The Concentrations.—By means of the formulas developed in the preceding section the calculation of c and p from (13) is easily carried out. The results are

$$\frac{c}{c_0} = \frac{I_0(2\sqrt{ABxy}) + \varphi(\alpha y, \beta x)}{I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x)} \quad (21)$$

and

$$\frac{p}{a} = \frac{\varphi(\alpha y, \beta x)}{I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x)} \quad (22)$$

It is instructive to rephrase the quantities involved in these formulas and write them explicitly in the velocity constants. This will show more clearly the physical quantities of significance in determining the performance of the zeolite. We put

$$r = c_0(t - l/R) = c_0 my$$

and $\quad (23)$

$$s = Mla/R v_0 = amx$$

When r and s are multiplied by the volume rate of flow, Rv_0, we get

$Rv_0 r$ = total milliequivalents of cations passed, and
$Rv_0 s$ = total milliequivalents of exchangeable cation per unit cross section of preceding zeolite.

In these terms the expression for the concentration of exchanging cation becomes

$$\frac{c}{c_0} = \frac{I_0(2\sqrt{k_1 k_2 rs}) + \varphi(k_1 r, k_2 s)}{I_0(2\sqrt{k_1 k_2 rs}) + \varphi(k_1 s, k_2 r) + \varphi(k_1 r, k_2 s)} \quad (21')$$

The application of these formulas to experimental results is entirely feasible. Extensive tables of the Bessel functions are available.[5] The compu-

(5) E. Anding, "Bessel'schen Funktionen Imaginären Argumentes," Leipzig, 1911.

tation of the integrals may be carried out by appropriate series expansions. Since the parameters of the integrals involve the unknown velocity constants k_1 and k_2, these quantities will probably best be obtained by fitting (21) to "break-through" data on a column run under known conditions. Preliminary experiments by Mr. Allen L. Solomon of this Laboratory indicate that the exchange reactions may be too rapid for an accurate determination of the constants by simply shaking the zeolite with solution.

It is hoped that the application and testing of the theory here presented may be made the subject of a further communication.

NOTE ADDED IN PROOF.—Very recently Nachod and Wood[6] have shown that the velocities of exchange of calcium for hydrogen or sodium follow a second order rate law. On the basis of their results the development of the present paper becomes the proper foundation for the description of the performance of packed ion exchange columns used in water softening.

In conclusion the author wishes to express his thanks to Professor Lars Onsager for his interest in this problem and for many most helpful conversations on the subject.

Summary

A mathematical description is given of the performance of a cation exchange column for the case in which the rate of the exchange is determined by a second order law. The effect of the reverse reaction is included without approximation.

(6) F. C. Nachod and W. Wood, THIS JOURNAL, **66**, 1380 (1944).

Aluminum Phosphide—Preparation and Composition[1]

BY WAYNE E. WHITE AND A. H. BUSHEY

Chemical literature records claims for the existence of five different binary compounds of aluminum and phosphorus. Wöhler[1a] first reported combination of the two elements and later A. Rossel and L. Franck[2] obtained a product reported to be Al_3P_5, by passing phosphorus vapor over heated aluminum. L. Franck[3] reported Al_3P_7,[4] Al_5P_3, Al_3P, and AlP as products which he obtained by slight variations in the general procedure of reacting aluminum with phosphorus vapor. In some cases air was entirely eliminated from the

(1) Original manuscript received October 21, 1943.
(1a) F. Wöhler, *Pogg. Ann.*, **11**, 160 (1827).
(2) A. Rossel and L. Franck, *Ber.*, **27**, 53 (1894).
(3) L. Franck, *Chem. Ztg.*, **22**, 237–240 (1898).
(4) Inspection of the analytical data supplied by Franck reveals that this product was 67% aluminum and 33% phosphorus. This composition corresponds to the formula Al_3P_3 rather than Al_3P_7 as reported.

glass reaction chamber by means of hydrogen; in other cases air was swept out with a stream of phosphorus vapor alone before the aluminum was heated. Unsuccessful attempts were made to secure effective reaction in sealed tubes. In all preparations the reacted masses were taken to high temperatures to volatilize any unreacted phosphorus.

