

The correlation of these two cases of contamination involving different analytical results gives strong support to the assumption that size as well as charge and configuration of the ions concerned are very important factors controlling the formation of solid solutions in precipitation systems. The fact that, so far as is known, barium sulfate has only an orthorhombic form, while barium nitrate has only a cubic form, shows that for cases of partial miscibility isomorphism or structural similarity between any two component ion-pairs of the contaminated precipitate is immaterial to the process. Either cation or anion or both can be replaced independently.

Summary

1. Several samples of permanganate-contaminated barium sulfate were prepared in the absence of all foreign ions except permanganate and hydrogen ions, using the procedure employed by Grimm and Wagner.^{3b}

2. Chemical analysis of the rose-colored precipitates shows that the total contaminant consists of hydrogen and permanganate ions in

equivalent quantity, and a variable amount of water.

3. The lattice parameters of these precipitates, obtained by X-ray powder photographs, are all greater than those of pure barium sulfate, and when these are plotted against the weight per cent. of total contaminant present, a reasonably smooth, rising curve is obtained. The precipitates are, therefore, solid solutions.

4. Chemical analysis of nitrate-contaminated barium sulfate prepared by Walden and Cohen² shows that the mole ratio of barium to sulfate is greater than unity, and therefore that the co-precipitated nitrate ions are balanced, at least partially, by barium ions.

5. Comparison of permanganate contamination with nitrate contamination of barium sulfate shows that primary factors controlling the formation of solid solutions in precipitation systems are the size, charge and configuration of the ions entering the lattice. Crystallographic isomorphism and similarity of ionic structure are proved to be unnecessary conditions for cases of limited miscibility.

NEW YORK, N. Y.

RECEIVED MARCH 20, 1937

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Vapor Pressure of Phosphorus Pentoxide

BY J. C. SOUTHARD AND R. A. NELSON

Introduction

The vapor pressure of phosphorus pentoxide has been subject to some uncertainty. The disagreement in existing data has already been pointed out by Kelley.¹ The uncertainty, however, is not so much one of magnitude as of reproducibility. Smits and co-workers² obtained measurements which varied from sample to sample. They believed this variation to be due to the presence of two forms of phosphorus pentoxide which could be partially separated by fractional distillation. It necessarily follows that these two postulated forms should be not readily transformable one into the other, and that true equilibrium between them could not have existed

at the time the vapor pressure measurements were made. Entirely reproducible results were obtained by Hoeflake and Scheffer³ but they point out that their distillations were carried out under fairly uniform conditions. Hence, their measurements were not necessarily at variance with those of Smits.

The present investigation was undertaken with the hope of determining definitely whether this phenomenon of Smits exists. The results are interpreted as showing that it does not and that the measurements of Hoeflake and Scheffer are substantially correct.

Description of Apparatus

The Jackson⁴ type gage was used by both Smits and Hoeflake and Scheffer. It consists essentially of a thin-

(1) K. K. Kelley, *Bur. Mines Bull.* 383, 1905, p. 82.
 (2) A. Smits and A. J. Rutgers, *J. Chem. Soc.*, 125, 2573 (1924);
 A. Smits with H. W. Deinum, *Z. physik. Chem.*, A149, 337 (1930).
 The same material is also presented in *Proc. Acad. Sci. Amsterdam*,
 33, 514 (1930).

(3) J. M. A. Hoeflake and F. E. C. Scheffer, *Rec. trav. chim.*, 45, 191 (1926).

(4) Jackson, *J. Chem. Soc.*, 99, 1066 (1911).

walled glass bulb collapsed on one side in such a manner that it is distorted easily by a difference in internal and external pressure. One end of the bulb is attached by a ring seal to an enveloping glass jacket and the other end to a long glass pointer. In practice the gage is used as a null instrument and the pressure in the external jacket is determined with a conventional mercury manometer. Hoeflake and Scheffer used such gages made of "fusible" glass, Jena glass and "verre dur"; Smits and Rutgers used gages made of high melting Jena glass and quartz while Smits and Deinum used quartz. The first measurements in this work were accordingly made with Jackson type gages constructed by Pyrex glass, Jena supremax glass and transparent silica glass (quartz).

