[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 528]

THE DISSOCIATION PRESSURES OF MONOPOTASSIUM AND MONOSODIUM ORTHOPHOSPHATES AND OF DIPOTASSIUM AND DISODIUM DIHYDROGEN PYROPHOSPHATES. PHOSPHATE IV

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Introduction

In 1833, Graham[1] prepared sodium metaphosphate, potassium metaphosphate and disodium dihydrogen pyrophosphate by heating their respective primary orthophosphates. He did not prepare the dipotassium dihydrogen pyrophosphate in the same manner in which he prepared the corresponding salt of sodium. Balareff,[2] however, claims that when primary potassium orthophosphate is heated it melts around 244° and forms a glassy mass which consists to a great extent of dipotassium dihydrogen pyrophosphate. For the formation of the disodium dihydrogen pyrophosphate, Graham gave 190–204° as the suitable temperature without assigning a reason beyond obtaining the product.

A review of the work done furnishes no information regarding the temperature-pressure equilibria of the phosphate system similar to that developed[3] for the various hydrates and other substances which dissociate, forming a gaseous phase.

Since in the preparation of the metaphosphate and pyrophosphate by heating the necessary orthophosphate, a vapor phase is developed, it seems evident that the dissociation is not different in general kind from the dissociations previously studied. Below, an account is given of an investigation to determine the temperature-pressure equilibria of the following phosphate systems:

$$2KH_2PO_4 \overset{\Delta}{\rightleftharpoons} K_2H_2P_2O_7 + H_2O$$

$$xK_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(KPO_3)_x + xH_2O$$

$$xKH_2PO_4 \overset{\Delta}{\rightleftharpoons} (KPO_3)_x + xH_2O$$

$$2NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$$

$$xNa_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(NaPO_3)_x + xH_2O$$

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[1] Graham, *Phil. Trans.*, **123**, 253 (1833).

[2] Balareff, *Z. anorg. Chem.*, **118**, 123 (1921).

[3] (a) Frowein, *Z. physik. Chem.*, **1**, 5 (1887). (b) Smith and Menzies, THIS JOURNAL, 1910–1920. (c) Johnston, *Z. physik. Chem.*, **62**, 330 (1908). (d) Baxter and Lansing, THIS JOURNAL, **42**, 419 (1920). (e) Carpenter and Jette, *ibid.*, **45**, 578 (1923). (f) Caven and Ferguson, *J. Chem. Soc.*, **121**, 1406 (1922).

$$x\mathrm{NaH_2PO_4} \overset{\Delta}{\rightleftharpoons} (\mathrm{NaPO_3})_x + x\mathrm{H_2}$$

(Whenever H_2O appears in the above equations, it is to be read as water in the gaseous state. When x is used in this article it means a unit, one or more. Three is generally used under the conditions of this investigation.)

In each of the above reactions there are two components, the choice of which is arbitrary. Furthermore, as long as there are three distinct and separable phases present at equilibrium the system is a univariant one—that is, at any given temperature there will correspond a certain definite maximum pressure (dissociation pressure) of the system, independent of the relative or absolute amounts of the solid or liquid phases present and of the volume of the vapor phase. In the above equilibria the possibilities of a univariant system are limited to the following: solid–solid–vapor, liquid–liquid–vapor, and solid–liquid–vapor. Which of these obtains at equilibrium will be mentioned under the discussion of results.

Preparation of Materials

Primary Potassium Orthophosphate, KH_2PO_4.—A quantity of the purest obtainable primary potassium orthophosphate was crystallized thrice from distilled water and dried in an air-bath at 100° to constant weight.

Dipotassium Dihydrogen Pyrophosphate, $K_2H_2P_2O_7$.—This salt cannot be prepared by heating the primary orthophosphate. The reason will be given later. It was prepared by dissolving the normal potassium pyrophosphate in a small amount of distilled water, cooling in ice water to prevent hydration to orthophosphate, adding acetic acid and then precipitating the dipotassium dihydrogen pyrophosphate by the addition of alcohol. This did not produce a deliquescent mass as stated in the literature,[4] but a crystalline monohydrate was obtained which was not deliquescent. It was dried in an air-oven at 155° to produce the anhydrous salt. If metaphosphate should be produced when the anhydrous salt is formed, it would not be detrimental as it is the phase produced on the dissociation in System I where it is used. Analyses indicated the expulsion of water of hydration.

