[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 519]

THE EFFECT OF HYDROGEN-ION CONCENTRATION UPON THE RATE OF HYDRATION OF SODIUM PYROPHOSPHATE. PHOSPHATE II

BY SAMUEL J. KIEHL AND WALDEMAR C. HANSEN

RECEIVED AUGUST 6, 1926 PUBLISHED NOVEMBER 5, 1926

During the study[1] of the hydration of sodium monometaphosphate to orthophosphate, pyrophosphate was found as an intermediate product by H. T. Beans and one of us.

From the results of the work it was deemed advisable to continue the research relative to the formation of the pyrophosphate. However, for a clearer understanding of the formation of pyrophosphate during the hydration of the monometaphosphate to orthophosphate and to facilitate an explanation of the somewhat complex reaction, a study of the hydration of pyrophosphate under the same conditions was considered worth while. In accordance with this idea a research was undertaken on the hydration of normal sodium pyrophosphate, $Na_4P_2O_7 + H_2O \rightleftharpoons 2Na_2HPO_4$, in such a manner as to show the influence of both pyrophosphate- and hydrogen-ion concentrations.

Of the work done previously on this problem, three researches are noteworthy. Berthelot and André[2] and Montemartini and Egidi[3] determined the rate of transformation by acidimetry at different time intervals on a prepared pyrophosphoric acid solution maintained at constant temperature. Abbott,[4] by conductivity measurements on a solution of pyrophosphoric acid, determined, at 75° and 100°, the rate of hydration by comparing the observed conductivities at intervals to the conductivities of synthetic solutions of pyrophosphoric and orthophosphoric acids representing stages in the progress of the hydration.

In previous work the concentration of hydrogen ion was dependent upon that actually furnished by the dissociation of the original acid left and the acid formed under equilibrium conditions at the moment. The effect of the concentration of hydrogen ion has been mentioned but no quantitative measurement of its influence has been made under conditions whereby it was possible to vary its concentration as well as that of pyrophosphate. It is the purpose of this paper to set forth the results of work done where independent variations were made both in the initial pyrophosphate and the initial acid concentrations.

---

[1] Published and submitted as a dissertation in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science in Columbia University by Samuel J. Kiehl in February, 1921.

[2] Berthelot and André, *Compt. rend.*, **123**, 776 (1896).

[3] Montemartini and Egidi, *Gazz. chim. ital.*, **32**, 1, 381 (1902).

[4] Abbott, THIS JOURNAL, **31**, 762 (1909).

Apparatus.—The temperature was regulated by a Freas thermostat. Hydrogen-ion concentration measurements were made with a direct-reading Leeds and Northrup potentiometer of low resistance in connection with a Leeds and Northrup Type R D'Arsonval galvanometer equipped with a telescope and scale; resistance, 510 ohms; sensitivity, 309 megohms; period, 2.7 seconds and a critical damping resistance of 1800 ohms. A Model 4, No. 4208, Weston standard cell with a value of 1.01872 volts at 22° served as a basis of measurement. The calomel and hydrogen cells were the same as those used by Fales and Vosburgh,[5] excepting a stopcock on the arm of the hydrogen cell leading to the salt bridge.

Preparation and Purification of Materials

Sodium Pyrophosphate, $Na_4P_2O_7.10H_2O$.—The purest obtainable sodium pyrophosphate was crystallized thrice from distilled water and analyses of the air-dried decahydrate for water of hydration and moisture content were made.

Disodium Orthophosphate.—By the addition of an equal volume of purified alcohol to a saturated solution of the purest obtainable disodium phosphate and cooling in ice water, uniform small crystals of this salt were obtained. After three of the above crystallizations, the salt was washed on a Büchner funnel thrice with purified alcohol and dried on a glass plate for an hour in the air. On account of its high dissociation pressure no attempt was made to prepare the pure dodecahydrate. The drying was done to insure the removal of free moisture. Analyses were carefully made for total water content by converting a weighed sample of the salt in platinum to normal sodium pyrophosphate. The salt was then kept in sealed bottles for use in the preparation of synthetic solutions of reference.

Hydrochloric Acid.—The hydrochloric acid used in all solutions was prepared from C. P. acid by distilling a constant-boiling solution through a quartz condenser. The first and last portions were rejected in each distillation.

Potassium Chloride.—The potassium chloride used in the calomel cells and salt bridges was prepared by fusing the product in platinum after three crystallizations from distilled water.