The sensitivity of the gages used in this work was such that a difference in pressure between the inside bulb and the enveloping jacket of less than one millimeter of mercury could be detected. This was accomplished by observing the motion of the 35-cm. long glass pointer relative to a fine pointed tungsten reference needle through a ten-power reading telescope.

The pressure in the enveloping glass jacket was determined with an 8-mm. bore, two-meter long mercury manometer. The height of the mercury column was read with the unaided eye on a mirror backed scale which had been tested at the National Bureau of Standards. The readings were reduced to 0° and a gravity correction of 0.04 cm. per atmosphere ($(980.091/980.665) \times 76$) applied.

The temperature of the gage was measured with a platinum-platinum-rhodium (10% rhodium) thermocouple. The noble metals of this couple were silver-soldered to copper wire and the junctions thus formed inserted in oil-filled glass protective tubes which in turn were immersed in a Dewar flask filled with crushed ice and distilled water. The e. m. f. developed by this couple was measured with a White potentiometer. Both the thermocouple and the potentiometer had been calibrated by the National Bureau of Standards.

Several furnaces were used, but all were provided with auxiliary heaters which permitted the temperature in the region surrounding the bulb to be maintained isothermal to $\pm 0.2^\circ$, as shown by difference thermocouples located at various points.

At the higher temperatures these glass gages were attacked by the phosphorus pentoxide. In order to remove this objection and to escape errors which might have been inherent in the Jackson gage, it seemed advisable to make some measurements with an entirely different type of vapor pressure gage, preferably one which could be made of platinum and one which did not depend on diaphragm distortion. A gage which meets these requirements, but made of glass or quartz, has been used by Maier⁵ in studying the vapor pressure of chlorides. This has been called the bulb type gage.

In this work it comprised a bulb of about 25-cc. volume connected by an approximately 30-cm. long, 1-mm. bore capillary to a glass U filled with mercury. The mercury in the capillary side of the U was kept at a reference mark by balancing an external pressure against it. In addition to the phosphorus pentoxide sample the bulb contained

an inert gas (dry nitrogen) at a pressure of 15 to 20 cm. of mercury. This gas served as a means for transmitting the pressure in the bulb to the U-trap outside of the furnace, while such gaseous phosphorus pentoxide as diffused up the capillary was condensed on the walls. The pressure observed was thus approximately equal to the sum of the vapor pressure of the phosphorus pentoxide in the bulb and the pressure exerted by the inert gas. The latter was determined by extrapolation of pressure readings taken at temperatures where the vapor pressure was negligible. Three such gages were used, two made of Pyrex glass and one of platinum.

The disadvantages of this type of gage are due principally to the necessary presence of the inert gas. (1) Measurements are made with the substance under a pressure higher than its equilibrium vapor pressure. Under the conditions of these measurements the correction may possibly amount to as much as 0.1% but it has been neglected for lack of necessary data. (2) Equilibrium measurements are dependent on the rate of evaporation and diffusion of the substance in the bulb being faster than its rate of diffusion up and condensation in the capillary. (3) During vapor pressure measurements the pressure in the system is higher than during the simple inert gas pressure measurements. This results in an excess of inert gas in external or "obnoxious" volume of system over that prevailing during the blank measurements and in a corresponding decrease in the inert-gas pressure in the bulb. Correction for this is made as follows

$$P_{\text{corr.}} = (P_2 - P_1)(1 + (T_B V_A / T_A V_B))$$

where $P_{\text{corr.}}$ is the corrected vapor pressure, P_2 is the observed total pressure of inert gas and substance, P_1 is the pressure of inert gas and T_A , V_A , T_B , V_B the temperatures and volumes of the external and internal volumes, respectively. In our work this correction amounted to more than 2% at the higher temperatures.

The temperature-pressure measurements made and the furnaces used with the bulb type gages were the same as in the experiments with the Jackson type gages.

Measurements with the Jackson Type Gages

C. P. phosphorus pentoxide was distilled in a stream of oxygen at 800° in an iron tube furnace as described by Finch and Fraser.⁶ This gave a product which showed a negative test for lower oxides with silver nitrate.⁷ This distilled phosphorus pentoxide was loaded in a "dry box" into a tube which was immediately sealed onto a vacuum system comprising the vapor pressure gage with from one to three intermediate distillation bulbs, and the conventional trap, McLeod gage and mercury diffusion pump. After the system had been evacuated to less than 10^{-5} mm., the pentoxide was distilled first into the intermediate bulb or bulbs, and then into the gage. After the final distillation, the gage was sealed off and placed in the furnace after the system was shown to have no leaks.