Potassium Metaphosphate, $(KPO_3)_x$.—The potassium metaphosphate was prepared by heating the primary orthophosphate and also by heating the dihydrogen pyrophosphate at a temperature of 290–300° for several days until analysis showed that all of the water of constitution had been expelled. This is the metaphosphate phase produced in the dissociations investigated.

Primary Sodium Orthophosphate, $NaH_2PO_4.2H_2O$ and NaH_2PO_4.—Chemically pure primary sodium orthophosphate was dissolved in distilled water and thrown out of solution by adding an amount of ethyl alcohol equal to the volume of the phosphate solution. This method, from the work of Beans and one of us,[5] produced a dihydrate which was unstable at room temperature and could not be heated above 40° without liquefying. The anhydrous salt was prepared by exposing the dihydrate to the air until it had lost about 7% of water of hydration and then heating it in an air-bath at 100° until all the water of hydration had been driven off. In this way the salt did not melt.

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[4] Roscoe and Schorlemmer, "A Treatise on Chemistry," Macmillan and Co., New York, 1923, vol. 2, p. 382.

[5] Published and submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York City, by Samuel J. Kiehl in February, 1921.

Disodium Dihydrogen Pyrophosphate, $Na_2H_2P_2O_7$.—This salt was prepared by heating the above anhydrous orthophosphate in an oven at 190° until the orthophosphate disappeared. If metaphosphate were formed during the preparation it would not interfere with subsequent attainment of equilibria according to experimental evidence and remarks under discussion.

Sodium Metaphosphate, $(NaPO_3)_x$.—The sodium metaphosphate was prepared by heating the above orthophosphate in an open vessel at 290–300° for several days until it was shown by analyses that it contained no water of hydration nor of constitution.

This is the metaphosphate phase produced in the dissociation under the conditions of this investigation.

Mercury.—The mercury for use in the manometer and as the enclosing liquid was twice distilled according to the method of Hulett.[6]

Reagents

In order to test qualitatively what phases were present at equilibrium, the following test reagents were prepared: (a) a 0.1 *M* solution of silver nitrate; (b) a 0.1 *M* solution of barium chloride; (c) a 0.2 *M* solution of zinc acetate whose hydrogen-ion concentration was adjusted to 5×10^{-4} moles per liter with glacial acetic acid; (d) 1 *M* nitric acid.

Tests

At equilibrium, quite appreciable amounts of each phase were present, so that the only procedure was to identify them. Accordingly, tests were made for the detection of orthophosphate ion in the presence of pyrophosphate ion, of pyrophosphate ion in the presence of metaphosphate ion and of metaphosphate ion in the presence of ortho- and pyrophosphate ions. The metaphosphates formed in these systems were insoluble in water and, therefore, did not interfere with the test for orthophosphate ion. Silver nitrate is sufficiently sensitive to detect 0.02 *M* orthophosphate in the presence of 0.1 *M* pyrophosphate. The barium chloride will detect 0.001 *M* metaphosphate in the presence of 0.1 *M* pyrophosphate in a 1 *M* nitric acid solution. The zinc acetate solution gives a precipitate with 0.006 *M* pyrophosphate in the presence of 0.1 *M* orthophosphate.

Apparatus

The apparatus was a modification of that used by Johnston[3c] in his study of the dissociation pressures of some metallic hydroxides. The system was inclosed in Pyrex. An arrangement of the apparatus is given in Fig. 1.

The manometer M, with mercury as the confining liquid mounted upon the beam bearing a scale S, was connected to a U-tube U by means of glass tubing and a short piece of shellacked, thick-walled rubber tubing G. By Stopcock B, air was admitted to balance any pressure developed in the system. C was connected to the vacuum pump. The U-tube was surrounded by a double-walled, glass jacket J, through which steam under a slight pressure was passed to maintain the temperature sufficiently high

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[6] Hulett, *Z. physik. Chem.*, 33, 611 (1900).

to prevent the water vapor developed in the decomposition from condensing. F represents the electric furnace, T the thermocouple, D the Dewar flask, P the potentiometer and K the galvanometer. The flexible rubber connection was used because it was necessary to tilt the U-tube to adjust the mercury in the legs which served as the gage. With both systems on either side of U evacuated, any pressure developed in E could be counterbalanced by admitting air. When the heights of the columns were equal, the pressures on each side were equal and could be measured independently on the manometer M.