Mercurous Chloride and Mercury.—The mercurous chloride for calomel cells was prepared by the electrolytic method of Ellis[6] from mercury according to Hulett,[7] and the hydrochloric acid as prepared above.

Magnesia Mixture.—The magnesia mixture was prepared by dissolving 320 g. of magnesium chloride hexahydrate, 225 g. of ammonium chloride and 250 cc. of ammonium hydroxide (d., 0.90) in 2250 cc. of distilled water.

Magnesium Chloride Solution.—The magnesium chloride solution used in the separation of orthophosphate from pyrophosphate was prepared by dissolving 110 g. of magnesium chloride hexahydrate in 50 cc. of distilled water, giving an approximate volume of 130 cc.

Method of Procedure

The measurement and control of the variable factors—concentration of pyrophosphate, concentration of orthophosphate, concentration of hydro-

---

[5] Fales and Vosburgh, THIS JOURNAL, **40**, 1291 (1918).

[6] Ellis, *ibid.*, **38**, 737 (1916).

[7] Hulett, *Z. physik. Chem.*, **33**, 611 (1920).

gen ion and temperature—which influence the rate of hydration, direct and determine the method of attack.

The temperature was controlled at 45° ± 0.02°. The amount of pyrophosphate changed to orthophosphate was determined by hydrogen-ion concentration measurement over the entire course of each hydration and by gravimetric analysis beyond 50%. By measurement of hydrogen-ion concentration it is possible not only to study the effect produced by different acid concentrations but also to determine the extent of transformation of pyrophosphate to orthophosphate.

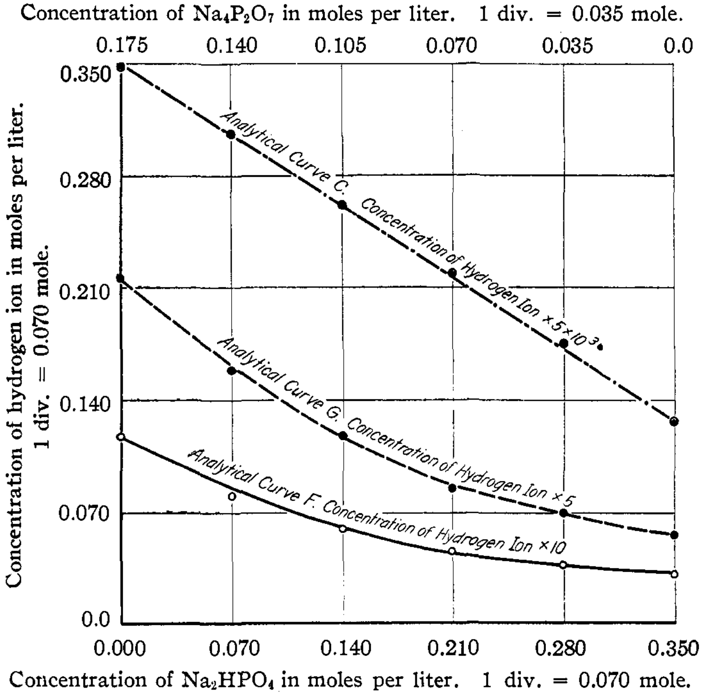

Fig. 1.—Analytical Curves *G*, *F* and *C*. $G = 0.175\ M$ $Na_4P_2O_7$ and $0.500\ M$ HCl; $F = 0.175\ M$ $Na_4P_2O_7$ and $0.425\ M$ HCl; $C = 0.175\ M$ $Na_4P_2O_7$ and $0.350\ M$ HCl.

Analogous to the method of Abbott,[4] synthetic solutions representing, 0, 20, 40, 60, 80 and 100% hydration for each different solution studied were made. From the hydrogen-ion concentration measurements of these synthetic solutions data were obtained for each solution studied. As examples of the type of data and curves, Table III and Fig. 1 are given. In order to minimize the number of figures, solutions of the same initial pyrophosphate concentration are, in all cases, put in the same figure. Also the hydrogen-ion values for each different initial acid concentration were multiplied by a factor, indicated on the curve to adapt them to the same scale as that used for plotting the concentrations of the phosphates. By referring to the respective analytical or reference curve one can establish the extent of hydration corresponding to the hydrogen-ion concentration determined at that time for the particular solution under investigation. Samples of each solution were pipetted at intervals into the hydrogen cell. The electromotive force was determined according to the method of Fales and Mudge,[8] from which the concentration of hydrogen ion was calculated by means of a relation $\log. (H^+) = (0.2342 - E)/0.063$, developed from the Nernst formula. The voltage (0.2997) of a 0.1 M hydrochloric acid solution standardized at 20° by Bureau of Standards benzoic acid with phenolphthalein as an indicator was used as a basis. Ninety-one and three-tenths, the value derived from the work of Noyes and others,[9] was employed as the percentage ionized in 0.1 M hydrochloric acid at 45° to make the calculations. E is the observed voltage.