The measurements obtained with the Pyrex glass gage are presented in Table I and Fig. 1. This gage without exception gave a reproducible zero position for the pointer on cooling down. Measurements in it on the vapor pressure of mercury gave results varying less than 0.2 cm. from the

(5) C. G. Maier, U. S. Bureau of Mines Tech. Paper 860, 1925.

(6) G. I. Finch and R. R. Fraser, *J. Chem. Soc.*, 117 (1926).

(7) G. I. Finch and Peto, *ibid.*, 121, 692 (1922).

values given in the "International Critical Tables." It was also subject to less attack by the phosphorus pentoxide than the gages made of either supramax or transparent silica glass. Readings were taken only when the temperature of the furnace was practically constant. As a rule check readings were made after a lapse of ten to fifteen minutes, and following a decrease as well as an increase in temperature. The data obtained with the Pyrex glass gage must accordingly be considered the most reliable of all those obtained by us with gages of the Jackson type. They differ but slightly from those obtained by Hoeflake and Scheffer. They show a metastable form (curve a, Fig. 1) existing below about 400°, a transient form (curve b, Fig. 1) and a stable form (curve c). The vapor pressure of the volatile form was entirely reproducible from day to day so long as the temperature did not exceed 360°. At

370° the rate of transition was such that satisfactory measurements could not be made. The transient form was considered by Hoeflake and Scheffer to be identical with that formed by supercooling the liquid. It could be obtained but once with the Pyrex gage. The curve c representing the stable form deviates from that of Hoeflake and Scheffer by an amount corresponding to about three degrees, which is not surely outside their limit of error. No satisfactory measurements on the vapor pressure of liquid phosphorus pentoxide could be obtained since the melting point lay above the workable range of a Pyrex gage.

TABLE I
VAPOR PRESSURE OF PHOSPHORUS PENTOXIDE IN PYREX
GLASS JACKSON GAGE

<i>t</i> , °C.	<i>P</i> _{cm.}	<i>t</i> , °C.	<i>P</i> _{cm.}
Feb. 18, 1935		Feb. 20, 1935	
216.2	0.5	475.6	9.3
253.0	2.2	476.5	9.7
252.2	2.1	498.8	15.6
278.4	5.5	497.2	15.0
278.4	5.6	522.5	26.4
300.9	12.3	524.9	24.1
301.3	12.4	549.2	29.7
324.8	27.2	549.3	30.0
324.8	27.1	549.2	29.7
350.2	59.1	549.2	29.7
350.1	59.2	537.9	21.8
350.0	58.9	538.0	22.0
335.1	37.2	514.0	11.0
337.6	40.2	513.9	11.0
339.7	43.1	489.0	5.0
342.2	46.3	489.2	5.0
342.9	47.2	462.2	1.8
300.2	11.8	462.4	1.8
300.4	11.9		
Feb. 19, 1935		Feb. 21, 1935	
283.6	6.6	449.3	1.4
283.7	6.6	474.1	3.4
316.5	20.7	474.1	3.3
316.1	20.6	474.2	3.4
316.0	20.5	498.4	7.1
336.6	39.6	498.0	7.1
337.2	40.2	525.1	15.1
337.7	41.1	525.1	15.2
358.7	76.0	561.7	40.9
360.7	79.1	562.1	41.3
360.9	79.6	562.8	42.2
361.2	80.2	562.9	42.4
361.3	80.3	534.3	19.9
362.3	82.1	534.3	20.1
362.7	82.3	534.3	20.1
367.9	83.8		
Feb. 25, 1935			
368.8	83.8	490.1	5.3
380.1	84.9	510.3	10.0
389.3	85.8	512.1	10.7