A determination of the vapor pressure of water at the boiling point demonstrated that the arrangement was satisfactory. It also gave the proper temperature at which to hold the steam jacket to prevent condensation of water within the system. Temperatures were determined by a copper-constantan thermocouple in connection with a potentiometer. An open-end mercury manometer with a 1mm. bore was mounted on a steel beam to which was attached an invar steel bar with a silver scale graduated in millimeters. To prevent oxidation of the mercury, the open end was protected by an alkaline pyrogallate solution. The beam was provided with a mirror back of the manometer and a hair-line reading device by which it was possible to read pressures with an accuracy of ±0.2 mm. The heat was furnished by an electric-resistance furnace, 12.7 cm. in depth and 7.6 cm. internal diameter. This was lined on the inside with asbestos rope to distribute the heat more evenly. With a sufficiently adjustable resistance in the circuit, any desired temperature within the range of that required could be obtained.

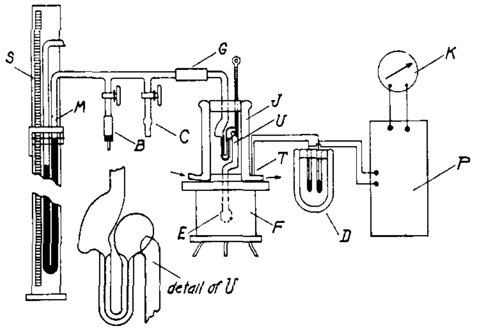

Fig. 1.

The thermocouple was checked against melting ice, boiling water and the freezing points of Bureau of Standards samples of tin and lead. A small Dewar flask containing crushed ice and distilled water served as the cold junction. A constant temperature of 0° was thus maintained and cold-junction corrections were eliminated.

A Leeds and Northrup Type K potentiometer was used in connection with a low-resistance Type R D'Arsonval galvanometer for measuring the electromotive force of the couple. The temperature was found by comparison with the regular electromotive force-temperature curve of the couple.

A Model 4 Weston standard cell served as the basis for all electrical measurements. Its voltage was compared frequently with that of a cell checked against a Bureau of Standards standard cell. Its voltage was constant throughout the entire investigation.

The system was evacuated by means of a two-stage oil pump capable of reducing the pressure to a fraction of a millimeter.

Method of Procedure

The sample was introduced carefully into the 15mm. bulb of Tube E (Fig. 1) made from Pyrex, of 10 mm. external and 7 mm. internal diameter. This tube of appropriate length was then sealed to U.

The volume from the enclosing liquid in the leg of U including the sample tube varied from 14–18 cc. This determined the size of the sample. One

g. of water at 100° and 760 mm. occupies about 1700 cc. Therefore our samples would necessarily have to contain more than 0.01 g. of water of constitution. Seven times the calculated amount, in general, was taken and our samples composed of the salt and the phase desired in decomposition weighed approximately 0.5 g. The samples were finely ground and intimately mixed.

Now, with the upper bulb of the U-tube containing sufficient mercury to fill each of the legs of it to a depth of 2–3 cm., the whole apparatus was adjusted for the determination in the following manner. The sample tube was immersed in boiling water to a depth of three inches and with the mercury still in the upper bulb of the U-tube, the system evacuated for an hour, during which all parts of the system were gently heated to remove moisture. The system was left evacuated overnight and the pump turned on for about half an hour the next morning. The mercury from the upper bulb of U was run into the legs while the pump was running, the stopcock was closed, the pump shut off and the vacuum read on the manometer. The barometer reading was taken and recorded. Corrections for differences between the two readings were used in calculating the correct equilibrium pressure. A paper millimeter scale was attached behind the legs of the U-tube to serve as a guide in leveling the enclosing liquid, the double-walled jacket adjusted to position with a cork stopper at either end and the tube containing the sample inserted through a hole in an asbestos board which fitted flush with the lower cork. The thermocouple was lashed to the bulb containing the sample. The bulb was then inserted into the furnace to a depth of about 8 cm. and the asbestos board brought tightly against the top of the furnace. The current and steam were then turned on and any pressure developed was balanced by admitting air through B. The jacket and manometer were tapped gently quite often to make sure that the mercury was not sticking. When the temperature and pressure remained constant for at least an hour the system was assumed to be in equilibrium and the heights of the mercury column, whose temperature was obtained by averaging the temperatures of three thermometers hung along the manometer, were read on the manometer and the barometer reading was taken. The columns of mercury in both the manometer and the barometer were corrected to 0° and the difference between them was taken as the pressure of the system, with allowance for any initial pressure in the system. The pressures are recorded in millimeters of mercury at 0°.

