VAPOR-LIQUID PHASE EQUILIBRIA IN THE P_2O_5–H_2O SYSTEM

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A mixture is formed on thermal degradation of orthophosphoric acid, or by its reaction with phosphoric anhydride, which contains various phosphoric acids: orthophosphoric, H_3PO_4; pyrophosphoric, $H_4P_2O_7$; triphosphoric acids: orthophosphoric $H_5P_3O_{10}$; and metaphosphoric acids having the general formula $(HPO_3)_n$. We will call such a mixture "strong phosphoric acid".

Mutual transformations of the stated acids, except for polymerized metaphosphoric acids, take place rather rapidly; consequently, the ratio of acids in the mixture is determined by the total phosphoric anhydride content and does not depend on the method by which the mixture was prepared [1, 2, 3], if formation of polymerized metaphosphoric acids is excluded. From this it follows that vapor pressure in the P_2O_5–H_2O system is uniquely determined by the liquid phase phosphoric anhydride content (with the above stated reservation).

Data published in the literature on variation of vapor pressure over phosphoric acids with temperature and composition [4-8] covers a wide range of phosphoric anhydride content. However, these data are limited – up to a pressure of only one atmosphere. Results of measuring vapor pressure over phosphoric acids at pressures of one atmosphere and higher are presented below.

Method of Measurement

Measurements were performed in an apparatus (Fig. 1), a novel feature of which was use of the liquid whose vapor pressure was being determined as a manometric fluid in a differential manometer. A U-shaped tube was used for this; its narrow arm was closed and filled with liquid at the start. Liquid level in the open arm was thus lower than its level in the closed arm (in selecting the difference in levels it is necessary to consider liquid expansion on heating). Inert gas pressure, measured with a manometer, was maintained over the liquid in the open arm. Subsequently, the U-tube was gradually heated. At some particular temperature a bubble of vapor is formed in the closed arm. At this moment, saturated vapor presses on the liquid in the closed arm and inert gas presses on the liquid in the open arm. On further increase in temperature, the liquid level in the closed arm decreases with a simultaneous rise in level in the open one. The levels are equal at equilibrium between the saturated vapor pressure and the inert gas pressure. The manometer reading directly gives the liquid vapor pressure corresponding to the temperature at which the levels are equal. For increasing measurement accuracy, one should proceed slowly close to this temperature. Since the vapor phase volume is small, its formation does not involve significant change in liquid composition. Measurements at atmospheric pressure were conducted in a pyrex glass tube; here air was used as the inert gas. Heating was provided by an air thermostat or by a bath containing a molten mixture of KNO_3 and $NaNO_2$. The moment the levels were equal was fixed by direct observation.

Our tests of a number of materials showed that copper was significantly more resistant to the action of strong phosphoric acid at high temperatures than various grades of steel, bronze, brass, and other alloys. Consequently, a tube prepared from a red copper ore (cuprite), was used for measurements at pressures above atmospheric. A molten mixture of KNO_3 and $NaNO_2$ was used for heating. The differential manometer null position in this case was determined by closing a contact employing the rather high electrical conductivity of phosphoric acid.

Apparatus construction is shown in Fig. 1. The copper U-tube 1, filled with phosphoric acid of known composition, was connected to manifold 2, on which were mounted two fine-regulating small gas valves 3, 4, a precision manometer 5 (one scale division was equal to 0 1 atm), a water cooling coil 6, and an airplane engine spark plug

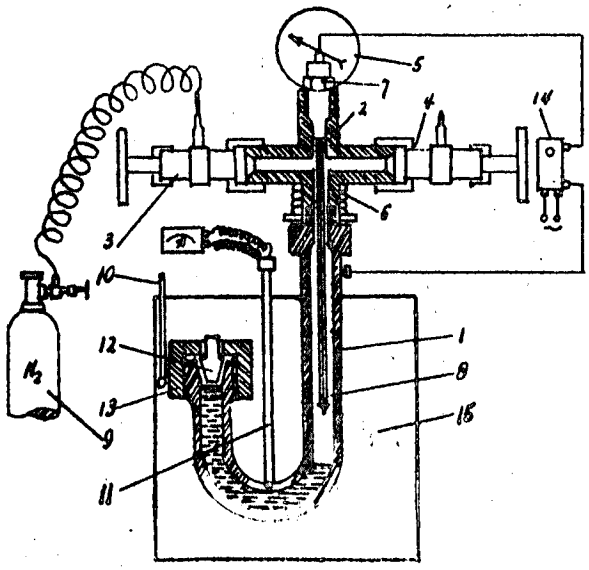

Fig. 1. Equipment arrangement for determining vapor pressures over phosphoric acids at pressures greater than 1 Explanation (of symbols) is given in text.