Unaware of earlier work except that of Granger[5] who concluded that aluminum phosphide was unstable and could not be prepared, Fonzes-Diacon[6] believed himself to be the first to make this compound. While mistaken in regard to discovery, he was original in his method of preparation. He mixed aluminum powder and red phosphorus in equal weights and ignited the mixture with a

(5) Granger, Doctorate Thesis, Paris, 1898.
(6) Fonzes-Diacon, *Compt. rend.*, **130**, 1315 (1900).

burning magnesium ribbon. No analyses were reported. Moser and Brukl[7] used the same procedure in their more recent work and they also failed to report a composition or formula. They did report, however, that the phosphine obtained from their product by its reaction with acid contained free hydrogen. Czochralski[8] obtained a phosphide on attempting to dissolve phosphorus in molten aluminum and ascribed to it the formula Al_3P. For study of crystal structure, Goldschmidt[9] prepared aluminum phosphide (AlP) by passing phosphorus vapor over aluminum.

The actual existence of these numerous aluminum phosphides is in question because of the meager information regarding their analyses. In order to determine the composition and learn more of the physical and chemical characteristics of aluminum phosphide, an investigation has been made of means of preparing and examining the compound (or compounds).

Experimental

Preparation.—The first preparations were made by igniting mixtures of red phosphorus and flake-type aluminum powder in an iron crucible. Upon thrusting a burning magnesium strip into a mixture and placing a cover on the crucible, rapid combination occurred and a porous, easily crumbled, dark solid was obtained. When approximately equal masses of the two elements were used in the mixture, only this dark product was obtained. When the ratio of phosphorus to aluminum was increased, yellow phosphorus collected on the underside of the crucible cover and ignited as soon as the cover was removed.

This procedure was obviously inadequate for preparing high purity phosphide. The avidity of phosphorus for oxygen and of aluminum for both oxygen and nitrogen made it essential that air be eliminated from the reaction mixture and vessel if the product were to be free of oxide and nitride contamination. The exclusion of air was accomplished in a series of preparations wherein the aluminum powder was placed in a Pyrex combustion tube which also contained some red phosphorus at a different spot or to which was attached a flask containing phosphorus and through which hydrogen could be passed to displace the air from the whole system. After passing hydrogen through until all of the air was flushed out, the aluminum powder was heated to about 500°, and then the phosphorus was heated to cause its vaporization. Upon contact of the vapor with the hot aluminum, combination occurred with increase in temperature to cause a glowing of the aluminum mass.

A general criticism of this method is that it yielded products retaining excessive amounts of

uncombined aluminum. Presumably this was caused by a sintering together of the metal during the preheating or during the reaction so that larger particles were formed. These particles then yielded phosphide only on their surfaces and this left a considerable amount of free metal remaining in the centers.

The next series of preparations was made by a variation of the original procedure—that of initially mixing the two elements. The powdered aluminum and red phosphorus were ground together in a mortar, transferred to a Pyrex test-tube or to some other container, and the air was displaced from the mixture and container by means of hydrogen or natural gas. Combination of the elements was then secured by quickly heating one spot in the mixture until the rapid, exothermic reaction was initiated. The heating was done by use of a small hot flame impinging on the outside of the glass or by means of a piece of resistance wire passed through the mixture and momentarily heated by an electric current. It was necessary that the heat input be localized and rapid so that a significant amount of phosphorus would not be volatilized to leave its equivalent of aluminum without a chance for combination.

The highest purity in the aluminum phosphide preparations was obtained by a procedure which was a partial combination of the two methods: passing phosphorus vapor over the aluminum and igniting a mixture of the two elements. In this method the intimate mixture was made, placed in a reaction tube, the air displaced by hydrogen and while the atmosphere around the mixture was rich in vaporized phosphorus, the mixture was ignited. Details of one particular experiment are given below. (The product of this experiment is designated as No. 12, see Table I.)

Materials Used.—From a commercial atomized aluminum powder 85% of which passed through a 325 mesh screen, that portion passing a 400-mesh sieve was secured. (In most cases commercial flake-type powders were used; they have an advantage in that they react more readily but they are unsuitable for the highest purity phosphide because of their relatively high aluminum oxide content. The atomized powder contains only about 0.15% Al_2O_3.) A commercial red phosphorus was purified by washing (by trituration and filtration) with carbon disulfide to remove any yellow phosphorus, then with dilute hydrochloric acid to take out iron or iron compounds. The hydrochloric acid together with oxides and acids of phosphorus was washed out with distilled water. When the washings were free of acid, absolute methanol was used to aid in drying. Drying was completed in an atmosphere of hydrogen at a temperature of 50°.