When a run was completed, the sample tube was removed from the furnace, the mercury in the legs of U drawn up into the upper bulb and the system evacuated in preparation for another run. Depending, however, upon the temperature and pressure at which the runs were made the same sample was generally used for more than one run. In the cases where there was partial liquefaction a new sample was taken for the next run. Equilibrium was reached fairly quickly with the potassium salts—in less than five hours. With the sodium salts, however, it required at least 70 hours before some of the equilibria were reached. In order to reduce the time required to reach equilibrium the system was heated above the temperature at which the equilibrium pressure was required and before the equilibrium pressure was reached the temperature was lowered to that desired. Some experiments were run continuously for 70 hours for one reading; others would give two or more readings in the course of 12 hours.

Discussion of Errors

As true equilibrium pressure is characterized by the production of exactly the same results when approached from both higher and lower pressures and temperatures, the results given here are most precise over the temperature ranges in which the systems were found to be feasibly reversible. Below these ranges the systems were assumed to be at equilibrium when no increase in pressure could be noticed for at least an hour, an assumption which we are not really justified in making as the reaction might still be going forward although too slow to give any noticeable increase in pressure for several hours. No metastable equilibrium was assumed to exist as the phases were the same over the entire range and curves were coincident when extended. However, as results were reproducible when held at constant temperature over varying lengths of time, they were accordingly recorded as the probably correct values. Naturally, the larger percentage errors occur at lower pressures. The error in reading the manometer, taken as 0.2 mm., would give a 2% error at a pressure of 10 mm. Another source of error is in leveling the enclosing liquid through the double-walled steam jacket. This may safely be taken as not exceeding 3%.

Since the copper-constantan thermocouple may be relied upon up to 360° for very precise work, the error from this source is indeed small and within the limit of other errors. The temperature of the furnace was maintained constant to within ±0.2°, so that the maximum error here in all but the system $NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$ would be not more than 2% when referred to pressures in millimeters of mercury. In the system mentioned above this would produce a maximum error of 4–5%.

Experimental Data

The results obtained for the equilibrium pressures of the systems are given in Tables I–V. They are shown graphically in Figs. 2 and 3.

In Table I both the actual determinations and the respective averages are given. Tables II, III and IV represent the averages only. All pressures are recorded in millimeters of mercury at 0°.

TABLE I

SYSTEM I

$xK_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(KPO_3)_x + xH_2O$. Reversible throughout.

Temp., °C.	Pressure, mm.	Av. press., mm.
165.0	19.5	19.5
167.0	21.2	21.2
170.0	24.3—24.6—24.5—24.6—23.7	24.3
180.0	44.1—44.3—41.1—42.0—42.8	42.9
186.0	58.8	58.8
190.0	63.8—66.2—64.0—63.2	64.3
190.5	67.7—68.6	68.1
200.0	97.6—95.8—98.9—100.4—100.2—99.9—99.6—99.2 95.7—98.8—96.0—99.0—101.5	98.3
202.0	104.4	104.4
210.0	134.5—138.0—135.3	135.9
211.0	145.5	145.5
212.0	150.3—148.3	149.3
220.0	203.1—203.2	203.1
230.0	313.3—307.8—304.1—311.9—303.6—313.7	309.1
240.0	471.3—468.5—474.0—469.3—467.6—466.8	469.4
250.0	627.3—638.0—637.6	634.3
260.0	728.5—733.5—737.9	734.8

TABLE II

SYSTEM II

$xNa_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(NaPO_3)_x + xH_2O$. Feasibly reversible above 240°.

