Aluminium Phosphates: Phase-diagram and Ion-exchange Studies of the System Aluminium Oxide–Phosphoric Oxide–Water at 25°.

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Phase-diagram studies in the range from 1% to 60% of phosphoric oxide have shown the following to be the stable solid phases at 25°: $Al_2O_3,P_2O_5,7H_2O$; $Al_2O_3,P_2O_5,4H_2O$; $2Al_2O_3,3P_2O_5,10H_2O$; $Al_2O_3,3P_2O_5,6H_2O$. With the possible exception of the first, all are crystalline solids. The last is probably $H_3[Al(HPO_4)_3]$, but the constitution of the others is less certain.

Anion-exchange experiments have indicated the presence in solution of the triphosphatoaluminium complex $[Al(HPO_4)_3]^{3-}$ which, together with free phosphate, is adsorbed by the exchanger. Cation-exchange studies have indicated the existence of cationic complexes, but very little phosphate was adsorbed with the aluminium by the exchanger.

GUERIN and MARTIN (*Compt. rend.*, 1952, **234**, 1777) reported some of the results of a study of the system aluminium oxide–phosphoric oxide–water at 60°, but they gave only incomplete data. Apart from this no other systematic examination appears to have been made, although several solid aluminium phosphates have been described. Thus a tertiary phosphate, Al_2O_3,P_2O_5,nH_2O (where n has been variously ascribed the values 2, 4, 6, 7, and 8) has been described by several workers, *e.g.*, Rammelsberg (*Pogg. Ann.*, 1845, **64**, 251, 405), Wittstein (*ibid.*, 1856, **97**, 158), Millot (*Compt. rend.*, 1876, **82**, 89), Erlenmeyer (*Annalen*, 1878, **194**, 176), and Guerin and Martin (*loc. cit.*).

Three hydrates $2Al_2O_3,3P_2O_5,nH_2O$ have been reported, two of them by Guerin and Martin (*loc. cit.*), who found the values of n to be 10 and 20 respectively, and the other, for which n is 16, by Millot (*loc. cit.*) and Travers and Perron (*Ann. Chim.*, 1924, **1**, 332). In addition, a compound, $Al_2O_3,2P_2O_5,4H_2O$, has been described by Guerin and Martin (*loc. cit.*) and $Al_2O_3,3P_2O_5,6H_2O$ by Erlenmeyer (*loc. cit.*), Hautefeuille and Margottet (*Compt. rend.*, 1888, **106**, 136), Travers and Perron (*loc. cit.*), and Guerin and Martin (*loc. cit.*).

From conductivity and pH measurements on solutions containing aluminium chloride and sodium dihydrogen phosphate, Bjerrum and Dahm (*Z. physikal. Chem., Bodenstein Festband*, 1931, 627) found evidence for complexes such as $[Al(H_2PO_4)]^{2+}$, $[Al(HPO_4)]^{+}$, $[Al(H_2PO_4)_2]^{+}$, $[Al(HPO_4)_2]^{-}$, $[Al(HPO_4)_3]^{3-}$, and $[Al(H_2PO_4)_3]^{0}$. Jensen (*Z. anorg. Chem.*, 1934, **221**, 1) found the solubility of aluminium tertiary phosphate in acid solutions containing phosphate and chloride to be dependent on the phosphate concentration, but independent of the chloride-ion concentration and so concluded that pure phosphato-complexes only (and not chlorophosphato-complexes) were present in solution.

The objects of the present work have been to determine the solubility isotherm of the system aluminium oxide–phosphoric oxide–water at 25°, to determine the compositions of the stable solid phases of that system, and to ascertain the nature of the ions present in the stable solutions.