All solutions were made at 20°. The measurements were made at 45°. The change of concentration due to thermal expansion is eight parts per thousand, for which a correction is possible, but this was deemed unnecessary since it falls within the limits of error of the method.

In making the acid solutions of the phosphates, the salts were transferred from a tared watch glass to a calibrated 1000cc. flask and enough distilled water was added to dissolve them quickly and still allow room to add from a buret the amount of standardized hydrochloric acid to give the molarity. By rotating the flask as the acid was added the hydration of the pyrophosphate by the strong acid was minimized as much as possible during the preparation of the solutions. The solutions were hurriedly brought to 1000 cc., put in Nonsol bottles, and placed in a thermostat. The time required from the beginning of the addition of the acid until the bottle was placed in the bath was, on the average, not more than ten minutes.

The specific gravity at 20° of three solutions, during hydration, was taken at the beginning and again at the end by means of a pycnometer. There was no change of volume greater than one part in 1000 during the hydration. The Westphal balance was used on the remaining six solutions as it gives results sufficiently accurate for the precision of the gravimetric analysis.

The specific-gravity determinations served a two-fold purpose. We were assured that no error greater than one part in one thousand was introduced in making up the synthetic solutions. They served also as a basis for the determination of volumes of samples weighed from a Bailey weighing buret. The total phosphorus content in a gravimetric sample could, therefore, be readily obtained for a solution of known molarity.

[8] Fales and Mudge, THIS JOURNAL, **42,** 2434 (1920).

[9] Noyes and co-workers, *Carnegie Inst. Pub.*, **1907,** pp. 141, 339.

After the hydration was beyond 50%, gravimetric determinations were made from samples pipetted from the bottles and weighed from the Bailey weighing buret. Due to the fact that magnesium pyrophosphate is soluble in an excess of magnesium salts, a method was developed whereby a separation of orthophosphate from a limited amount of pyrophosphate was possible. The magnesium chloride solution referred to above was used with the standard magnesia mixture to effect the quantitative separation according to the method developed in the following paragraph.

One hundred and seventy cc. of the magnesia mixture was added to 85 cc. of the magnesium chloride solution. This was called "magnesium chloride mixture." A weighed quantity of pyrophosphate dissolved in a few cubic centimeters of water was added drop by drop and stirred until the precipitate formed was dissolved. This process was continued until the entire amount of the pyrophosphate was added and the final solution remained clear. Orthophosphate was then added slowly from a standard solution by means of a buret during stirring until the precipitation was complete and the product crystalline. After standing for 12 hours this precipitate was separated from the solution by filtration, dissolved on the filter by a minimum amount of 3 *M* hydrochloric acid, and again precipitated. By allowing the hydrochloric acid solution to run into 20 cc. of a 6 *M* ammonium hydroxide solution, the hydration of any adsorbed pyrophosphate during the separation was minimized. The final washings brought the solution to 120 cc. A few drops of magnesium mixture were added to the alkaline solution to insure an excess of magnesium ion. After standing for six to twelve hours the magnesium ammonium phosphate was filtered into a Gooch crucible, washed, ignited and weighed as magnesium pyrophosphate.

In Table I are given the results of 29 determinations under the conditions stated above.

