Non-polar compounds, on the other hand, crystallize presumably with the molecule as the unit. Since the intermolecular forces are of the nature of stray fields from the atoms, which are relatively weak, non-polar compounds do not have high melting points. The "ionizing solvents" are, however, quite different in properties from a non-polar liquid of the type of liquid nitrogen. The atoms of the nitrogen molecule are "saturated." This is another way of saying that the stray fields around the molecule are not strong enough nor diversified enough to produce much interaction between the molecules. On the other hand, the properties of the "ionizing solvent" depend upon the existence of moderately strong intermolecular fields.[1] Dielectric constant is a measure of this type of "polarity" but has no significance with regard to highly polar compounds.

The metals in the middle of the long groups of the periodic table, which we have previously avoided discussing, form compounds intermediate in character between the highly polar salts and the non-polar acids. They show to a high degree the property which Werner has designated as coördination number. Abegg and Bodlander[2] point out that the solubility and ionization of the salts of these metals is connected with this tendency to form ionic complexes. In other words the simple salts of these elements, which are in themselves not highly polar, become more polar through reaction with the solvent or other molecules. It is not surprising that a salt such as cadmium chloride should be slightly dissociated in water solution but rather that any salt of these metals should be a good electrolyte.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE S. S. WHITE DENTAL MANUFACTURING COMPANY.]

THE SYSTEM ZINC OXIDE, PHOSPHORUS PENTOXIDE AND WATER AT 25° AND 37°.

BY N. E. EBERLY, C. V. GROSS AND W. S. CROWELL.

Received May 4, 1920.

Introduction.

The zinc salts of phosphoric acid are of interest in the study of dental cements. The following is a part of a more extended investigation of the reactions and equilibria involved in the manufacture and use of such plastic compounds.

The phosphates of zinc, particularly the acid salts, have been very little studied. Graham describes an acid salt, $ZnHPO_4.H_2O$. Heintz[3]

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[1] Cf. Harkins and King, THIS JOURNAL, 41, 971 (1919).

[2] Abegg and Bodlander, *loc. cit.*

[3] Heintz, *Ann.*, 143, 356 (1867).

was not able to prepare it. Demel[1] describes the salt $Zn_2(HPO_4)_2.2H_2O$ as separating in stable, triclinic crystals from concentrated acid solutions of sp. gr. 1.5 or more, and states that it is decomposed by water.

The neutral zinc orthophosphate, $Zn_3(PO_4)_2$, has been studied more fully. The tetrahydrate has been obtained from zinc carbonate and orthophosphoric acid at 100°. A monohydrate is also reported.[2]

Various investigators have reported the preparation of hydrates of zinc orthophosphate by precipitation. The evidence of higher hydrates than $4H_2O$ is based upon the analyses of precipitates filtered from solutions. Owing to the colloidal nature of these preciptiates, the existence of such hydrates is questionable. The tetrahydrate occurs in nature as the mineral hopeite.

In view of the scanty information obtained from the literature, the investigation of the ternary system, zinc oxide, phosphorus pentoxide and water, was undertaken. Since we are concerned with the stability of the system at ordinary temperatures and the reactions occurring in it at body temperature, the isotherms at 25° and 37° were traced.

Materials Used.

The zinc oxide used was the U. S. P. grade. Careful analysis indicated that it contained only traces of impurities, chiefly iron and silica. It was practically 99.8% zinc oxide.

The phosphoric acid used was U. S. P. 85% phosphoric acid. It was found to contain traces of nitrates (diphenylamine gave a faint blue color), and an undeterminably small quantity of alkali. It was free from chlorides, sulfates and pyrophosphoric acid.

Experimental Method.

The experiments were carried out as follows. After preliminary experiments had shown the approximate course of the curve, solutions were made in small Erlenmeyer flasks of Pyrex glass containing zinc oxide and phosphorus pentoxide in sufficient quantity to be slightly supersaturated. The more dilute solutions, up to 35% of phosphorus pentoxide, were allowed to crystallize spontaneously. The more concentrated were seeded with the proper crystalline phase, since they showed great reluctance to crystallize of themselves.

In the case of the equilibrium at 25°, the tightly-stoppered flasks and their contents were placed in a mechanically-stirred gas-heated water bath, provided with a toluene regulator which kept the temperature constant without attention to about 0.1° for months at a time. With occasional agitation, the flasks were allowed to remain in the bath for some weeks. The liquid and solid were removed and analyzed, returned

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[1] Demel, *Berl. Ber.*, **12**, 1171 (1879).