The reaction tube consisted of two pieces of 20-mm. Pyrex tubing joined together by a ground joint. The outer end of each section was drawn to 6 mm. diameter. Weighed quantities of 2.9 g. of the purified phosphorus and 1.8 g. of the minus 400-mesh aluminum powder were ground together in a mortar and placed in the tube at a point near the joint. The tube was then attached to a distilling flask containing red phosphorus. Hydrogen, freed from oxygen by passage over hot copper and dried through sulfuric acid and Activated alumina, was passed through the flask and tube. With the phosphorus flask in boiling water to increase the phosphorus content of the

(7) L. Moser and A. Brukl, Z. anorg. allgem. Chem., **121**, 73-94 (1922).

(8) J. Czochralski, Z. Metallkunde, **15**, 280 (1923).

(9) V. M. Goldschmidt, Skrifter Norske Videnskaps Akad. i Oslo, I. Mat. Natur. Klasse, **1926**, No. 8, 33 (1927).
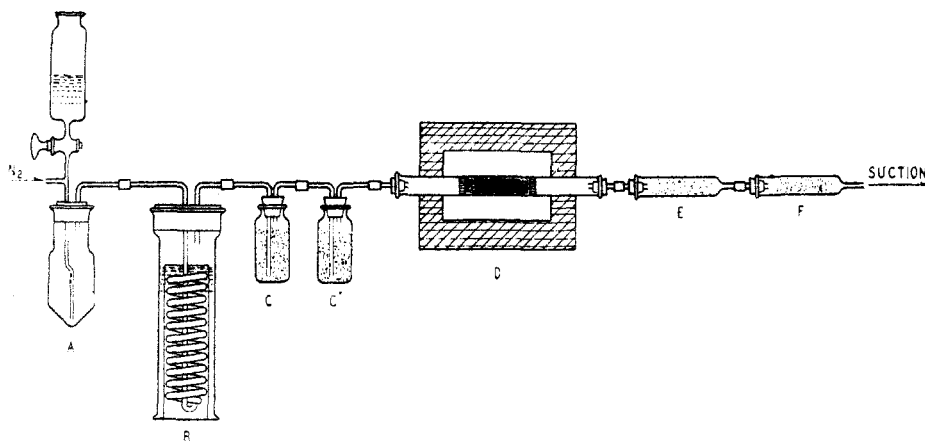
Fig. 1.—Train for aluminum phosphide analysis.

gas stream, the reaction tube containing the mixture was outwardly heated with steam for forty-five minutes to dry the tube and contents without losing phosphorus from the mixture.

A slow stream of hydrogen was allowed to continue through the system for several hours to assure removal of air from the mixture. Then the phosphorus was warmed again sufficiently to introduce an appreciable amount into the gas stream and to allow some to condense out on the cold aluminum–phosphorus mixture. By means of a small, hot, oxygen–gas flame impinging on the reaction tube, the mixture was ignited. After the short, vigorous reaction the phosphorus flask was allowed to cool and the reaction tube was heated over its whole length to drive out the condensed, unreacted phosphorus.

Upon cooling, and with a stream of phosphorus-free hydrogen still flowing, the reaction tube was disconnected at the joint and the product was allowed to slide into a small mortar which was closed with a rubber cover permitting grinding with the pestle and still maintaining the hydrogen atmosphere. After slight grinding to secure homogeneity, the product was quickly transferred to a dried sample bottle and was stored in a desiccator. Analysis (cf. Table I) revealed it to be 94.0% aluminum phosphide.

Unsuccessful attempts were made to prepare aluminum phosphide by evaporating the solvent from a carbon disulfide solution of yellow phosphorus mixed with aluminum powder and igniting the resultant mass. Also, aluminum chloride would not react with phosphorus. Phosphorus and phosphorus pentachloride vapors were separately passed into molten aluminum with no more than meager amounts of phosphide being formed.

Analysis.—In addition to the various aluminum phosphides which have been mentioned in the introduction, one might expect that the products obtained in the preparations described above should contain aluminum oxide, aluminum phosphate, and unreacted aluminum. Free phosphorus would probably not be present; the relatively high temperatures attained during the reactions would cause volatilization of this element. In order, then, to obtain significant results from analyses, it was necessary that procedures be used which would differentiate between the elements in their various possible conditions of combination.

After considerable experimentation, an ana-

lytical procedure was developed which permitted the determination, from one sample, of the phosphide phosphorus, free aluminum, total aluminum, and phosphoric oxide. The evolution and absorption train which was used is diagrammed in Fig. 1.