Attempts with a greater amount of pyrophosphate present than given

TABLE I

SEPARATION OF ORTHOPHOSPHATE FROM PYROPHOSPHATE

In milligrams

P used as ortho	P found as ortho	P used as pyro	P used as ortho	P found as ortho	P used as pyro	P used as ortho	P found as ortho	P used as pyro
30.60	30.38	40	45.00	45.20	30	45.00	46.13	30
30.53	30.38	40	45.00	44.83	none	45.00	45.77	20
30.53	30.16	40	45.00	44.52	none	45.00	45.91	20
30.53	30.75	40	44.90	45.69	30	45.00	44.83	none
30.53	30.58	30	45.00	46.41	30	45.00	44.74	none
30.53	30.30	30	45.00	45.88	30	45.00	46.41	30
30.53	30.61	30	45.00	45.74	20	45.00	45.88	30
30.53	30.53	20	45.00	45.91	20	21.50	21.74	30
30.53	30.38	20	45.00	45.55	30	21.60	21.49	30
45.00	45.52	30	45.00	45.29	30			

in the table were not satisfactory. From the results tabulated, the deviation within the limits of conditions outlined above is on the average about 1.5 parts per 100.

However, in sampling from solutions under investigation, a difficulty was encountered. Orthophosphate and pyrophosphate were simultaneously added. Small amounts of pyrophosphate were probably brought down with the orthophosphate, which upon dissolving with strong acid always gave high results on account of hydration at the beginning of the gravimetric procedure for each solution. These high results occur at a point in the progress of hydration where the hydrogen-ion concentration method is still reliable. As the hydration nears completion, the slopes of most of the hydrogen-ion concentration curves decrease with a consequent decrease in precision. On the other hand, the pyrophosphate has so decreased that the gravimetric method is dependable to a degree of variation not greater than that shown in Table I. The amount of phosphorus present as pyrophosphate was in all experiments not more than 10 mg. The samples were so taken that we would have an ignited magnesium pyrophosphate residue of about 0.15 g. This residue required 40 mg. as orthophosphate. The orthophosphate was therefore precipitated beyond 75% hydration in the presence of less than 10 mg. of phosphorus as pyrophosphate—decreasing constantly as completion was approached.

The taking of samples was done by pipetting some of the solution into a Bailey weighing buret from which a definite amount could be added to the "magnesium chloride mixture," drop by drop, during stirring, and the weight obtained.

In Tables II to VII the percentage hydrated, as determined by hydrogen-ion concentration measurement and analytical or reference curves of the type represented by Fig. 1, is designated Method M. The percentage determined by gravimetric procedure is designated Method N.

Tables IV to VI inclusive contain results of three hydrations outlined at the beginning of the Experimental Part. Table VII contains the data of a duplicate of the hydration whose values are given in Table VI.

The data in Table VII show how closely results may be duplicated, and what precision may be expected from the potential measurements. Omitting the first and last two measurements, the average difference between two corresponding measurements is one-half millivolt. In the first measurement, temperature and equilibrium conditions which were to be attained may not have been reached. In the last two the reactions had run for a period of three and one-third months with a difference between the two readings of one millivolt. For the whole range the average deviation from the mean of two corresponding times is less than 0.3 mv. By using the same wooden plugs for the hydrogen cells throughout the experiments it was possible to duplicate the potential measurements of synthetic solutions to within 0.3 mv. The precision of each individual measurement is, therefore, subject to a variation caused by an error of plus or minus 0.3 mv. The results selected to represent precision of measurement include the four hydrations where there is a change of but 4.0 mv. for a change of 20% in phosphate concentration. The five others have an average change of 8.0 mv. for a change of 20% phosphate concentration. Therefore, the precision of each individual percentage determination is subject to a deviation of 1 to 1.5 from the mean. By using both the potentiometric and gravimetric determinations and plotting the results, the course of the reaction may be followed with dependability and the error near completion will be on the average not greater than plus or minus two parts per hundred.

Experimental Part

Table II outlines the plan adopted for securing experimental data on the hydration of solutions of different hydrogen-ion and pyrophosphate concentrations.

TABLE II

SOLUTIONS INVESTIGATED

	A	H	I	C	F	G	B	D	E
Molar concn. $Na_4P_2O_7$	0.125	0.125	0.125	0.175	0.175	0.175	0.225	0.225	0.225
Molar concn. HCl	.350	.425	.500	.350	.425	.500	.350	.425	.500
d^{20}	1.029	1.030	1.031	1.041	1.041	1.043	1.052	1.054	1.056

All hydrations were run in duplicate.

For convenience, synthetic solutions were lettered the same as those under investigation. An example of such solutions is given in Table III and is represented graphically by Fig. 1.