[2] Fredel, *ibid.*, **9**, Ref. 794 (1876); Friedel and Sarasin, *J. Ber.*, **1892**, p. 519; also Debray, *Compt. rend.*, **52**, 46 (1861) and **59**, 40 (1864).

and the analyses repeated at 2-week intervals until constant results were obtained. At 37° the flasks were kept in a bacteriological incubator which was observed to be constant to 0.25° over a long period.

Considerable difficulty was experienced in making up solutions with less than 20% phosphorus pentoxide, since the solid phase was more soluble in the cold than at the boiling point. The following procedure was adopted. The preliminary experiments had shown the approximate course of the curve. Concentrated solutions were prepared such that on dilution they would be of the proper composition. They were cooled rapidly in ice and diluted with the proper quantity of cold water, shaken vigorously and placed at once in the bath at the proper temperature. The rise in temperature caused crystallization.

Methods of Analysis.

Samples of the liquid phase were withdrawn with a pipet provided with a filter of cotton wool. Zinc and phosphoric acid were determined in the same solution. It was found that phosphoric acid in such large quantities caused errors in the determination of zinc by titration with potassium ferrocyanide. The phosphoric acid was removed by precipitation with magnesia mixture. The first precipitate was washed with 2.5%

Equilibrium at 25°.

No.	Solution.		Crystals and mother liquor.		
	% P_2O_5.	% ZnO.	% P_2O_5.	% ZnO.	
1......	5.08	2.38	15.62	22.75	Locate $Zn_3(PO_4)_2 : 4H_2O$ ZnO 54.3%. P_2O5 31.0%. H_2O 14.7%.
2......	9.76	4.65	17.04	20.89	
3......	12.42	6.13	.....	.....	
4......	13.52	6.56	.....	.....	
5......	14.00	6.74	.....	.....	
6......	14.15	6.92	.....	.....	
7......	14.37	6.97	.....	.....	
8......	14.83	7.34	.....	.....	
9......	15.98	7.71	.....	.....	
10......	17.15	8.26	.....	.....	
11......	18.33	8.73	19.50	11.15	Indeterminate.
12......	22.75	10.74	23.92	13.70	
13......	26.48	12.47	27.05	14.18	Locate $ZnHPO_4: 3H_2O$. ZnO 37.8%. P_2O_5 33.0%. H_2O 29.2%.
14......	28.70	13.48	29.82	19.47	
15......	30.09	14.16	31.03	20.78	
16......	32.55	15.40	33.07	23.98	
17......	33.79	15.82	33.82	21.58	
18......	37.15	17.30	36.73	21.50	
19......	37.76	17.65	.....	.....	
20......	39.61	18.04	.....	.....	
21......	42.05	16.14	47.77	27.48	Locate $Zn(H_2PO_4)_2 : 2H_2O$ ZnO 27.3%. P_2O_5 47.9%. H_2O 24.8%.
22......	44.53	13.20	.....	.....	
23......	48.70	9.58	48.00	27.13	
24......	52.25	7.64	.....	.....	
25......	55.97	7.23	.....	.....	

Equilibrium at 37°.

	Solution.		Crystals and mother liquor.		
No.	% P_2O_5.	% ZnO.	% P_2O_5.	% ZnO.	
1......	4.87	2.08	.....	.....	
2......	9.46	4.12	.....	.....	
3......	13.60	6.27	.....	.....	
4......	18.13	8.78	.....	.....	
5......	19.48	9.66	.....	.....	
6......	20.32	10.16	.....	.....	
7......	21.96	10.88	.....	.....	
8......	26.75	13.26	.....	.....	
9......	29.65	14.77	.....	.....	
10......	33.39	17.06	.....	.....	
11......	34.58	17.92	.....	.....	
12......	36.13	16.00	.....	.....	
13......	37.80	15.78	38.92	34.38	Locate $ZnHPO_4 : H_2O$ ZnO 44.1%. P_2O_5 38.5%. H_2O 17.4%
14......	39.93	16.12	39.54	41.30	
15......	42.42	15.81	40.58	34.05	
16......	42.65	16.82	40.09	39.08	
17......	44.89	17.83	.....	.....	
18......	46.11	18.05	.....	.....	
19......	46.41	14.74	.....	.....	
20......	48.99	12.55	.....	.....	
21......	51.35	11.26	.....	.....	
22......	51.92	11.12	.....	.....	
23......	54.32	10.82	.....	.....	

ammonium hydroxide, dissolved and reprecipitated carefully by the method of Schmitz,[1] filtered on a Gooch crucible, dried, ignited and the phosphoric acid weighed as magnesium pyrophosphate. The zinc oxide, was determined in the combined filtrate by careful titration with potassium ferrocyanide by the method of Lowe.[2]

The drained crystals, with mother liquor adhering, were analyzed in the same way, thus giving 2 points on the straight line connecting the composition of the solid phase and that of the liquid phase.