Temp., °C.	Av. press., mm.	Temp., °C.	Av. press., mm.
170.0	10.6	240.0	289.0
180.0	34.5	250.0	411.6
190.0	59.0	260.0	526.5
200.0	84.9	267.0	595.6
210.0	115.0	270.0	650.0
220.0	154.0	275.0	717.4
230.0	208.2	278.5	754.8

TABLE III

SYSTEM III[a]

$xKH_2PO_4 \overset{\Delta}{\rightleftharpoons} (KPO_3)_x + xH_2O$. Feasibly reversible above 215°.

Temp., °C.	Av. press., mm.	Temp., °C.	Av. press., mm.
170.0	6.3	250.0	673.3
180.0	25.5	254.5	715.8
191.0	46.5	254.8	721.2
200.0	68.3	255.5	728.2
210.5	118.7	256.5	733.6
220.0	188.3	257.0	734.9
230.0	306.5	258.5	739.1
240.0	467.9	264.0	751.0

[a] See discussion on this system above 248°.

TABLE IV

SYSTEM IV

$2NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$. Feasibly reversible above 145°.

Temp., °C.	Av. press., mm.	Temp., °C.	Av. press., mm.
110.0	17.9	140.0	245.0
120.0	36.1	148.0	521.0
128.0	55.3	148.5	621.0
130.0	66.1	150.0	750.0

TABLE V

COMPARISON OF SYSTEMS I–IV

Temp., °C.	System I Press., mm.	System II Press., mm.	System III Press., mm.	System IV Press., mm.
95	...	...	...	...
100	...	...	...	6.7
105	...	...	...	11.7
110	...	...	...	17.9
115	...	...	...	26.3
120	...	...	...	36.1
125	...	...	...	48.4
130	...	...	...	66.1
135	...	...	...	109.0
140	...	...	...	194.0
145	...	...	...	360.0
150	...	...	...	750.0
155	5.0	...	...	...
160	11.0	...	...	...
165	18.0	1.0	...	...
170	24.5	10.6	6.3	...
175	33.0	21.0	16.0	...
180	42.8	33.0	25.0	...
185	52.5	45.0	34.7	...
190	64.0	59.0	44.5	...
195	80.0	71.0	55.0	...
200	98.3	85.0	69.0	...
205	115.5	100.0	89.0	...
210	136.0	115.0	115.0	...
215	161.0	133.0	152.0	...
220	199.0	154.0	190.0	...
225	246.0	179.0	242.0	...
230	309.0	208.0	303.0	...
235	386.0	250.0	380.0	...
240	469.0	296.0	468.0	...
245	553.0	345.0	570.0	...
250	634.0	395.0	673.0	...
255	684.0	451.0	720.5	...
260	734.0	517.0	739.0	...
265	...	578.0	...	...
270	...	643.0	...	...
275	...	710.0	...	...
280	...	760.0	...	...

For comparison, Table V contains the average pressures for each of the four systems in five-degree intervals from 95° to 280°.

Discussion of Results

A comparison of the data in Table V and curves in Figs. 2 and 3 for Systems I and III shows quite conclusively why dipotassium dihydrogen pyrophosphate cannot be prepared by heating the primary orthophosphate. Its dissociation pressure at lower temperatures is higher than that of the orthophosphate when it forms metaphosphate under the same conditions. Consequently, if it were possible for any dihydrogen pyrophosphate to be formed from orthophosphate it would be converted into metaphosphate under equilibrium conditions of the system. We are dealing with a two-component, univariant system. The vapor phase must always be present. Therefore, the maximum number of solid phases which may coexist are two. If, then, we start with a mixture of primary potassium orthophosphate and dipotassium dihydrogen pyrophosphate in a closed system and apply heat, we know that the dihydrogen pyrophosphate will and should disappear in a stable system because its dissociation pressure is the higher, or it will produce another solid phase, giving us ortho-, dihydrogen pyro- and metaphosphates as solids, and one vapor phase, in a system consisting of two components. We should have, therefore, an invariant system or a system not in equilibrium. From experimental data the system is univariant in the range of experimentation. This allows the coexistence of two solid phases only. So the disappearance of the most unstable phase is required for equilibrium. At 170°, with equilibrium established by tests, orthophosphate and metaphosphate alone existed as solid phases.