TABLE III

DATA FOR ANALYTICAL OR REFERENCE CURVES OF FIG. 1

	Soln. no.	Molar concn. $Na_4P_2O_7$	Molar concn. Na_2HPO_4	Voltage	$[H^+] \times 10^5$
Soln. C	1	0.175	0.000	0.4961	6.96
0.350 *M* HCl	2	.140	.070	.4999	6.13
	3	.105	.140	.5038	5.25
	4	.070	.210	.5086	4.41
	5	.035	.280	.5149	3.50
	6	.000	.350	.5235	2.55
					$[H^+] \times 10^3$
Soln. F	1	0.175	0.000	0.3557	11.80
0.425 *M* HCl	2	.140	.070	.3661	8.06
	3	.105	.140	.3738	6.08
	4	.070	.210	.3809	4.58
	5	.035	.280	.3865	3.82
	6	.000	.350	.3910	3.24

TABLE III (*Concluded*)

	Soln. no.	Molar concn. $Na_4P_2O_7$	Molar concn. Na_2HPO_4	Voltage	$[H^+] \times 10^2$
Soln. G	1	0.175	0.000	0.3201	4.33
0.500 *M* HCl	2	.140	.070	.3285	3.18
	3	.105	.140	.3367	2.36
	4	.070	.210	.3445	1.77
	5	.035	.280	.3509	1.40
	6	.000	.350	.3565	1.14

TABLE IV

SOLUTION G

0.175 *M* $Na_4P_2O_7$ and 0.500 *M* HCl
Data for Curves in Fig. 2

Sample	Voltage	$[H^+] \times 10^2$	Time Hrs. mins.	Percentage hydrated Method M	Percentage hydrated Method N
1	0.3200	4.35	...	..	..
2	.3217	4.09	7:00	4.0	..
3	.3256	3.54	23:52	14.0	..
4	.3310	2.91	51:55	26.6	..
5	.3349	2.52	78:31	35.4	..
6	.3383	2.22	119:27	44.0	..
7	.3421	1.95	154:12	53.4	..
8	.3440	1.81	201:00	59.4	61.3
9	.3466	1.64	269:53	67.2	69.7
10	.3497	1.47	368:19	76.4	77.8
11	.3517	1.36	488:30	83.0	84.6
12	.3531	1.29	632:35	88.6 ?	92.0
13	.3543	1.24	824:48	92.0 ?	95.5
14	.3554	1.19	1016:27	96.6 ?	99.7
15	.3554	1.19	1160:23	96.6 ?	100.5

TABLE V

SOLUTION F

0.175 *M* $Na_4P_2O_7$ and 0.425 *M* HCl
Data for Curves in Fig. 2

Sample	Voltage	$[H^+] \times 10^3$	Time Hrs. mins.	Percentage hydrated Method M	Percentage hydrated Method N
1	0.3555	11.90	...	..	..
2	.3583	10.70	21:18	5.6	..
3	.3640	8.70	67:55	16.8	..
4	.3683	7.44	116:00	26.0	..
5	.3709	6.76	168:00	32.2	..
6	.3770	5.41	284:30	48.0	..
7	.3805	4.76	413:30	58.6	..
8	.3838	4.22	581:30	70.0	..
9	.3860	3.89	773:52	78.6	..
10	.3872	3.72	941:35	83.4	87.6
11	.3891	3.47	1277:15	92.2	95.1
12	.3915	3.17	1493:38	100.0	99.6

TABLE VI

SOLUTION C

0.175 *M* $Na_4P_2O_7$ and 0.350 *M* HCl

Data for Curves in Fig. 2

Sample	Voltage	$[H^+] \times 10^5$	Time Hrs., mins.	Percentage hydrated Method M	Percentage hydrated Method N
1	0.4962	6.94	...	..	..
2	.4982	6.45	71:41	11.6	..
3	.5001	6.01	143:27	21.0	..
4	.5010	5.82	244:05	26.0	..
5	.5050	5.03	365:53	44.0	..
6	.5063	4.79	479:04	51.0	..
7	.5091	4.33	579:00	60.0	..
8	.5117	3.93	752:32	69.2	67.4
9	.5134	3.70	896:26	73.8	74.1
10	.5149	3.50	1063:54	78.4	79.9
11	.5186	3.06	1447:36	87.8	89.0
12	.5196	2.95	1712:00	91.0	93.0
13	.5212	2.78	2072:12	95.0	95.5
14	.5217	2.73	2383:47	97.0	98.6

TABLE VII

SOLUTION C_2[a]