used for introducing electrode 7. A copper wire, insulated by a porcelain sleeve along its entire length, served as electrode 8 and was soldered to the spark plug. The bare end of the wire was placed at the zero level. The moment contact was made by the acid touching the bare electrode end was indicated by the signal lamp of electronic relay 14. The apparatus is connected to a compressed nitrogen cylinder 9 by valve 3. Valve 4 is used for regulating pressure. Temperature is measured by thermometer 10 immersed in bath 15 and by thermocouple 11 mounted on the measuring tube. For convenience in filling the measuring tube with acid, the seal on the short arm was made using a conical plug 12 and union-nut 13. To establish the necessary difference in levels, excess acid was removed from the open arm by connecting the tube to an evacuated tube via a glass capillary set at the zero level.

Strong phosphoric acid was prepared by heating crystalline orthophosphoric acid (analytically pure) with previously distilled phosphorous pentoxide in a pyrex glass flask at 180° for a 8-50 hour period until the solution was completely homogeneous. Samples were analyzed for total phosphoric anhydride by a gravimetric procedure – precipitation of phosphoric anhydride using ammonium molybdate [9], by a method of potentiometric titration with quinhydrone and calomel electrodes [10], and by directly titrating a sample of acid being analyzed after first boiling it in water – using thymolphthalein.

The difference between results determined by the several methods did not exceed 0.5% P_2O_5. The samples prepared contained from 29 to 80 weight% phosphoric anydride.

Results of Measurement

The first series of measurements involved determining the temperature at which the vapor pressure over phosphoric acid was equal to 1 atm. The low volatility of phosphoric acid enables assuming that the gas phase over it consists almost entirely of water vapor up to temperatures of 350-380°. According to Brown and Whitt [8], the gas phase over phosphoric acid contains 0.47 wt. % P_2O_5 at 300° and 1.96 wt % P_2O_5 at 385°. On this basis, we may assume that the values obtained by us for vapor pressures over phosphoric acids correspond to the water vapor pressure. Measurement results are given in Table 1 and illustrated graphically in Fig. 2.

It should be particularly noted that a singular point is present on the composition – temperature isobar (Fig. 2.) which corresponds to transition from aqueous orthophosphoric acid solutions to strong phosphoric acid. Phosphoric anhydride content at this point corresponds to the formula H_3PO_4. This fact was not noted in any of the earlier papers on determining vapor pressures in the P_2O_5–H_2O System.

In Fig. 2 we compare literature data on dependence of phosphoric acid composition on temperature at constant vapor pressure with results from the present study. The data of the several authors agree very well for orthophosphoric acid solutions. Our data are somewhat different from literature values for strong phosphoric acids; this, evidently, is explained by the difference in methods used in performing the measurements.

TABLE 1

Dependence on Liquid Phase Composition of Temperature at which Vapor Pressure was 1 atm in P_2O_5–H_2O System.

Wt. % P_2O_5	Temperature	Wt. % P_2O_5	Temperature
29.0	103°	73.2	290°
50.7	123°	74.0	297°
53.5	130°	74.5	301°
57.5	141°	74.7	304
65.9	180°	76.3	318°
67.6	200°	77.8	335°
69.8	220°	78.7	350°
70.7	240°	79.0	355°
71.7	260°	80.0	380°
72.4	284°		

The curve given in Fig. 2 may be used for determining phosphoric anhydride content of phosphoric acids. For this it is necessary to determine the temperature at which test sample vapor pressure becomes equal to atmospheric pressure.

In the second series of measurements, we determined vapor pressure dependence on temperature for constant acid compositions using seven samples having P_2O_5 contents ranging from 69.8 to 76.3 wt. %. Measurement results are given in Tables 2, 3, and 4, and are presented graphically in Fig. 3.