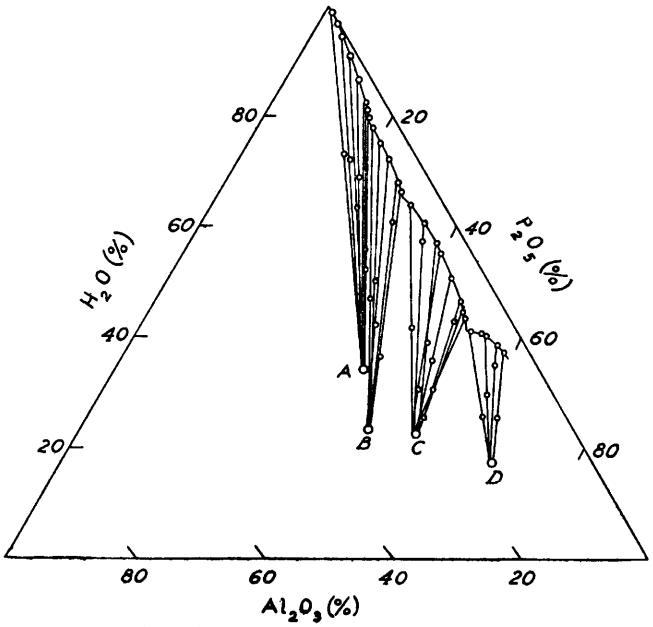
RESULTS

Phase-diagram Studies.—A study of the system at 25° for the range of solutions up to 60% of phosphoric oxide has indicated the following as the stable solid phases (Table 1 and Figure): (*A*) $Al_2O_3,P_2O_5,7H_2O$ as a microcrystalline powder, (*B*) $Al_2O_3,P_2O_5,4H_2O$ as

minute hexagonal plates, (*C*) $2Al_2O_3,3P_2O_5,10H_2O$ as small triangular plates with bevelled edges, and (*D*) $Al_2O_3,3P_2O_5,6H_2O$, as hexagonal prisms.

The degree of hydration of the two tertiary salts cannot be established accurately from the intersections of the appropriate tie-lines, but taken in conjunction with those of Guerin and Martin (*loc. cit.*) for the system at 60° our results indicate the existence of a hepta- and a tetra-hydrate. Whilst Guerin and Martin found both to occur in microcrystalline form, we have observed that the lower hydrate forms hexagonal plates.

Stable equilibria in the system, Al_2O_3–P_2O_5–H_2O *at* 25°.



For *A*, *B*, *C*, and *D*, see text p. 4013.

TABLE 1. *The system aluminium oxide–phosphoric oxide–water at* 25°.

Solutions			Moist solids			Solutions			Moist solids		
P_2O_5 (%)	Al_2O_3 (%)	$\frac{[PO_4]}{[Al]}$	P_2O_5 (%)	Al_2O_3 (%)	Type *	P_2O_5 (%)	Al_2O_3 (%)	$\frac{[PO_4]}{[Al]}$	P_2O_5 (%)	Al_2O_3 (%)	Type *
1·063	0·0791	9·64	15·89	10·68	*A*	30·96	5·08	4·38	42·31	16·03	*C*
3·016	0·2906	7·45	—	—		34·88	4·84	5·17	36·07	6·87	
4·832	0·558	6·22	17·19	10·49		38·45	4·85	5·69	46·00	15·35	
8·111	1·124	5·18	22·76	13·77		40·03	5·06	5·68	49·13	20·76	
11·23	1·984	4·06	20·01	10·96		44·16	5·60	5·66	48·55	16·04	
14·86	2·845	3·75	29·89	18·06		47·67	6·17	5·54	48·23	9·11	
15·14	3·354	3·24	27·87	16·50		49·00	6·78	5·20	52·34	22·56	
16·42	3·803	3·10	33·09	22·33		49·96	6·89	5·21	51·02	17·51	
		†									
17·89	4·054	3·17	33·21	19·69	*B*	51·86	7·15	5·23	61·43	13·01	*D*
20·21	4·270	3·40	32·33	17·67		53·77	5·75	6·70	—	—	
23·18	4·516	3·69	36·29	21·70		54·34	5·57	7·00	60·07	10·55	
27·12	5·150	3·78	29·54	9·62		57·21	4·64	8·86	58·88	6·64	
28·23	5·382	3·76	39·86	24·00		59·13	4·30	9·88	63·91	10·87	

* See p. 4013. † The minimum value of the mol. ratio occurs at this transition point.

The compound $2Al_2O_3,3P_2O_5,10H_2O$ was found, in agreement with Guerin and Martin (*loc. cit.*), to crystallise as small triangular plates with bevelled edges and $Al_2O_3,3P_2O_5,6H_2O$ as hexagonal prisms of varying length; Guerin and Martin describe it as crystallising as large rods.

The compound $Al_2O_3,2P_2O_5,4H_2O$ reported for the system at 60° by Guerin and Martin (*loc. cit.*) does not appear at 25°.