0.175 *M* $Na_4P_2O_7$ and 0.350 *M* HCl

Sample	Voltage	$[H^+] \times 10^5$	Time Hrs. mins.	Percentage hydrated Method M	Percentage hydrated Method N
1	0.4974	6.64	...	..	..
2	.4987	6.33	73:50	14.0	..
3	.5005	5.93	145:41	23.6	..
4	.5016	5.69	245:35	28.0	..
5	.5045	5.12	368:12	42.2	..
6	.5070	4.67	481:14	53.4	..
7	.5095	4.27	581:15	61.4	..
8	.5119	3.91	754:45	69.2	67.8
9	.5136	3.67	898:40	74.4	73.8
10	.5156	3.41	1066:32	79.4	79.1
11	.5191	3.00	1449:50	90.0	89.0
12	.5194	2.97	1714:35	90.6	91.4
13	.5220	2.70	2074:20	96.8	97.9
14	.5227	2.63	2385:55	98.4	97.1

[a] A duplicate of C_1 to show the reproducibility of results and the precision of measurement of Methods M and N.

Discussion

In Figs. 2, 3 and 4 the results of the several hydrations are shown graphically. The data for curves in Figs. 3 and 4 have been omitted as they differ in degree and not in character. The significant facts emphasized in each figure are the comparative effects of the different acid concentrations on the rate of hydration with the same phosphate concentration and the progressive decrease of hydrogen-ion concentration as the reaction proceeds.

The length of time required for the attainment of the same percentage hydration in each case decreases as the initial concentration of acid is increased—a fact that was known but not substantiated previously by extended quantitative measurement on solutions of normal sodium pyrophosphate with acids of different concentrations.

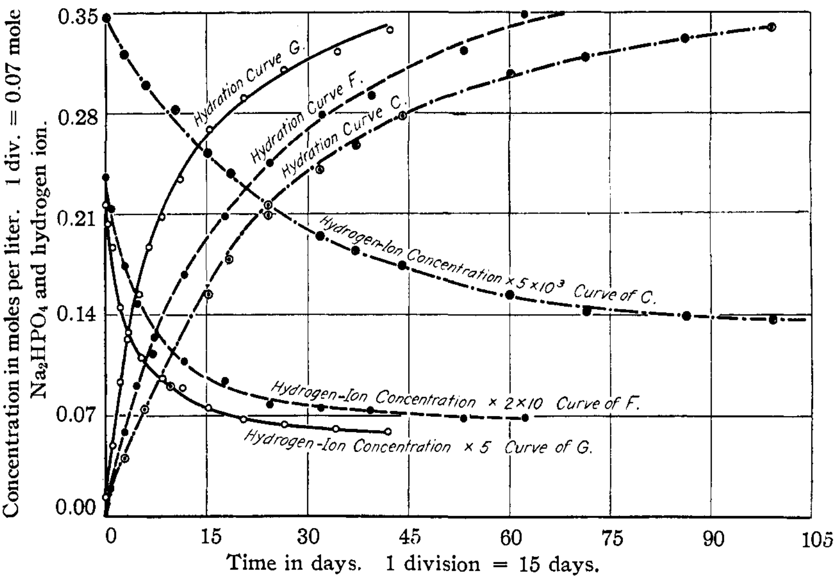

Fig. 2.—Hydration and hydrogen-ion concentration curves of *G*, *F* and *C*. *G* = 0.175 *M* $Na_4P_2O_7$ and 0.500 *M* HCl; *F* = 0.175 *M* $Na_4P_2O_7$ and 0.425 *M* HCl; *C* = 0.175 *M* $Na_4P_2O_7$ and 0.350 *M* HCl.

In the work of H. T. Beans and one of us with sodium monometaphosphate, the decrease of hydrogen-ion concentration during each separate hydration was found to occur. Likewise in this work, there is a decrease in hydrogen-ion concentration as the pyrophosphate is hydrated to orthophosphate. Therefore, in going by hydration from the monometaphosphoric acid through pyrophosphoric acid to orthophosphoric acid, the acids become respectively less active, the more they are hydrated.