Before considering the ternary system, the binary systems zinc oxide water and phosphorus pentoxide water should be considered. The first can be dismissed by stating that zinc oxide is relatively insoluble in water at ordinary temperatures. The second has been very completely investigated by Smith and Menzies.[3] Their results were expressed in terms of orthophosphoric acid and water. We have recalculated them in terms of phosphoric pentoxide and water and find that the solubility of phosphoric pentoxide in water will not affect our results until high concentrations are reached. The isotherm at 25° intersects the solubility curve in 3 points, 62.5%, 68.4% and 68.7% pentoxide. It would be

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[1] Schmitz, *Z. anal. Chem.*, **45**, 512 (1906).

[2] Low, "Technical methods of Ore Analysis," Sixth edition, p. 284.

[3] Smith and Menzies, THIS JOURNAL, **31**, 1183 (1909).

interesting to trace the equilibrium relations around these concentrations. Unfortunately, the experimental difficulties are great and lack of time restricted our work to concentrations below 55%.

The isotherms at 25° and 37° are plotted in Fig. 1. The first branch of the curves represents the solubility of neutral zinc orthophosphate tetrahydrate, $Zn_3(PO_4)_2.4H_2O$, in phosphoric acid of increasing concentration. It will be noted that the 37° isotherm lies below the 25°, showing that the solubility decreases as the temperature increases. At 25° this branch of the curve ends at P_2O_5 = 15.2%, ZnO = 7.5%. At 37° it ends at P_2O_5 = 20.3%, ZnO = 10.1%. The lower solubility and higher acidity at the quadruple point at 37° can be attributed to greater hydrolysis at the higher temperature. The tetrahydrate separates in shining plates similar in appearance to magnesium ammonium phosphate. If caused to form slowly, large transparent plates or short prisms can be prepared.

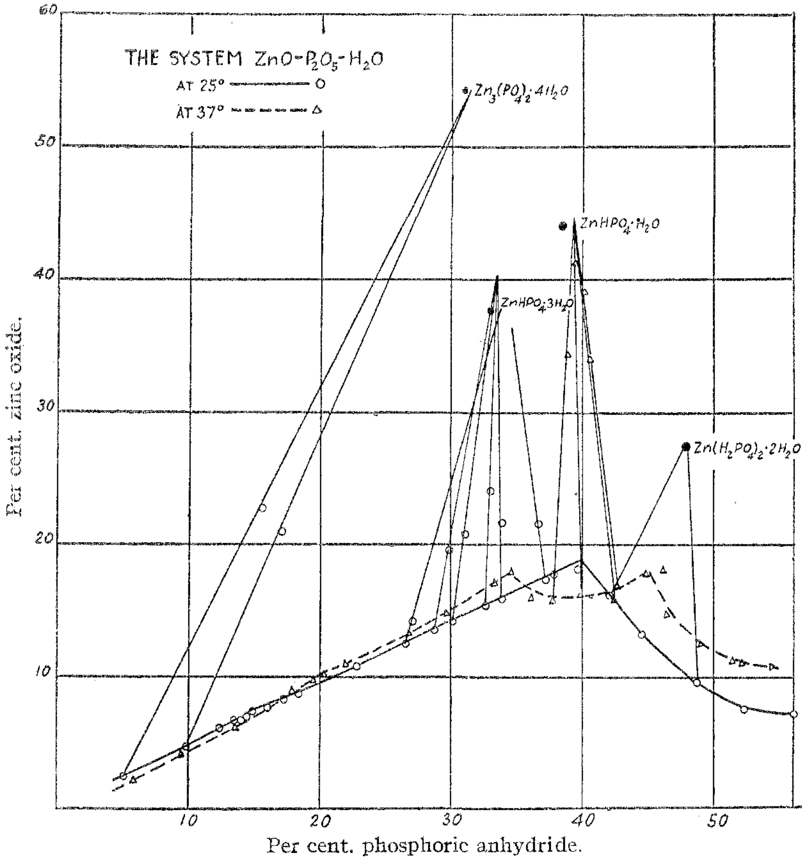

Fig. 1.

At the quadruple point $Zn_3(PO_4)_2.4H_2O$, $ZnHPO_4.3H_2O$, solution and vapor are in equilibrium.

