	1.24
		7.00	671	2.32	1.21
		9.00	488	2.32	1.15
		11.00	363	2.22	1.01
		1.00	287	1.80*	0.85
			Mean,	2.28	1.36**

It will be seen from Table V that in each of the series of experiments (at any rate in those at 75°) the values of k_1 remain nearly constant throughout the course of the reaction, while those of k_2 diminish rapidly as the reaction proceeds. A comparison of the specific reaction rates (k_1 and k_2) for the two different series at 75° has, however, much greater significance. Here a fourfold decrease in the initial concentration causes the mean values of k_1 to increase and those of k_2 to decrease, which shows that the truth lies between the two assumptions. It is to be noted also that the two series of k_2 values are nearly continuous, the value in the last part of the first series being only 1.3-fold greater than in the first part of the second one. Since the concentration of pyrophosphoric acid is nearly the same at these two points, while the hydrogen ion concentration is nearly twice as great at the end of the first series, it follows that the H^+ concentration does not have a nearly proportional influence on the rate.

The conclusion seems therefore justified that the hydration of pyrophosphoric acid in dilute aqueous solution takes place at a rate which is approximately proportional to its own concentration and which increases with that of the hydrogen ion in the solution but not nearly so rapidly as proportionality would require.

The deviations that exist may well be due largely to the complicated ionization relations of the acid. Indeed, a full interpretation of the molecular mechanism of the reaction necessarily involves a consideration of the concentrations of the different forms of the acid existing in the solution, namely of the $H_4P_2O_7$, $H_3P_2O_7^-$, and $H_2P_2O_7^{--}$ molecules. Since the calculations of Abbott and Bray have shown that at the concentrations in question (0.0125–0.05 formular) pyrophosphoric acid

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* Omitted in calculating the mean.

** Value at the time when the change was about one-third completed—not a mean.

exists at 18° mainly (from 54 to 68 per cent.)[1] in the form $H_3P_2O_7^-$, and since the proportion of this at 75° and 100° is still larger,[2] it seems probable that the rate of the reaction is approximately proportional to the concentration of the $H_3P_2O_7^-$ ion, which last may be taken as roughly proportional to the total concentration of the pyrophosphoric acid in the solution.

Summary.

In this article there have been described determinations of the rate of hydration of pyrophosphoric acid in aqueous solution made by measuring in a platinum-lined bomb the change of conductance of a 0.05 formular solution at 75° and 100° and also of a 0.0125 formular solution at 75°.

The specific reaction rate was calculated (1) on the assumption that the rate of hydration is proportional both to the hydrogen-ion concentration and to that of the pyrophosphoric acid undergoing hydration, and (2) on the assumption that the rate is independent of the hydrogen-ion concentration and is determined only by the concentration of the pyrophosphoric acid. The results indicate that the rate of the reaction is approximately proportional to the concentration of the total pyrophosphoric acid present (or to that of the $H_3P_2O_7^-$ ion which is roughly proportional to it) and that it increases with the concentration of the hydrogen-ion but by no means to the extent that proportionality would require.

The actual rate of the reaction is most clearly shown by a statement of the times required for a certain fraction of the acid to undergo hydration under the different conditions. Such data, derived from those in Table V, are brought together in the following table. The values are only approximate:

Concentration.	0.0125 formular 75°.			0.05 formular 75°.			0.05 formular 100°.		
Per cent. hydrated	25	50	75	25	50	75	25	50	75
Times in minutes	88	220	470	52	135	290	5	12.5	27

Since the specific reaction rates are inversely proportional to these times of equal percentage hydration, it follows (from the results for 0.05 formular solution) that the rate is 10.6 times as great at 100° as at 75°. From the general principle approximately valid for almost all reactions that equal increments of temperatures produce equal multiplication of the reaction rate we may conclude that at 25° and 0° the rate would be $1/(10.6)^2$ and $1/(10.6)^3$ as great, respectively, as at 75°,

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[1] From 36 to 18 per cent. exists in the form $H_2P_2O_7^{--}$ and 10 to 14 per cent. in the form $H_4P_2O_7$.

[2] This must be so since the ionization of the $H_3P_2O_7^-$ ($= H^+ + H_2P_2O_7^{--}$) is known from the heat of neutralization measurements to evolve heat. See Abbott and Bray, *loc. cit.*, p. 730, foot-note 9.

and that therefore the time required to produce 25 per cent. hydration in a 0.05 formular solution would be about 100 hours at 25° and 1030 at 0°, and even greater in more dilute solutions. From the same principle (expressed more generally by the equation $\log (k_{t_2}/k_{t_1}) = \text{const.} \times (t_2—t_1)$, it follows that the multiplication of the rate of this reaction for each 10° rise of temperature is about 2.57-fold, in conformity with the usual effect of temperature on reactions.

BOSTON, April, 1909.

[CONTRIBUTION FROM THE PHYSIKALISCH-CHEMISCHES INSTITUT, UNIVERSITY OF LEIPZIG.]

A QUANTITATIVE STUDY OF THE PHOTOCHEMICAL REACTION BETWEEN QUININE AND CHROMIC ACID.

BY ROBERT LUTHER AND GEORGE SHANNON FORBES.

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The original intention of this research was to follow the kinetics of a photochemical reaction in monochromatic light over a considerable period, and to construct equations showing the relation between speed of reaction and absorption of light throughout a long range of concentrations of the reacting substances. We chose the reaction between quinine and chromic acid, already studied by Goldberg,[1] whose results seemed to show that the velocity was dependent on the quantity of light absorbed by the chromic acid. Experiments with monochromatic light, however, soon convinced us that the *quinine* was the substance sensitive to light, and that the chromic acid acted only as an indifferent light filter, absorbing a part of the light and turning it into heat. This and other considerations led us to modify somewhat the plan of the research. The initial velocities of the reactions induced in various solutions by monochromatic light were measured, and the quantities of light absorbed by the quinine and by the chromic acid were calculated from measurements of extinction coefficients. The concentrations of the reacting substances, the intensity of the incident light, and the wave length of the same were varied, one at a time, in successive experiments. Finally the results were generalized and explained from the theoretical standpoint.

The apparatus in which the reaction mixtures were exposed to light is shown in Fig. 1. Three cylindrical glass tubes, *A*, *B*, and *C*, were set in a ring-shaped pan of sheet tin, *P*; their lower edges were made concentric by suitable pieces of brass soldered to the floor of the pan, their upper edges by bits of wood. The average distance between *A* and *B* was 0.71 cm., between *B* and *C* 1.56 cm. Two small glass tubes, not shown in the cut, were passed through holes in the pan, barely projecting into the spaces between *A* and *B*, and *B* and *C*, respectively; through

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[1] Dissertation, Leipzig, 1906.