Due to the simultaneous change in concentration of both hydrogen ion and pyrophosphate, it is the influence of both which affects the rate of transformation. A comparison of the hydrations of the different pyrophosphate concentrations with the same acid concentration emphasizes that the effect of hydrogen-ion concentration upon the rate is much more pronounced than that of pyrophosphate. For example 0.125 *M*, 0.175

M and 0.225 *M* pyrophosphate solutions with a 0.350 *M* HCl reached 98 ± 2% in 1302, 2384 and 4029 hours, respectively. The initial and

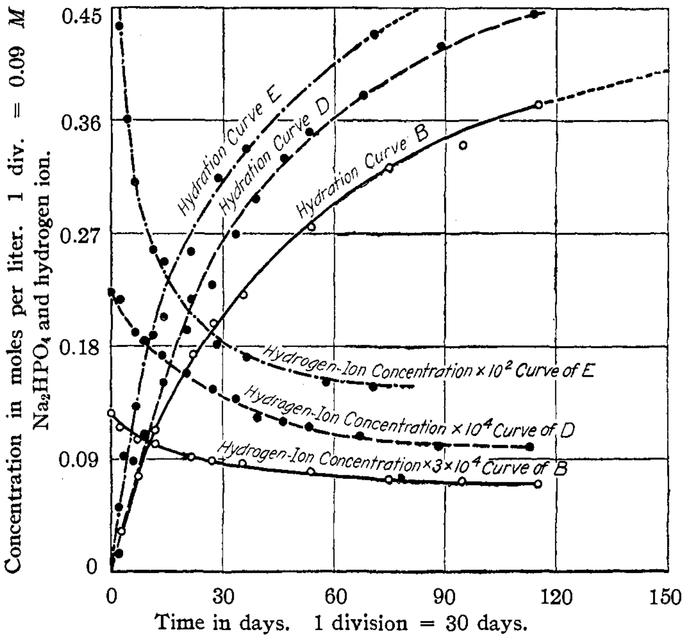

Fig. 3.—Hydration and hydrogen-ion concentration curves of *E*, *D* and *B*. *E* = 0.225 *M* $Na_4P_2O_7$ and 0.500 *M* HCl; *D* = 0.225 *M* $Na_4P_2O_7$ and 0.425 *M* HCl; *B* = 0.225 *M* $Na_4P_2O_7$ and 0.350 *M* HCl.

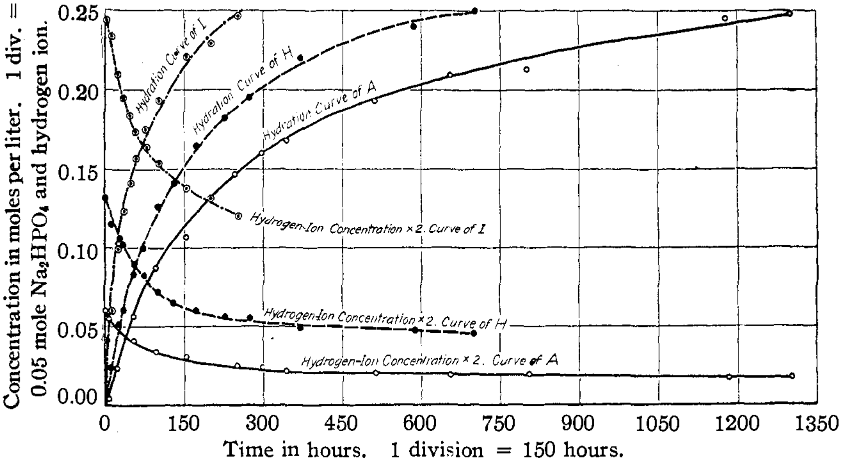

Fig. 4.—Hydration and hydrogen-ion concentration curves of *I*, *H* and *A*. *I* = 0.125 *M* $Na_4P_2O_7$ and 0.500 *M* HCl; *H* = 0.125 *M* $Na_4P_2O_7$ and 0.425 *M* HCl; *A* = 0.125 *M* $Na_4P_2O_7$ and 0.350 *M* HCl.

final hydrogen-ion concentrations are quite different in each case. The initial molar hydrogen-ion concentrations for a 0.125 *M*, a 0.175 *M* and a 0.225 *M* were respectively 2.9×10^{-2}, 6.9×10^{-5} and 4.2×10^{-6} while their corresponding final concentrations were 0.9×10^{-2}, 2.7×10^{-5} and 2.2×10^{-6}. The initial hydrogen-ion concentration and the changing concentration as the reaction proceeds toward the complete transformation to orthophosphate offer an interesting study in the comparative activities of the hydrochloric, pyrophosphoric and orthophosphoric acids, respectively.