In the diagram, A is the evolution vessel made of Pyrex and closed with a ground-glass stopper bearing a dropping funnel with side tube for admittance of nitrogen and an exit tube to permit passage of the evolved gases to B. B is a Milligan wash bottle containing a 1.5% solution of mercuric chloride. C' is a drying tower filled with calcium chloride, and C" is filled with magnesium perchlorate. Copper oxide is contained in D which may be heated to oxidize hydrogen in the stream. The resulting water is absorbed in the weighing tube, E, which is filled with magnesium perchlorate. F is a similar drying tube which prevents diffusion of moisture from the outside into E. Sufficient suction is applied to F to nearly balance the back pressure developed in B and the other absorption and drying tubes.

In making an analysis, the train was set up as indicated in Fig. 1, with A having been carefully dried. The whole system was flushed out with oxygen-free nitrogen and a blank run was made on the water absorption tube E. As soon as water pick-up by E became very low, a 100 to 200 mg. sample of the phosphide preparation was weighed in a covered porcelain micro crucible. The crucible and its contents were transferred quickly to the evolution flask A. This flask was disconnected only long enough to insert the crucible. The cover of the crucible was removed, the flask re-attached to the stopper, and the nitrogen was allowed to flow through again until the air was flushed out. Then water was admitted in very small amounts by opening the stopcock from the dropping funnel until a little water ran through; this small amount was carried on down through the tube by the nitrogen stream. The crucible bearing the sample had been placed in such a position that the water dropped into it.

The first contact with water occasionally produced a very rapid gas evolution, and for this reason the first additions of water were made slowly and gradually. Thereafter, more water was added—enough to cover the micro crucible—and finally about 5 ml. of 50% sulfuric acid was added. To complete the reaction, the flask was slowly heated by means of a burner until no more gas evolution could be observed. The whole procedure of gas evolution required over an hour.

During the addition of water and acid to the sample in the evolution flask, a yellow to orange colored precipitate collected in the mercuric chloride solution. Its origin and composition

have been previously described[7,10] as being represented by the equation

$$PH_3 + 3HgCl_2 = P(HgCl)_3 + 3HCl \quad (1)$$

After all of the phosphine from the phosphide sample had been evolved and absorbed in the mercuric chloride solution, the precipitate was removed by filtration, washed to remove all of the acid from it, and the combined filtrate and washings were titrated with standard caustic to an end-point at pH 3.78. The pH was measured by glass electrode. This pH value was selected for the end-point because it was that shown by the mercuric chloride solution alone.

The tube E was weighed as a measure of the water produced from hydrogen evolving during the reaction in A. The solution left in A on completion of the gas evolution was used for determination of the total aluminum content. In some instances this solution was aliquoted and phosphorus pentoxide was determined by phosphomolybdate. When there was insoluble matter left in A after the gas evolution, it was filtered off, fused with potassium bisulfate, dissolved, and returned to the main portion of the solution before beginning the alumina precipitation.

For comparison of results with those from the evolution method just described, some of the preparations were analyzed by conventional methods for total aluminum and total phosphorus after careful dissolution of the sample in potassium bromide solution saturated with bromine. It appeared that the sample could be dissolved without appreciable loss of phosphine by slow, cautious addition of the bromine solution to the solid.

Brook and Waddington[11] have discussed the use of dry hydrogen chloride for the determination of alumina in aluminum. Using a similar procedure, a direct determination of the alumina content of one phosphide sample was made by treatment in a stream of dry, oxygen-free hydrogen chloride at 500°. Under these conditions free aluminum was removed by volatilization as the chloride and aluminum phosphide was decomposed, and both constituents were volatilized. The residue remaining was weighed as aluminum oxide (*cf.* footnote *e*, Table I).

The fate of the phosphorus in the hydrogen chloride treatment presented an interesting possibility; it collected on the exit tube as a yellow or orange sublimate which may have been elemental phosphorus or a solid hydride, $P_{12}H_6$, which has been reported[12] to form when phosphine contacts dry aluminum chloride.