Anion-exchange Experiments.—The adsorption of aluminium and phosphate by Amberlite IRA-400 in the phosphate form from stable solutions (*i.e.*, of compositions decided on the basis of the solubility isotherm for 25°) has been determined under equilibrium conditions. The results are given in Table 2 *a*, and those for a corresponding series of experiments with pure phosphoric acid solutions in Table 2 *b*. A significant adsorption of aluminium by the exchanger (Table 2 *a*) indicates the presence in the aluminium phosphate solutions of anionic complexes.

TABLE 2. *Adsorption of aluminium and phosphate by* IRA-400-*phosphate* (1·000 *g.*).

(*a*) *From aluminium phosphate solutions* (100 *ml.*)

Solutions		Resin							
		Moles adsorbed/equiv. resin :		Capacity accounted for (%) *					
P_2O_5 (%)	$[PO_4]/[Al]$	Al	PO_4	E	F	G	H	J	L
2	8·58	0·005	0·660	101	100	101	99	97	98
5	6·30	0·016	0·672	106	101	103	99	95	97
10	4·51	0·028	0·679	108	100	105	99	92	95
20	3·42	0·050	0·697	115	100	108	98	90	95

* Assuming the following to be adsorbed : $E = [Al(PO_4)_3]^{6-}$; $F = [Al(HPO_4)_3]^{3-}$; $G = [Al(PO_4)_2]^{3-}$; $H = [Al(HPO_4)_2]^{-}$; $J = [Al(H_2PO_4)_2(HPO_4)]^{-}$; $L = [Al(H_2PO_4)(HPO_4)_2]^{2-}$.

(*b*) *From phosphoric acid solutions* (100 *ml.*)

Solutions : P_2O_5, %	Mols. adsorbed/equiv. of resin : PO_4 (= [*y*])	Solutions : P_2O_5, %	Mols. adsorbed/equiv. of resin : PO_4 (= [*y*])
5	0·654	15	0·643
10	0·660	20	0·643

Cation-exchange Experiments.—The results of similar experiments with the hydrogen form of the cation-exchange resin Zeo-Karb 225, which are given in Table 3, show that the amount of phosphate retained by the exchanger is slight, but that this increases slowly with increasing phosphate content of the solutions. It is sufficient to indicate the presence, albeit in small amounts, of cationic complexes in the solutions.

TABLE 3. *Adsorption of aluminium and phosphate by Zeo-Karb* 225-H (0·500 g.) *from aluminium phosphate solutions* (100 ml.).

Solutions			Resin	
			Moles adsorbed/equiv. of resin :	
P_2O_5 (%)	$[PO_4]/[Al]$	pH	Al	PO_4
2	8·58	1·49	0·319	Nil
5	6·30	1·39	0·301	Trace
10	4·51	1·12	0·276	Trace
20	3·42	1·01	0·259	0·012

DISCUSSION

Nature of the Solutions.—Although the cation-exchange studies (Table 3) show the presence in the solutions of cationic complexes, the amount held by the exchanger is too small for the composition of the complex (or complexes) adsorbed to be determined by the method used for the cationic ferric phosphate complex (Salmon, *J.*, 1953, 2644). Nevertheless, it is significant that there is a difference in behaviour between the ferric and the aluminium phosphate system in that in the former no evidence was found for the presence of cationic complexes in pure ferric phosphate solutions (Jameson and Salmon, *J.*, 1954, 28). A further difference is that in the aluminium phosphate system the amount of aluminium adsorbed by the cation-exchanger is higher than the corresponding amount of iron adsorbed in the ferric phosphate system (Jameson and Salmon, *loc. cit.*) and rises in the more dilute solutions to the value expected for the Al^{3+} ion (namely 1/3 mole per equiv. of resin). It thus appears that there must be a higher concentration of free aluminium ions in the aluminium phosphate system than of ferric ions in the ferric phosphate system.