Summary

1. Three concentrations of normal sodium pyrophosphate each in three different concentrations of hydrochloric acid were studied.

2. By use of analytical or reference curves obtained by making hydrogen-ion concentration measurements on synthetic solutions and plotting molar concentration of hydrogen ion against molar concentration of disodium orthophosphate, each hydration was followed to completion by hydrogen-ion concentration measurements.

3. Beyond the last 50%, each hydration was followed by the standard gravimetric method for orthophosphate. The separation of orthophosphate from a limited quantity of pyrophosphate was made by use of a "magnesium chloride mixture."

4. The hydrogen-ion concentration decreased progressively with time, tending to reach a final fixed value as complete conversion to orthophosphate was approached. This fact indicates that pyrophosphoric acid is a more active acid than orthophosphoric acid in spite of the formation of potential hydrogen ions during the reaction.

Table VIII

Summary of Results

Solution		A	H	I	C	F	G	B	D	E
Concentration of $Na_4P_2O_7$, *M*		0.125	0.125	0.125	0.175	0.175	0.175	0.225	0.225	0.225
Concentration HCl, *M*		0.350	0.425	0.500	0.350	0.425	0.500	0.350	0.425	0.500
	%									
Time in hours for the hydration of the percentage indicated.	5	11	5.2	1.8	28	18	7	40	39	20
	10	23	10.8	3.8	57	38	15	85	79	42
	15	35	17.0	5.8	89	61	24	140	123	67
	25	62	33.2	11.0	165	113	46	277	222	127
	35	97	54.0	18.8	256	177	74	463	337	203
	45	144	79.6	29.0	369	254	110	694	477	298
	55	207	114.5	42.8	507	344	162	1012	648	416
	65	291	161.5	61.7	686	460	242	1468	860	559
	75	404	224.5	88.5	926	625	337	1955	1140	749
	85	580	319.0	133.0	1263	900	506	2722	1605	1060
	90	722	393.0	165.5	1538	1290	636	3235	1976	1280
	95	982	527.0	214.0	1992	1300	830	4035	2448	1553

5. Table VIII summarizes the results of duplicate hydrations on each solution. The values were obtained from a smooth curve representing the most probable curve for the two hydrations in each case.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE POISONING ACTION OF OXYGEN ON IRON CATALYSTS FOR AMMONIA SYNTHESIS

BY J. A. ALMQUIST AND C. A. BLACK

RECEIVED AUGUST 11, 1926 PUBLISHED NOVEMBER 5, 1926

Heterogeneous catalytic gas reactions in general are characterized by a marked sensitivity to inhibition or poisoning by the presence in the reacting gases of small concentrations of certain foreign substances. The substances that are known to act as catalyst poisons are many and the effect of each has been found to be dependent upon the type of catalyst that is being employed. It has been noted previously[1,2] that oxygen compounds are poisons for iron ammonia catalysts and that the inhibiting effect of small concentrations of several different oxygen compounds is proportional to their oxygen content. The present investigation was undertaken with the view of studying in a quantitative way the mechanism of the poisoning action of oxygen with particular regard to its effect on iron catalysts containing various promoters.

Experimental Part

The experiments were made at atmospheric pressure in a glass apparatus arranged as in Fig. 1. The catalysts used were of the series whose composition, preparation and activity at 100 atmospheres' pressure are described in connection with another investigation.[3]

Approximately 5 cc. of the catalyst to be studied was placed in the tube, 6, in the form of 10–14 mesh granules of the oxide. The weight of the oxidized catalyst used in each case was 12.95 ± 0.02 g. The tube was then sealed into place and heated to 444° by means of a boiling sulfur-vapor bath. Reduction was then begun by passing through a gas mixture of three parts of hydrogen to one of nitrogen. This gas was expanded from the high-pressure system, where it had undergone purification by passage over heated copper and nickel catalysts, soda lime and alumina gel. In order to insure a high degree of gas purity for these tests, the expanded gas was passed in order through Tube 1 containing platinized asbestos at about 300°, drying tubes containing soda lime and fused potas-

---

[1] Larson and Tour, *Chem. Met. Eng.*, **26**, 647 (1922).

[2] Almquist and Dodge, *ibid.*, **33**, 89 (1926).

[3] Almquist and Crittenden, *Ind. Eng. Chem.*, to be published later.