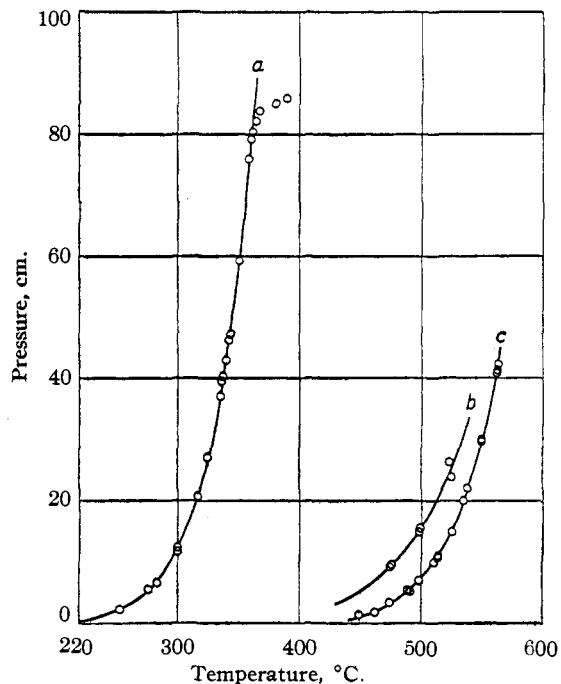


Fig. 1.—Vapor pressure of phosphorus pentoxide in Pyrex Jackson gage.

A gage was constructed from transparent quartz glass in an effort to obtain data on liquid phosphorus pentoxide. Also, it was thought desirable to duplicate Smits' working conditions as exactly as possible. Data obtained with this gage are given in Fig. 2. This gage showed a tendency for the position of the pointer to shift. At times this shift was equivalent to 5 cm. pressure. In most cases a suitable correction could be applied, but even then the measurements may be in doubt by more than a centimeter of mercury pressure.

The greatest fault of the quartz gage is the ease with which it is attacked by phosphorus pentoxide. Fairly reproducible measurements were obtainable at temperatures near 300°, but on maintaining the furnace at 350° overnight the pressure fell from about 50 to 18 cm. That this was not due to a transition to a more stable form is shown by the fact that a vapor pressure curve differing but slightly from the first measurements was obtained as soon as the temperature was lowered to a point where the gaseous phase was saturated. Furthermore, on three separate days (curves b, c, d, Fig. 2) measurements were obtained which were characteristic of a saturated vapor at

the lower pressures and of a gas at the higher pressures. On each succeeding day not only was the temperature lower at which this break in the curve took place, but the pressure curves were lower. This could be explained by assuming that the phosphorus pentoxide was reacting with the walls of the gage. This assumption proved warranted as the gage was later found to be badly etched. In fact when the apparatus was inspected at the end of the series of runs, no phosphorus pentoxide at all was visible.

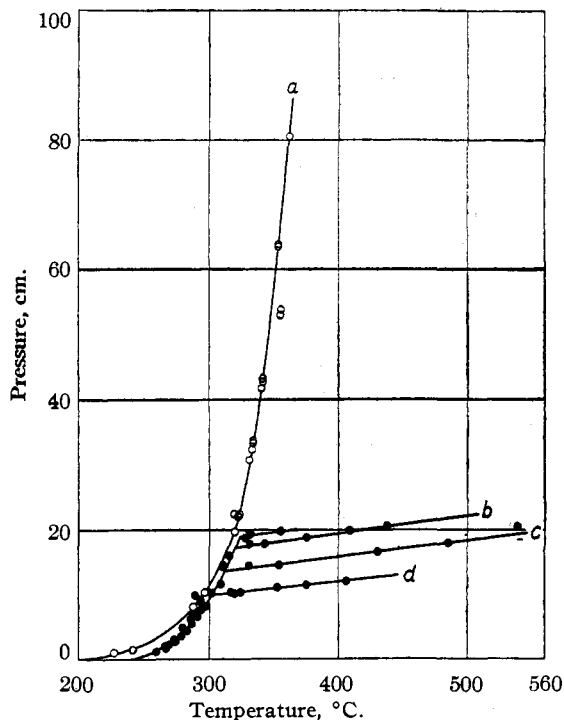


Fig. 2.—Vapor pressure of phosphorus pentoxide in transparent quartz Jackson gage.

Below 350°, however, some data were taken on the volatile form which do not differ by more than a centimeter or two from those obtained in the Pyrex glass gage. They were in general lower, as would be expected should contamination of the phosphorus pentoxide with silica have been occurring.