On the other hand, if we start with a mixture of primary sodium orthophosphate and sodium metaphosphate and apply heat to the closed system, we find by experiment that when equilibrium is reached we have the orthophosphate and dihydrogen pyrophosphate as the solid phases. Here, moreover, the orthophosphate decomposes to form the stable dihydrogen pyrophosphate. We would again have four phases and either an invariant system or a system not in equilibrium. In this case the metaphosphate is the metastable phase and must disappear in order that the system may reach equilibrium. The absence of data for the systems, $2KH_2PO_4 \overset{\Delta}{\rightleftharpoons} K_2H_2P_2O_7 + H_2O$ and $xNaH_2PO_4 \overset{\Delta}{\rightleftharpoons} (NaPO_3)_x + xH_2O$, is therefore explained.

By comparing the data and curves in Fig. 3 for Systems I and II in Table V we find that the dipotassium dihydrogen pyrophosphate–metaphosphate–vapor system has a higher dissociation pressure at any given temperature than the corresponding sodium system. This would predict that potassium metaphosphate could be prepared at a lower temperature than the sodium metaphosphate. Pascal found this to be the case.[7]

The solid phases of the potassium systems have a tendency to cake into a hard mass, with considerable shrinkage in volume. Partial liquefaction is also produced between 245° and 250°. In the system $xK_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(KPO_3)_x + xH_2O$ the metaphosphate appears to be suspended in a solution of the dihydrogen pyrophosphate; some of it is possibly dissolved, which probably accounts for the falling off in the vapor-pressure curve in Fig. 3 above 250°. In the system $xKH_2PO_4 \overset{\Delta}{\rightleftharpoons} (KPO_3)_x + xH_2O$, liquefaction takes place at about 248° with the formation also of dihydrogen pyrophosphate. Here it seems, since the phosphates were formed with the system in equilibrium, that the orthophosphate dissolves the dihydrogen pyrophosphate formed and that the meta- behaves as in the above system, giving in both cases a solid–liquid–vapor system. If this is so, then it accounts for the greater falling off of the curve in Fig. 2 for this system above 250°. Inasmuch as three solid phases and one vapor phase could not coexist at

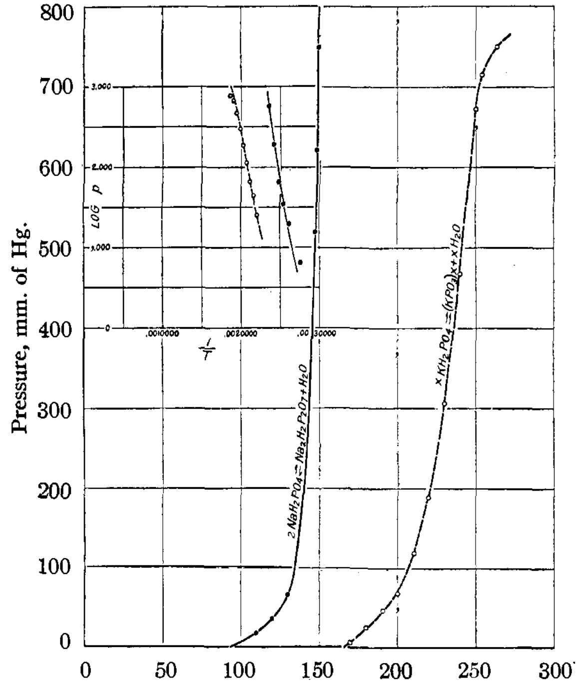

Fig. 2.—Full line = sodium salt system. Broken line = potassium salt system.

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[7] Pascal, *Compt. rend.*, **178**, 211 (1924).

equilibrium in a two-component system without a well-defined intersection of two curves, this seems to be the only logical explanation.

By reference to the curve in Fig. 2 for the system $2NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$, it is seen that most of the pressure is produced between 140° and 150°. Therefore, disodium dihydrogen pyrophosphate may be prepared near 150° if heated in an open vessel, or at a lower temperature if the partial pressure of the water vapor is kept low by removal as soon as formed.