The dependence of log P on $\frac{1}{T}$ for a given composition, and likewise that of log a_{H_2O} on $\frac{1}{T}$, is not linear (a_{H_2O} was calculated as the ratio of vapor pressure over phosphoric acid to the vapor pressure of water at the same temperature). A linear dependence exists between log P and phosphoric anhydride content of the acid at constant temperature. Isotherms of this type are shown in Fig. 4. The slope angle of the straight lines with respect to the composition axis changes sharply on transition from aqueous orthophosphoric acid solutions to strong phosphoric acids. Consequently, the relationships between composition, vapor pressure, and temperature must be expressed by different equations for aqueous H_3PO_4 solutions and for a strong phosphoric acids. For strong phosphoric acids, isotherms illustrated in Fig. 4 may be fitted by equations of the form:

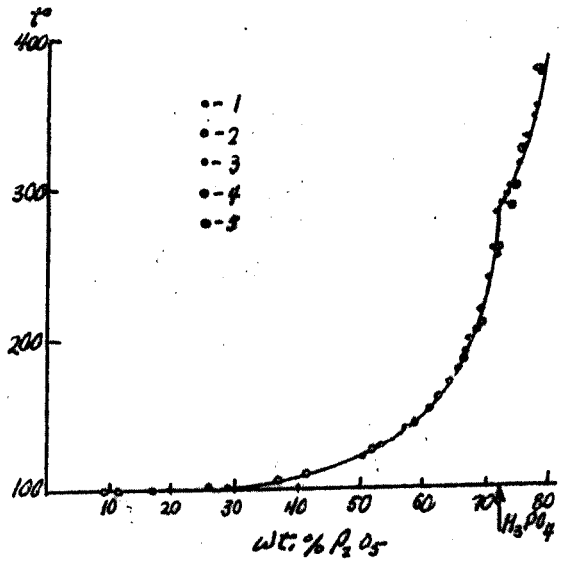

Fig. 2. 1 atm Pressure Isobar for the P_2O_5-H_2O System. Data sources: 1) Ours; 2) I. Kablukov and K. Zagvozdkin [4]; 3) E. Britske and N. Pestov [5]; 4) Brown and Whitt[8].

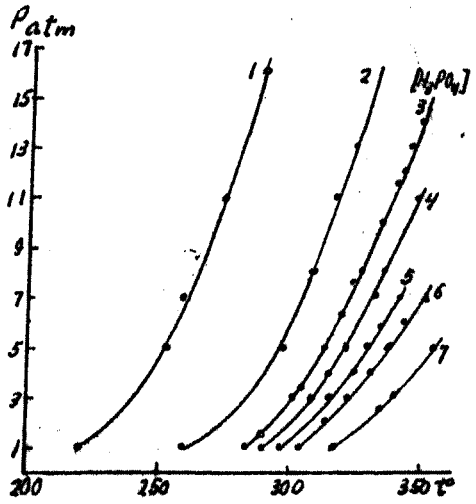

Fig. 3. Dependence of phosphoric acid vapor pressure on temperature. P_2O_5 content: 1) 69.8; 2) 71.7; 3) 72.4; 4) 73.8; 5) 74.9; 6) 74.7; 7) 74.3.

TABLE 2

Dependence of Aqueous Orthophosphoric Acid Solution Vapor Pressure on Temperature.

Weight % P_2O_5	Temperature	Vapor Pressure (atm).
69.8	220°	1.0
	253°	5.0
	260°	7.0
	275°	11.0
	290°	16.0
71.7	260°	1.0
	298°	5.0
	309°	8.0
	318°	11.0
	325°	13.0
	345°	20.0

TABLE 3

Dependence of Orthophosphoric Acid Vapor Pressure on Temperature (72.4% P_2O_5).

Temperature	Vapor Pressure (atm).
284°	1.0
290°	1.5
302°	3.0
305°	3.4
214°	5.0
320°	6.3
325°	7.6
327°	8.0
335°	10.0
341°	11.5
343°	12.0
346°	13.0
350°	14.0

$$\log \frac{P}{P_0} = -k\Delta C, \qquad (1)$$

where: P is the pressure of water vapor over acid of the given composition; P_0 is the pressure of water vapor over pure H_3PO_4 (i.e., at 72.4 wt. % P_2O_5) at the same temperature; k is a coefficient depending on temperature; ΔC is the difference between water contents of H_3PO_4 and strong phosphoric acid, expressed in weight percent: ΔC = 27.6 − wt. % H_2O = wt. % P_2O_5 − 72.4.

Values of k calculated by equation (1) are given in Table 5; values of P and P_0 used in the calculations were obtained by graphical interpolation of data in Tables 3 and 4.