The Jena suprema glass gage was not entirely satisfactory either. In spite of its higher than Pyrex softening point its pointer was subject to some variation in zero position. The phosphorus pentoxide also finally disappeared into the glass walls although not so rapidly as in the quartz gage. The data obtained with this gage are shown in Fig. 3. No measurements could be obtained on the stable high temperature form. Curve b, Fig. 3, is almost identical with that of the amorphous form of Hoeflake and Scheffer. A reasonable explanation is that the phosphorus pentoxide suffered sufficient contamination by the suprema glass to prevent crystallization into the stable form.

Regardless of the glass used, the results obtained were not entirely above suspicion because some reaction with the walls occurred in all cases. This made measurements in a platinum system highly desirable.

Measurements with the Bulb Type Gage

Before building a gage from platinum, a series of measurements was made with the Pyrex bulb gages. This not only afforded an opportunity to study the reliability of the method, but offered an opportunity for comparing results obtained in the two types of gages made of the same material (Pyrex glass). There seems to be no systematic deviation between the observations obtained on the low temperature form with the two types. From necessity data on the bulb type gages had to be taken "on the fly" because if they were extended over too long a period the capillary tube would plug. The temperature of the furnace was consequently changing at a rate of about one to two degrees a minute during most readings. As a result the curves representing data taken during an increase in temperature will in general lie a degree or so higher than those representing the data taken during cooling. The mean, though, checks with the more static experiments of the Jackson gage.

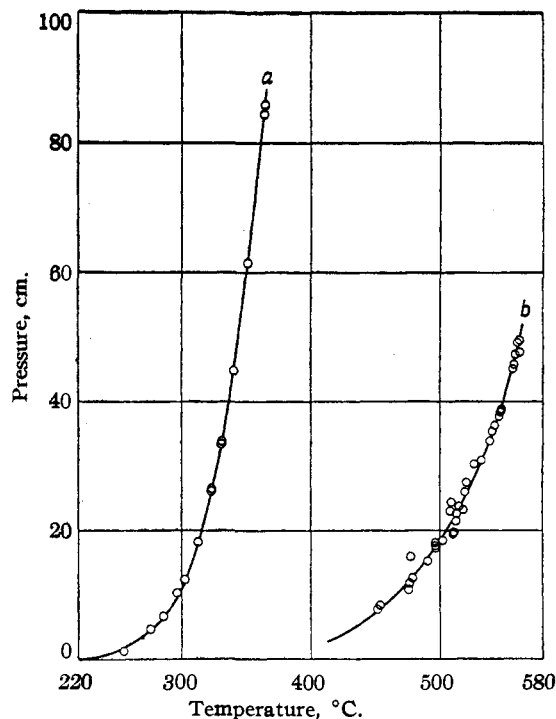


Fig. 3.—Vapor pressure of phosphorus pentoxide in suprema glass Jackson gage.

The platinum bulb gage presented a special problem in filling and sealing off, since dry phosphorus pentoxide cannot be handled in the open air. The upper end of the bulb was attached to a high vacuum system through the 30-cm. long platinum capillary tubes. The lower end of the bulb was provided with a short 1-mm. bore, gold lined, platinum capillary tube. To this was sealed a soft glass distillation apparatus which consisted of a bulb loaded with the pentoxide and but one intermediate bulb. The phosphorus pentoxide was first distilled under high vacuum into the intermediate bulb, the original container sealed off, and the phosphorus pentoxide finally distilled into the platinum bulb. These distillations were per-

formed with the aid of an electrically heated tubular furnace at a temperature of about 300°. After the distillation, dry nitrogen was admitted to the system, the short platinum capillary was pinched shut and then sealed with gold. The bulb was then again evacuated to test for leaks and filled with dry nitrogen to a pressure of 15 to 20 cm.

The data obtained with the platinum bulb gage are presented in Fig. 4. They agree with the results obtained with the Pyrex Jackson gage on the two forms and in addition include five points which follow a curve assigned to the liquid phase by Hoeflake and Scheffer. The higher temperature measurements of August 20, 1936, obviously do not represent equilibrium since at one point the pressure rose from 90 to 110 cm. while holding the furnace temperature constant. This phenomenon took place in the course of about one hour. The possibility of such a pressure increase being due to a transition to another form having a higher vapor pressure is thermodynamically inconceivable. These data (of August 20) are included as being illustrative of the relative difficulty of obtaining equilibrium vapor pressure measurements on the high temperature form. Smits and Deinum (pp. 347, 348) experienced a similar difficulty and believed it to be due to lack of "internal equilibrium" between the postulated co-existent forms. If this had actually been the case it seems more reasonable that the pressure would have decreased rather than increased.