Interpretation of Analytical Results, Composition of Aluminum Phosphide.—Several questions

were considered in appraising the merits and meanings of the results obtained from the analyses made by the methods just described. In the first place, the question was that of the mode and products of interaction between water or acid and phosphides such as Al_3P_5, Al_3P_7, Al_5P_3, and Al_3P, if these should be present in the preparations. It seems certain that the compound AlP would react only as typified by the equation

$$2AlP + 3H_2SO_4 = 2PH_3 + Al_2(SO_4)_3 \quad (2)$$

but one might suspect a compound such as Al_5P_3 to produce a different phosphorus hydride upon reaction with water or an acid. An equation can be written, for example, to get a hypothetical PH_5 from an aluminum phosphide of formula, Al_5P_3. If such unusual phosphorus hydrides were formed, additional acid might be produced by a reaction with mercuric chloride similar to that of Equation (1), or the excess hydrogen might be liberated as the free gas to be collected later as water.

It was strongly suspected, even before analyses were made, that some of the preparations retained uncombined aluminum. On treatment with acid in the evolution flask, this would release its equivalent of hydrogen which would be recovered as water. Computation of the free aluminum content of the sample from the amount of water recovered in E (of Fig. 1) would not be valid, however, if hydrogen were released from aluminum combined in any of the reported phosphides or from unusual hydrogen phosphides produced by their interaction with water or acid.

X-Ray diffraction analyses were made[13] of four of the phosphide preparations in order to establish the hydrogen evolution as being a true measure of the free aluminum present in the samples. By assuming the hydrogen (recovered as water) to have come from free aluminum reacting with water and acid, the four samples were found to contain, respectively, 3.5, 4.8, 6.2, and 15.3% Al. Visual comparison of the intensities of the aluminum lines on the Debye type, X-ray diffraction patterns allowed the operator to arrange the samples in this order without previous knowledge of the chemical analytical results.

In order to learn if the absolute magnitude of the free aluminum content as shown by the X-ray diffraction patterns was in agreement with the chemical analyses (and computations based on the assumption that the water collected was equivalent to free metal), a series of standards was made by thoroughly mixing 400-mesh aluminum powder with 325-mesh quartz in proportions to give 2.0, 4.0, 6.6, 10.1, 14.1, and 18.0% aluminum. Comparison of diffraction line intensities from these mixtures with those from the phosphide preparations showed definitely that the free metal contents of the latter were in the range indicated by

(10) P. Lemoult, *Compt. rend.*, **145**, 1175 (1907); M. Wilmet, *ibid.*, **185**, 206–208 (1927); K. Beyer, *Z. anorg. allgem. Chem.*, **250**, 312–320 (1943).

(11) G. Brook and A. Waddington, *J. Inst. Metals*, **61**, 309 (1937).

(12) W. Peters with M. Müller, *Z. anorg. allgem. Chem.*, **89**, 191 (1914); A. Stock, W. Böttcher and W. Lenger, *Ber.*, **42**, 2839 (1909); L. Hackspill, *Compt. rend.*, **156**, 1466 (1913).

(13) The authors acknowledge indebtedness to Dr. W. L. Fink and Mr. R. V. Milton for the X-ray analyses.

TABLE I
COMPOSITION OF ALUMINUM PHOSPHIDE PREPARATIONS

Sample	Method of preparation	Analyses, %			Computed composition, %		
		Total Al	Free Al	P (by evoln.)	AlP	Al	Al₂O₃ᵃ
1	15.2 g. aluminum flake powder put in Pyrex tube, large excess of phosphorus vapor passed over in atmosphere of hydrogen and at an initial temp. of 500°	57.9	16.5	36.7ᵇ	68.7	16.5	17.8
2	Initially similar to no. 1 but this analysis made two years after prepn.	56.7	15.3	30.6	57.2	15.3	27.9ᶜ
3ᵈ	Similar to no. 1 but atomized aluminum powder (80-85% through 325 mesh screen) used instead of flake type	..	57.7	16.7	32.9	57.7	..
4	2 g. of flake aluminum powder mixed with 3 g. of red phosphorus; ignited in iron crucible with burning magnesium strip; remaining yellow phosphorus eliminated from sample	53.1	10.3	35.7ᵉ	66.7	10.3	22.2ᵉ
5	Similar to no. 4 but the analysis was made two years after prepn.	50.3	6.2	18.5	34.6	6.2	53.0ᶠ
6	Similar to no. 4 but the phosphorus was purified before use and was mixed more intimately with the aluminum	47.3	2.4	42.8	79.9	2.4	14.8
7	2.5 g. of flake aluminum powder mixed with 3.0 g. of red phosphorus, mixture put into tube and ignited by a flame on the outside of the tube after the air had been flushed out with natural gas	50.4	4.8	44.2	82.7	4.8	13.3
8ᵈ	Similar to no. 7, but phosphorus was purified before use	..	3.3	46.7	87.2	3.3	..
9ᵍ	Similar to no. 8 but mixture ground together in presence of chloroform to possibly facilitate intimate mixing	..ᵈ	3.3	47.5	88.8	3.3	..
		47.8	3.5	46.0	86.0	3.5	8.1
10	1.2 g. of flake aluminum powder which had been washed with benzene and with methanol and dried in hydrogen at 50°, ground with 2.1 g. of purified red phosphorus, mixture in hydrogen atmosphere, ignited by hot flame on tube	48.8	4.1	48.2	90.2	4.1	5.2
11	1.2 g. minus 400-mesh atomized aluminum ground with 1.8 g. of purified red phosphorus, mixture ignited in tube, hydrogen atmosphere	47.9	1.7	49.2	92.0	1.7	6.2ʰ
12ᵈ	As described in detail under *Experimental* in body of this paper	..	5.0	50.3	94.0	5.0	..