A plot of k versus $1/T$ gives a straight line (Fig. 5) which corresponds to the equation:

$$k = \frac{500}{T} - 0.671. \qquad (2)$$

TABLE 4

Dependence of Strong Phosphoric Acid Vapor Pressure on Temperature

Wt. % P_2O_5	Temperature	Vapor pressure, atm: Experimental	Vapor pressure, atm: According to Equation (3)
73.2	290°	1.0	1.0
	309	3.0	2.9
	315	4.0	3.8
	322	5.0	5.0
	332	7.0	7.0
	336	8.0	7.8
	348	10.8	10.5
74.0	297	1.0	1.1
	316	3.0	2.8
	325	4.0	4.2
	330	5.0	4.9
	335	5.8	5.7
	342	7.0	7.0
74.7	304	1.0	1.1
	315	2.1	2.0
	323	3.0	2.9
	331	4.0	3.9
	338	5.0	4.9
	344	6.0	5.9
	352	7.0	7.3
76.3	318	1.0	1.2
	335	2.5	2.6
	340	3.1	3.1
	355	5.0	5.1

Equations (1) and (2) give:

$$\log \frac{P}{P_0} = \left(0.671 - \frac{500}{T}\right) \Delta C. \qquad (3)$$

Experimental values of vapor pressure over strong phosphoric acid are compared with values calculated from Equation (3) in Table 4. The discrepancies do not exceed experimental error. Thus, Equation (3) may be used as an interpolation equation for calculating strong phosphoric acid vapor pressures.

Equation (3) expresses a linear dependence of log P on P_2O_5 weight percent at constant temperature. Weight percents were used for convenience in calculation; an analogous dependence would be obtained in the given composition range by expressing composition in mole fraction. This kind of dependence is observed in other systems. Thus, for example, the logarithm of HCl vapor pressure (or the logarithm of HCl activity) over concentrated aqueous solutions varies approximately linearly with solution composition, as can be easily demonstrated by examining the corresponding data [12]. These relation-

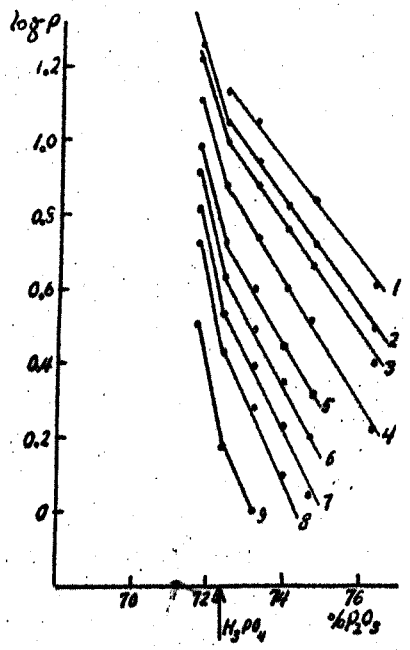

Fig. 4. Isotherms of log pressure versus composition at given temperatures.

1) 350°, 2) 340°, 3) 335°, 4) 325°, 5) 315°, 6) 310°, 7) 305°, 8) 300°, 9) 290°.

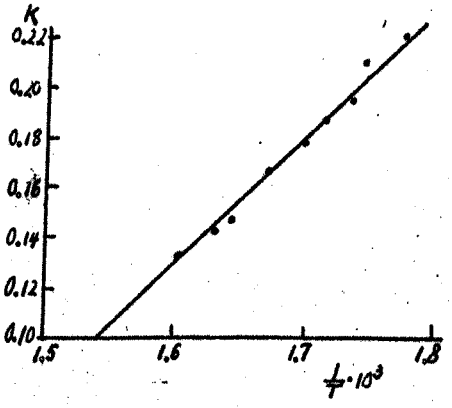

Fig. 5. Dependence of coefficient k on T.

TABLE 5

Temperature Dependence of k

Temperature	k	Temperature	k
290	0.2201	325	0.1662
300	0.2101	335	0.1470
305	0.1945	340	0.1440
310	0.1866	350	0.1331
315	0.1780		

ships can be regarded as a generalization of I. M. Sechenov's law [13].

SUMMARY

1. A new method for measuring vapor pressure was developed.

2. Temperatures were measured at which vapor pressures in the P_2O_5-H_2O system were equal to 1 atm in the composition range from 29.0 to 80 wt.% P_2O_5.

3. A singular point, corresponding to the compound H_3PO_4 (72.4% P_2O_5) was found on the isobar.

4. Vapor pressure dependence on temperature was measured for acids having P_2O_5 compositions ranging from 69.8 to 76.3 wt. % at vapor pressure values from 1 to 20 atm.

5. The logarithm of vapor pressure is a linear function of water content for strong phosphoric acids (i.e., for P_2O_5 content above 72.4%). An interpolation equation is given for calculating vapor pressure of strong phosphoric acids.

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