Results

The data obtained in this investigation together with those of previous workers are interpreted as showing that phosphorus pentoxide exists in two crystalline modifications. These are designated as the low temperature and high temperature forms, respectively.

The low temperature form has a vapor pressure which may be represented by equation (1)

$$\log_{10} p_{cm.} = -(5000/T) + 9.792 \quad (1)$$

the high temperature form by equation (2)

$$\log_{10} p_{cm.} = -(7930/T) + 11.113 \quad (2)$$

and the liquid by equation (3)

$$\log_{10} p_{cm.} = -(4320/T) + 6.809 \quad (3)$$

Equation (1) gives 358.9° as the atmospheric sublimation temperature for the low temperature form. A temperature of 359.0° has been calculated from Hoeflake and Scheffer's³ work by Frandsen.⁸ Similarly the data of Smits and Deinum² give the three values 356.6, 362.0, 370.5° and the data of Smits and Rutgers 354.9 and 346.1°. The mean of these values based on the work of earlier investigators was thus estimated by Frandsen to be 358 ± 7°, which compares favorably with the value obtained here.

A solution of equations (2) and (3) determines the triple point between the liquid, high tempera-

ture solid form and gas as being at a pressure of 45.6 cm. and a temperature of 565.6°. The triple point pressure and temperature were found by Smits and Rutgers to be 0.59 atm. (44.8 cm.) and 563°; by Hoeflake and Scheffer to be 46 cm. and 569°; and by Smits and Deinum to be 55 cm. and 580°.

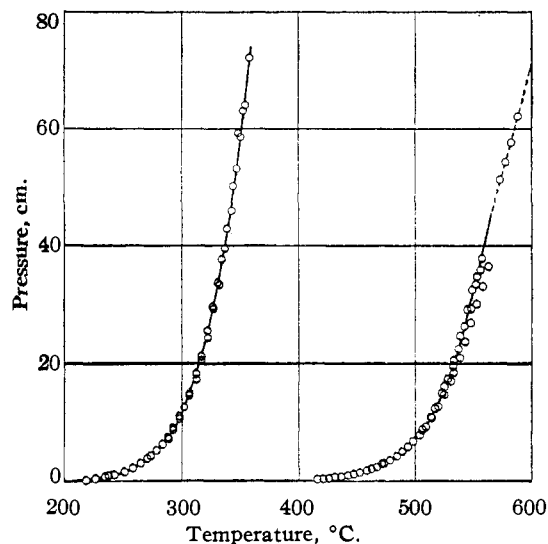


Fig. 4.—Vapor pressure of phosphorus pentoxide in platinum bulb gage: —, vapor pressure of solid; - - - - -, vapor pressure of liquid.

The heats of vaporization per gram molecule are determined from eq. (1) and (3) as 22,800, 36,200, 19,700 calories for the low temperature form, high temperature form and liquid, respectively. The heat of fusion is thus 16,500 cal. The only available calorimetric heat of vaporization work is that of Frandsen⁸ on the low temperature form. He obtained the value 8800 ± 1300 cal. per gram formula weight of phosphorus pentoxide.

To compare this calorimetric value with that calculated from the vapor pressure data it is necessary to have some knowledge of the molecular weight of the vapor. Vapor density determinations by West⁹ at 1400° indicate a molecular weight of about 300, while measurements by Tilden and Barnett¹⁰ at about 1000° range from 307 to 370. The molecular formula most nearly approaching these values is P₄O₁₀ with a gram molecular weight of 284. The errors inherent in the vapor density determinations are such that they cannot definitely be said to disagree with this formula. However, the possibility

(9) C. A. West, *J. Chem. Soc.*, **81**, 923 (1902).

(10) Tilden and Barnett, *ibid.*, **69**, 154 (1896).