The second branch of the curve represents the solubility of zinc hydrogen orthophosphate trihydrate, $ZnHPO_4.3H_2O$, in phosphoric acid solutions. The curve at 37° lies above that at 25°, showing an increase of solubility with increasing temperature. The curve at 37° ends at about 34% phosphorus pentoxide, while that at 25° continues to the quadruple point at 40% pentoxide and 18.8% zinc oxide. At 37° a new phase makes its appearance at 34% pentoxide. Transparent needles of Graham's phosphate, $ZnHPO_4.H_2O$, separate from solutions of this and higher concentrations. The salt seldom separates pure, but is always contaminated at first with the adjacent phases. Equilibrium is very slowly reached even when the solutions are seeded with crystals of the proper phase. Efforts were made to crystallize this salt at 25°, but without success, and no evidence of its existence could be obtained except from a slight irregularity of the curve near the second quadruple point. Either the upper end of the curve at 25° represents a metastable condition which we were not successful in destroying or the monohydrate does not appear at this temperature. In any event, Heintz' failure to prepare this salt can be readily understood.

At 25° the second quadruple point represents the equilibrium between $ZnHPO_4.3H_2O$, $Zn(H_2PO_4)_2.2H_2O$, solution and vapor. Above this point large, transparent rhombohedrons of the latter salt separate slowly from the solutions. The solubility decreases rapidly as the concentration of the pentoxide increases.

At 37° another branch is inserted between the $ZnHPO_4.3H_2O$ curve and the $Zn(H_2PO_4)_2.2H_2O$ curve, which represents the solubility of the $ZnHPO_4.H_2O$, Graham's phosphate. Great difficulty was experienced in determining the curve since equilibrium was reached very slowly. Nearly 6 months elapsed before the composition of the solutions became constant. In some instances the trihydrate separated first in spite of seeding with the monohydrate, and a long time elapsed before this salt redissolved. In the more concentrated solutions a salt of the composition $Zn(H_2PO_4)_2$ separated, and the crystals slowly broken down into needles of the monohydrate. There is some uncertainty as to the exact location of these 2 quadruple points, but we feel that they are located to within 1%. The quadruple point $ZnHPO_4.3H_2O$, $ZnHPO_4.H_2O_7$ solution, vapor, is at 34.6% pentoxide and 17.6% zinc oxide. The quadruple point $ZnHPO_4.H_2O$, $Zn(H_2PO_4)_2.2H_2O$ solution, vapor, is at 45.7% pentoxide and 18.5% zinc oxide.

The hydrolytic precipitation of the zinc orthophosphate tetrahydrate from dil. phosphoric acid solutions leads to a simple method for its preparation in a pure state. A solution containing 50% pentoxide (85% phosphoric acid diluted with $^1/_5$ of its weight of water) is saturated at the boiling point with zinc oxide. The water lost by evaporation is replaced and the solution rapidly cooled first to room temperature, then in cracked ice. About 10 volumes of ice-cold water are added and the solution violently stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated with stirring on a water bath. A large quantity of shining plates of the neutral tetrahydrate will separate. The crystals are filtered out and washed clean with boiling water, sucked dry on a plate and spread out in a thin layer to air dry. This gives a pure product of constant composition, uncontaminated with alkalies and without excess zinc or phosphoric acid.

A microscopic study of the various phases was made with the following results.

$Zn_3(PO_4)_2 : 4H_2O$. Shining orthorhombic plates.

$ZnHPO_4 : 3H_2O$. Sticky, threadlike crystals agglomerating into cotton-wool-like masses. Optical properties could not be observed.

$ZnHPO_4 : H_2O$. Small, hard, transparent needles. Extinction oblique to long axis, probably triclinic.

$Zn(H_2PO_4) : 2H_2O$. Large, transparent triclinic rhombohedra.

Summary.

The isotherms at 25° and 37° of the ternary system $ZnO.P_2O_5 : H_2O$ have been traced to 55% phosphorus pentoxide.

The following solid phases separated at 25°: $Zn_3(PO_4)_2.4H_2O$, $ZnHPO_4.3H_2O$ $Zn(H_2PO_4)_2.2H_2O$.

At 37° an additional phase was noted, *viz.:* $ZnHPO_4.H_2O$.

A method of preparing pure neutral zinc orthophosphate tetrahydrate has been described.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

THE DETERMINATION OF ZIRCONIUM AND TITANIUM IN ZIRCONIUM ORES.

BY G. E. F. LUNDELL AND H. B. KNOWLES.[1]

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CONTENTS.

I. Introduction.

Zirconium ores may be expected to contain besides zirconium such elements as silicon, iron, aluminum, titanium, calcium, magnesium, sodium and potassium. In addition to these elements others such as thorium, cerium, tin, yttrium, uranium, manganese and phosphorus are often found,

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[1] Published by permission of the Director of the Bureau of Standards.