ᵃ Except where indicated, the values for Al₂O₃ have not been corrected for the slight amount of phosphate which they may contain. ᵇ Total phosphorus by direct determination was 37.1%. ᶜ In this case the Al₂O₃ is corrected for P₂O₅; 1.5% P₂O₅ was found. ᵈ Complete analysis was not made on this sample. ᵉ Total phosphorus by direct determination was 34.8%; a direct determination of Al₂O₃ (by dry hydrogen chloride) gave 22.5% as compared to the calculated value of 22.2%. ᶠ This does not include the 5.8% P₂O₅ which was found. ᵍ The second analysis was made six months after the first one which was soon after prepn. ʰ This sample was found to contain 2.0% P₂O₅; this has not been included in the Al₂O₃ percentage.

the chemical analyses. Thus we had confirmation, by an independent means, of the chemical analyses and our interpretation thereof.

In addition to confirming the presence of elemental aluminum in the phosphide preparations, the X-ray analyses demonstrated the identity of crystallinity in the four preparations which were examined. The aluminum–phosphorus ratios as indicated by chemical analysis can be approximated by the formulas Al₆P₅, Al₄P₃, Al₈P₃, and Al₂P, again in the order as listed above. Were the composition and formula based only on analyses for the two elements, it could be stated that the products were represented by these various formulas. The X-ray diffraction patterns were identical for the principal constituent, however, and this fact rules out the existence of the four different phosphides in the four samples.

The principal constituent of the four samples subjected to X-ray analysis was the same in each case. Moreover, it was very probably the same crystal variety as that studied by V. M. Goldschmidt,[9] who reported the lattice parameter of aluminum phosphide to be 5.541 Å. and by L. Passerini[14] who found the value to be 5.42 Å. The four samples studied in the present work yielded values varying between 5.445 and 5.451 Å.

With this evidence in support of the belief that there is but one variety of aluminum phosphide in spite of variations in ratio of total aluminum to

(14) L. Passerini, *Gazz. chim. ital.*, 58, 655 (1928).

total phosphorus in the preparations, it remained to determine the composition of this one variety. Consideration of the known combining characteristics of the two elements favors the simple formula, AlP. Assumption of this formula as correct and calculation on this basis from chemical analyses permit reasonable compositions to be assigned to all of the analyzed preparations. From the titration of the acid produced in the mercuric chloride solution, the original AlP content was calculated on the basis of the molar ratios indicated:

$$AlP \longrightarrow PH_3 \longrightarrow P(HgCl)_3 + 3HCl \quad (3)$$
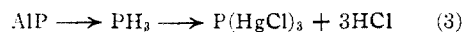
From the water collected in the weighing tube at the exit end of the hot copper oxide tube, the free aluminum was calculated and the balance of the total aluminum over that present as free metal and as the phosphide was calculated to alumina. Table I shows how well this method of computation accounts for the whole of many of the preparations.

Summation of the reported compositions for each of the samples listed in Table I yields values ranging from 97.1 to 103.0%. Recognized errors in the determinations are sufficient to account for this deviation from 100%. Aluminum phosphide picks up moisture quite rapidly and hydrolyzes according to the reaction

$$2AlP + 6H_2O = Al_2O_3 \cdot 3H_2O + 2PH_3 \quad (4)$$
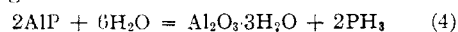
The chemical analyses gave no direct evidence of

the presence of combined water, but the X-ray diffraction pattern of sample no. 9 did show the strongest line of α-Al$_2$O$_3$·3H$_2$O.