(8) M. Frandsen, *Bur. Standards J. Research*, **10**, 54 (1933).

that the vapor is an equilibrium mixture of several forms must be considered. The composition of such a mixture would necessarily depend on the pressure, which in this case is the vapor pressure. Any wide variation in this composition would be reflected in the heat of vaporization, which would result in abnormal curvature of a $\log p$ vs. $1/T$ plot. The experimental data do not reasonably permit a variation in the slope of this line by more than a few per cent. between one atmosphere and one-tenth atmosphere pressure. This lack of curvature limits the concentration of the lowest polymer (P_8O_{20}) to something less than 5% at one atmosphere, if the variation of the association equilibrium constant in this temperature range be considered of secondary importance to the change of the degree of association with pressure. The molecular formula P_4O_{10} must therefore be nearly correct. On this basis the calorimetric value of the heat of vaporization becomes $17,600 \pm 2,600$ cal. per gram mole. This deviates considerably from the value 22,800 obtained here and 22,600 calculated from the data of Hoeflake and Scheffer.

Considerable importance is attached to the fact that phosphorus pentoxide vapor will con-

dense only as the low temperature form. This indicates, at least, that the transition occurs only through the solid phase.

Acknowledgments.—The authors are indebted to P. H. Emmett, S. B. Hendricks, R. T. Milner and P. H. Royster for their advice and encouragement. Special mention should be made of the skillful glassblowing of Leonardo Testa in the construction of the Jackson type gages.

Summary

1. The vapor pressure of phosphorus pentoxide has been found to be entirely reproducible and independent of the rate of distillation of the sample.

2. The data are interpreted to show that phosphorus pentoxide exists in a low temperature and a high temperature crystalline form and as a liquid. The atmospheric sublimation temperature of the low temperature form was found to be 358.9° . The triple point between the high temperature crystalline form, the gas and the liquid was found to be at a pressure of 45.6 cm. of mercury and at a temperature of 565.6° . The rate of transition from the low to the high temperature form is undetectable below 360° .

WASHINGTON, D. C.

RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

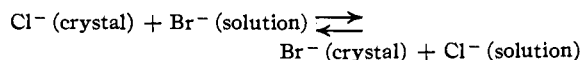
Aging of Fresh Precipitates. XII. The Equilibrium between Mixed Crystals of Silver Chloride and Bromide and Solutions

BY H. C. YUTZY¹ AND I. M. KOLTHOFF

It is well known² that solid silver chloride and bromide form a complete series of mixed crystals. Küster,³ preparing the mixed crystals by precipitation from solutions at 19° , was the first to study the equilibrium conditions existing between solid and solution. Various studies, more or less related to the subject, are found in the literature.⁴⁻⁶ In connection with a study of the aging of precipitated silver chloride it was desirable to know the equilibrium conditions of distribution at 27 and 98° .

The relation between the distribution con-

stant K and the composition of the liquid and the solid phase is found from the following considerations.



in which Cl (crystal) and Br (crystal) denote the chloride and bromide in the mixed crystals. At equilibrium it is found that

$$K' = \left(\frac{a_{\text{Br}^-}}{a_{\text{Cl}^-}} \right)_{\text{crystal}} \left(\frac{a_{\text{Cl}^-}}{a_{\text{Br}^-}} \right)_{\text{solution}} = \frac{\left(\frac{f_{\text{Br}^-} N_{\text{Br}^-}}{f_{\text{Cl}^-} N_{\text{Cl}^-}} \right)_{\text{crystal}} \left(\frac{f_{\text{Cl}^-} N_{\text{Cl}^-}}{f_{\text{Br}^-} N_{\text{Br}^-}} \right)_{\text{solution}}}{1} \quad (1)$$

in which a represents the activity of the particular component, f the activity coefficient, N the mole fraction. With the justifiable assumption that $f_{\text{Cl}^-} = f_{\text{Br}^-}$ in the solution (or that their ratio is constant over a wide range of ionic strengths) expression (1) can be written as

(1) From a thesis submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the degree of doctor of philosophy, 1936.

(2) R. B. Wiley, *J. Franklin Inst.*, **200**, 739 (1925).

(3) F. W. Küster, *Z. anorg. allgem. Chem.*, **19**, 81 (1899).

(4) A. Thiel, *ibid.*, **24**, 1 (1900).

(5) O. Ruff and E. Ascher, *ibid.*, **185**, 369 (1929).

(6) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 444 (1933).