The adsorption of aluminium by the anion-exchanger (Table 2 *a*) is low, but an attempt has been made to account for the capacity of the resin in terms of the adsorption of free

phosphate [as a mixture of H_2PO_4' (for which 1 mole takes up 1 equiv. of resin) and HPO_4'' (0·5 mole takes up 1 equiv. of resin) ions, in the proportions indicated in Table 2 *b*] together with one of several possible anionic complexes (Table 2 *a*). The calculation, in the case of the complex $[Al(PO_4)_3]^{6-}$, for example, is made as follows: the free (*i.e.*, non-complex) phosphate is given by $[PO_4] - 3[Al]$ (where $[PO_4]$ and $[Al]$ refer to moles adsorbed per equivalent of resin—Table 2 *a*). Then if $[y]$ represents the moles of phosphate adsorbed per equivalent of resin from the phosphoric acid solutions (Table 2 *b*), the number of equivalents of exchanger taken up by the free phosphate is given by $([PO_4] - 3[Al])/[y]$. But each aluminium atom which is adsorbed as the ion $[Al(PO_4)_3]^{6-}$ takes up six equivalents of resin and hence the fraction of the capacity accounted for is $6[Al] + ([PO_4] - 3[Al])/y$ It is apparent from Table 2 *a*, in which the results have been given as percentages, that it is difficult to decide which of the possible complexes is being adsorbed; $[Al(HPO_4)_3]^{3-}$ seems most likely to be predominant, but $[Al(HPO_4)_2]^-$ is also possible. The following points, however, all suggest that it is the $[Al(HPO_4)_3]^{3-}$ ion that is adsorbed in major proportion: (1) the adsorption of phosphate is consistently above that for the phosphoric acid solutions (Table 2 *a* and *b*) which is consistent with the adsorption of $[Al(HPO_4)_3]^{3-}$ ions, for which each of the three phosphate groups effectively takes up one equivalent of resin per mole only, as compared with the value of 1·5 equivalents per mole in the case of phosphate adsorbed as simple phosphate ions [*i.e.*, the reciprocal of $[y]$ in Table 2 *b*]. In the case of the adsorption of $[Al(PO_4)_2]^{3-}$ ions, on the other hand, the adsorption of phosphate should be the same as for the phosphoric acid solutions, whilst for the adsorption of $[Al(PO_4)_3]^{6-}$ ions (which might be expected by analogy with the ferric phosphate system) the adsorption of phosphate would be lower; (2) the lowest value of the ratio of phosphate to metal in the saturated solutions is almost exactly 3 (Table 1), suggesting that, as in the ferric phosphate system, a triphosphato-complex predominates (Jameson and Salmon, *loc. cit.*), in contrast to the chromic phosphate system at 40° where the ratio is 2 and the diphosphato-complex predominates (Jameson and Salmon, unpublished work) (this argument assumes that the concentration of cationic complexes is not high enough to alter the phosphate : metal ratio in solution, as in fact appears to be the case from the cation-exchange experiments); (3) the general similarity of the behaviour of the aluminium phosphate system to that of the ferric phosphate system where a triphosphato-complex $[Fe(HPO_4)_3]^{3-}$ was present (Jameson and Salmon, *loc. cit.*).

The results are in accord with those of Bjerrum and Dahm (*loc. cit.*) in indicating the presence in the solutions of both cationic and anionic complexes, but since their studies were of a system containing chloride as well as phosphate attempts at a closer correlation would not be justified.

Nature of the Solid Phases.—Little concerning the nature of the solid phases can be deduced from the present work, but the compound $Al_2O_3,3P_2O_5,6H_2O$ may be $H_3[Al(HPO_4)_3]$, since the corresponding anion appears to be present in solution.

Experimental

Preparation of Aluminium Tertiary Phosphate.—Sodium hydroxide solution was added dropwise to "AnalaR" ammonium alum (50 g.) in water (500 ml.) containing "AnalaR" syrupy phosphoric acid (10 ml.) until a permanent precipitate was just visible. The solution was filtered and the filtrate heated on a steam-bath whereupon, as a result of its negative temperature coefficient of solubility, the tertiary phosphate was precipitated. After being heated for 6 hr. the precipitate became granular. The supernatant liquor was siphoned off and replaced by 5 ml. of phosphoric acid in 500 ml. of water and the suspension was again heated for several hours. Two further treatments with water, followed by washing with boiling water on a Buchner funnel, yielded a dazzling-white solid free from sodium (by flame test). Analysis of a typical batch of the air-dried material gave the results: Al_2O_3, 32·20; P_2O_5, 44·89; H_2O, 22·90% (Calc. for $Al_2O_3,P_2O_5,4H_2O$: Al_2O_3, 32·25; P_2O_5, 44·94; H_2O, 22·81%). It was thus assumed to be the compound $AlPO_4,2H_2O$.