The determination of high percentages of aluminum is subject to numerous errors. In the analyses discussed here, a further complication is introduced by the presence of small amounts of phosphate which must be determined in the ignited precipitate and for which correction must be made.

The analytical procedure for determining phosphine by absorption in mercuric chloride solution and subsequent alkalimetric titration is referred to, in the early literature,[10] as being only approximate. The method as given there called for titration to a colorimetric end-point. It was noted in preliminary work that the precision of the analysis was poor, especially so because the volume of the absorbing solution was large. However, when the glass indicator electrode was substituted to identify the proper end-point, the quality of the results showed a marked improvement. In the present investigation, the only suggestion of failure in this phase of the analysis was an apparent slight increase in acidity with increase in free aluminum content of the sample. Addition of more aluminum to a sample of phosphide was found to increase slightly the titrated acid; the aluminum without the phosphide had no effect. An explanation of this behavior is not apparent.

It was observed that the initial precipitation in the mercuric chloride solution was frequently nearly white in color and that in later stages it was orange colored. The relationship between phosphide decomposed and acidity produced was found to be the same in each case, however, and X-ray examination of the two precipitates indicated them as being the same.

Considering the chemical analytical methods and computations therefrom to have been substantiated by X-ray analyses and by the satisfactory summations of constituents as shown in Table I, it is seen that AlP becomes the most probable formula of aluminum phosphide. No other simple formula can fit so well the established facts. Since some of the preparations described in Table I were made by the procedures used by earlier investigators[1a,2,3,6,7,9] and also show aluminum–phosphorus ratios corresponding to some of the reported formulas other than AlP, it may be assumed that we are dealing with the same substances. These preparations are now, however, represented as being mixtures containing AlP as the only binary aluminum–phosphorus compound. When aluminum in excess over the ratio required by the formula AlP is used, it remains in the product as the free element if sufficient care is exercised to prevent its combination with oxygen or nitrogen during the preparation reaction and during storage. When phosphorus is in excess, it is vaporized out and is not found in the products,

unless it, too, partially oxidizes and remains as phosphorus pentoxide or as aluminum phosphate.

Assuming the above arguments as adequate proof that AlP is the phosphide found in the analyzed products, a possibility remains that some other combination of these two elements may be attained under other conditions. Attempts were unsuccessful, however, in preparing phosphides slowly at low temperature (under 300°).

The results recorded in Table I reveal that purity as high as 94% AlP was obtained. It appears that highest quality is obtained by making an intimate mixture of the elements in as high purity as possible and causing them to combine in an inert atmosphere such as that of hydrogen or in such an atmosphere enriched with phosphorus vapor to aid in preventing loss from the mixture during its reaction. The extremely fine atomized aluminum powder is superior to the flake type powder because its initial oxide content is lower. High purity of reactants is essential for high quality of products because no means are available for purifying the reacted mass except to heat it further to ensure volatilization of uncombined phosphorus.

Great care is necessary to protect the products against moisture before and during the first steps of analysis else a sample initially of high purity and low alumina content will be found by the analysis to be of only mediocre quality.

Properties of Aluminum Phosphide.—The phosphide samples, described in Table I, have varied in color from almost black through gray shades to a dark greenish-yellow. The samples of high purity show yellowish tinges. The preparations have all appeared crystalline. When made by ignition of a mixture of the two elements, the products are obtained as porous, friable masses. When the preparation is one of interaction of aluminum with phosphorus vapor, the apparent density of the product is higher and it is less easily pulverized.

Goldschmidt[9] reported aluminum phosphide to possess the cubic, zinc blende structure with a unit cube edge length, $a_0 = 5.451$ Å. and an Al–P distance of 2.360 Å. Passerini[14] found $a_0 = 5.42$ Å.; Al–P distance 2.34 Å. and the density by X-ray to be 2.424. Measurements made on preparations of the present investigation give a_0 values of 5.445 to 5.451 Å.

Aluminum phosphide does not melt, sublime, or thermally decompose at temperatures as high as 1000°. Even at this temperature the vapor pressure is very low as was demonstrated by maintaining a sample at 1000° for two hours in a purified hydrogen stream and finding that no loss in weight occurred. It is possible that in the absence of moisture, aluminum phosphide would show nearly as great chemical stability and resistance to fusion and vaporization as does aluminum oxide. Its low volatility should preclude the exhibition of an odor by aluminum phosphide,

but sufficient hydrolysis is caused by atmospheric moisture so that the odor of phosphine may be observed.