Figs. 2 and 3 also show that when the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, the points so obtained lie very nearly on straight lines. Antoine[8] developed an equation of the form $\log p = A - [B/(T + C)]$ (where A, B and C are constants), by which the relation between pressure and temperature may be calculated when the ($\log p$, $1/T$) points lie on straight lines. Inasmuch as the points obtained here conform very closely to lying on straight lines, this equation was applied to Systems I and II and was found to hold with an average deviation of less than 8% at intermediate temperatures.

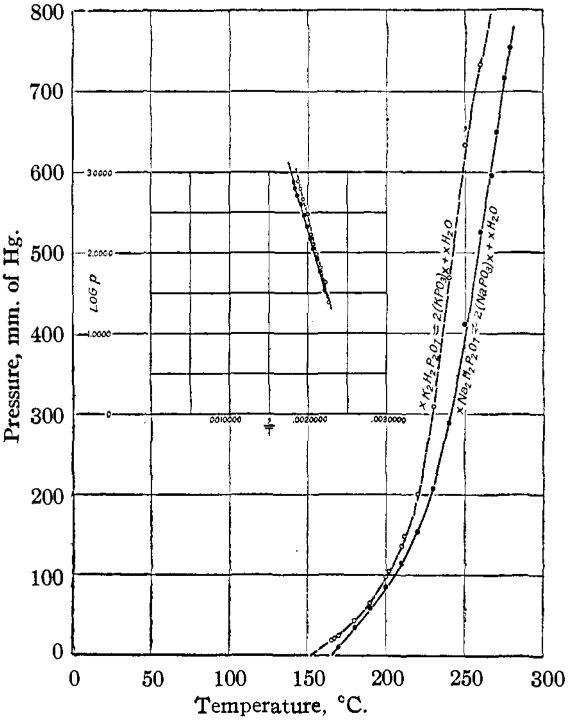

Fig. 3.—Full line = sodium salt system. Broken line = potassium salt system.

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[8] Antoine, *Compt. rend.*, **107**, 681, 778, 836 (1888).

Summary

An apparatus, with mercury as the confining liquid, for measuring by the static method dissociation pressures of compounds giving a condensable vapor, has been described.

Temperatures were measured by the thermocouple-potentiometer method with the cold junction at 0°.

Equilibrium was reached from higher temperatures and pressures where reactions were found to be feasibly reversible as indicated in the tables.

The dissociation pressures of the following closed systems have been measured: $xK_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(KPO_3)_x + xH_2O$; $xNa_2H_2P_2O_7 \overset{\Delta}{\rightleftharpoons} 2(NaPO_3)_x + xH_2O$; $xKH_2PO_4 \overset{\Delta}{\rightleftharpoons} (KPO_3)_x + xH_2O$; $2NaH_2PO_4 \overset{\Delta}{\rightleftharpoons} Na_2H_2P_2O_7 + H_2O$.

No equilibrium-pressure relations in the closed systems, $2KH_2PO_4 \overset{\Delta}{\rightleftharpoons} K_2H_2P_2O_7 + H_2O$ and $xNaH_2PO_4 \overset{\Delta}{\rightleftharpoons} (NaPO_3)_x + xH_2O$, were obtained in the temperature ranges studied.

New York, N. Y.

[Contribution from the Bureau of Mines, United States Department of Commerce, and the Safety in Mines Research Board, British Mines Department]

MECHANISM OF THE UNIFORM MOVEMENT IN THE PROPAGATION OF FLAME[1]

By H. F. Coward[2] and G. W. Jones[3]

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When an inflammable gas mixture is ignited at the open end of a tube closed at the other end, flame is propagated at first at uniform speed. In weak mixtures this "uniform movement" may persist during the whole passage of flame throughout the tube, but in most cases the uniform movement sooner or later gives place to a vibratory movement which may either develop into detonation or result in spontaneous extinction of the flame during some particularly violent vibration.[4]

When ignition is effected near the *closed* end of a tube, flame is propagated toward the open end at an accelerated rate which may ultimately

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[1] This is a joint report on one of a series of investigations to decrease accidents in mines, being conducted under the coöperation between the Bureau of Mines, U. S. Department of Commerce, and the Safety in Mines Research Board, British Mines. Department. Published with approval of the Director, United States Bureau of Mines.

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[4] Mallard and Le Chatelier, *Ann. Mines*, [8] **4,** 274 (1883).