Preparation of Solutions for Phase-diagram Studies.—The solid tertiary phosphate was added in small amounts over a period of days with continuous (mechanical) stirring to phosphoric acid solutions of varying concentrations at 25° until no more would dissolve. Solutions thus

prepared were found to be supersaturated and hence on further stirring a solid phase separated from them. When precipitation appeared to be complete the tube was closed with a glass stopper (instead of a mercury-sealed stirrer) and the suspension left to settle for 2—3 weeks. Sometimes the initial crystallisation was slow and had to be started by gentle scratching. High viscosity seemed to be the cause of the low rate of crystallisation in most cases. The time taken for equilibrium to be reached varied from 5 to 8 weeks. The method of analysing alternate tubes in any given batch of six was employed. Two weeks were allowed to elapse between the analysis of the first and the second sets of solutions (and solids) and a smooth solubility isotherm was taken as a criterion of the attainment of equilibrium.

The method often employed in phase-diagram studies of saturating solutions at a higher temperature before cooling rapidly to the equilibrium one was not adopted since no crystals separated from such solutions, even after several months. The range of solutions studied was determined by the concentration of the commercially available " AnalaR " syrupy phosphoric acid; no attempt was made to concentrate it further.

Resins.—The strongly acidic, monofunctional cation-exchanger Permutit Zeo Karb 225 and the strongly basic monofunctional anion-exchanger Amberlite IRA-400 were used for the ion-exchange experiments. The former was in the hydrogen form and the latter in the form of its phosphate to avoid the introduction of foreign ions into the solutions on exchange.

At least three weeks, with frequent shaking, were allowed for solutions and resin to come to equilibrium. The solution was then filtered through a dry column (1-cm. internal diameter, 10 cm. long, with sintered disc of grade 2 porosity) and the filtrate kept for analysis and pH measurements. The resin was then transferred to the column and washed rapidly with water (*ca.* 50 ml.) under suction—in this way any solution adhering to the resin was quickly displaced and interaction between partly diluted solution and the resin was avoided. The column was filled with water and the resin washed with water until the washings were neutral to methyl-orange, before elution with 500 ml. of 2—3N-nitric acid. Aliquot portions of the eluate were used for analysis.

Capacity of the Resins.—The capacity of the cation-exchanger was determined by passing 250 ml. of 0·5N-sodium chloride through a column containing 0·500 g. of resin in the hydrogen form and determining the acid liberated in the effluent. For the anion-exchanger 500 ml. of 2—3N-nitric acid were passed through a column containing 1·000 g. of the chloride form of the resin and the chloride content of the effluent was determined gravimetrically. The capacities of the air-dried resins, which were determined separately on every sample of resin used, were found to be in the ranges 2·45—2·48 milliequivs./g. for IRA-400 (weighed as the phosphate form) and 3·68—3·78 milliequivs./g. for Zeo Karb 225 (hydrogen form).

Analytical Methods.—Aluminium was determined gravimetrically by means of 8-hydroxyquinoline (" oxine "). The solids were first dissolved in perchloric acid and this was also added to the solutions to prevent precipitation of phosphate on dilution. Interference by phosphate in the aluminium determination was avoided as follows: the solution was made alkaline with sodium hydroxide (added until the precipitate that formed had just redissolved), 5 ml. of a 5% solution of " oxine " in acetic acid added to the hot solution, the solution brought to the boil, and ammonium acetate solution added until precipitation was complete. The precipitate, after standing for 2 hr., was filtered off, washed, and dried in the usual way. After each analysis, the precipitate was redissolved in sulphuric acid and tested for the presence of phosphate by means of ammonium molybdate reagent.

Phosphate was determined by weighing as ammonium phosphomolybdate after drying at 115°. Efforts to separate the aluminium and phosphate by means of ion-exchange resin columns failed and the method of estimating phosphate with bismuthyl perchlorate (Salmon and Terrey, *J.*, 1950, 2813) could not be employed, since the presence of aluminium interferes with the titration. The difficulty in the ion-exchange separation was the incomplete retention of the aluminium by the exchanger—possibly caused by the high acidity required to keep the aluminium phosphate in solution.

Apparatus.—The samples, contained in Pyrex boiling-tubes fitted with B24 standard sockets to fit either stoppers or mercury-sealed stirrers, were kept at 25° ± 0·1°.

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