A sample of high purity aluminum phosphide reacts readily with water to release phosphine and with acid or alkaline solutions the reaction rate is higher. Ordinarily the evolved gas does not ignite spontaneously in the air as does the impure phosphine generated from hot, concentrated alkaline solutions reacting with yellow phosphorus. The ignition temperature is low—about 100°—however, and combustion of the gas is easy to initiate. When small portions of the phosphide are dropped onto the surface of aqua regia, explosive reaction and combustion of evolved gases occur. When the vapors above the aqua regia become rich in the fumes from the acid mixture and air is excluded, dissolution of the phosphide is not accompanied by the pyrotechnics which otherwise occur. Aluminum phosphide is decomposed by dry hydrogen chloride so that this reagent cannot be used to remove elemental aluminum from an aluminum phosphide preparation. The simultaneous evolution of phosphine

and aluminum chloride from interaction of hydrogen chloride and the phosphide results in the formation of yellow to orange deposits which may be of the solid phosphorus hydrides as previously described.[11]

Summary

Five different binary combinations of aluminum and phosphorus have been reported in the literature. Evidence is presented in this paper to support the belief that only the one compound, AlP, exists and that the previously reported products have been mixtures of AlP with free aluminum and aluminum oxide. An analytical procedure has been used which permits determination of phosphide phosphorus, free aluminum, and total aluminum. Preparations have been made with over 90% AlP. Aluminum phosphide is dark gray to yellowish-gray in color, crystalline, and it does not melt nor thermally decompose at temperatures up to 1000°. It is readily hydrolyzed and reacts with water, acids, or bases to give phosphine.

Isotonic Solutions: Activity Coefficients of Sodium Bromate and Potassium Chlorate

BY JAMES HOMER JONES AND H. R. FRONING[1]

Physical measurements on aqueous solutions of sodium bromate are very limited. No measurements of activity coefficients by any method were revealed by the literature search. Scatchard[1a] and co-workers have determined the activity coefficients of potassium chlorate in aqueous solution from freezing point measurements. The solubility of the saturated solution is only about 0.25 molal at the freezing point, whereas, it is 0.7000 molal[2] at 25°.

This investigation was undertaken to obtain the activity coefficients of sodium bromate and potassium chlorate in aqueous solution at 25°. The method and apparatus have been described in an earlier paper.[3]

Experimental

Purification of Materials: Sodium Chloride.—This has been described previously.[3]

Sodium Bromate and Potassium Chlorate.—Reagent grade sodium bromate and potassium chlorate were recrystallized from conductivity water. The hot solutions were filtered through sintered glass filters to remove any insoluble material. Two successive crops of crystals were collected from each solution. The salts were partially

dried in an oven at 100°, the lumps broken up, and the drying completed in a vacuum desiccator over solid potassium hydroxide.

Preparation of Solutions.—All solutions were made up directly by weight. The samples of the salt were always reheated for two to three hours before they were weighed. The samples were weighed in two ways. Part of the samples were weighed into the cups from weight burets. In the other cases, 2 ml. of the solution was pipetted into the weighed cups and the cups covered and immediately reweighed. The precision in weighing was at least ±0.5 mg.

Data Obtained

The concentrations of solutions of sodium bromate and potassium chlorate that were isotonic with solutions of sodium chloride of known molality were determined from about 0.2 molal to saturation of the least soluble salt. The results are collected in Table I. In this table, R_0 refers to the observed ratios of M_{NaCl}/M_x, M_x to the molality of either sodium bromate or potassium chlorate, and R_s to the ratios above as read from a smoothed curve through the experimental points. The fourth column gives the difference between the observed ratios and the smoothed curve value corresponding. The deviations from the smoothed curve are seen to be well within the allowable experimental error. The concentration of sodium bromate or potassium chlorate isotonic with the concentration of sodium chloride listed can be obtained readily by dividing column 1 by the corresponding ratio given in column 2.

(1) Taken from a thesis submitted to the Graduate School, Indiana University, in partial fulfillment of the requirements for the degree of Master of Arts.

(1a) Scatchard, Prentiss and P. T. Jones, THIS JOURNAL, **56**, 805 (1934).

(2) Swenson and Ricci, *ibid.*, **61**, 1974 (1939).

(3) J. H. Jones, *ibid.*, **65**, 1353 (1943).