546. *The Systems Zinc Oxide–Phosphoric Oxide–Water and Manganous Oxide–Phosphoric Oxide–Water at Temperatures between 25° and 100°.*

By J. E. Salmon and H. Terrey.

The evidence provided by phase-diagram studies has indicated the existence of an unstable zinc phosphate, $Zn(H_2PO_4)_2,2H_3PO_4$, and an anhydrous manganous phosphate, $Mn(H_2PO_4)_2$, neither of which has been previously reported.

Apart from one point concerning zinc secondary phosphate monohydrate, $ZnHPO_4,H_2O$, the results of Eberly, Gross, and Crowell on the zinc phosphates have been confirmed, and have been extended.

In the case of the manganous phosphates, no evidence has been found to support the results of Grube and Staesche. Amadori's data for the system at 25° have been found to be correct and have been extended to cover the range up to 100°.

It has been observed that the phosphates which separate from the more dilute solutions in these two systems all have a negative temperature coefficient of solubility. A similar behaviour has been found in the system ferrous oxide–phosphoric oxide–water. The inference is drawn that this behaviour is connected with the decrease in the degree of ionisation of phosphoric acid with rise of temperature, for which evidence was indicated by earlier investigators.

The effect of temperature variations on the two systems mentioned in the title has hitherto received only slight attention. The zinc phosphate system was examined by Eberly, Gross, and Crowell (*J. Amer. Chem. Soc.*, 1920, **42**, 1433) at 25° and 37°. Over this comparatively short range of temperature they found that one of the stable solid phases, namely, the tertiary zinc phosphate, $Zn_3(PO_4)_2,4H_2O$, had a negative temperature coefficient of solubility. Their results also implied that zinc secondary phosphate monohydrate showed a similar behaviour.

TABLE I.

Zinc phosphate solutions.

Solution.			Moist solid.*			Solution.			Moist solid.*		
P_2O_5, %.	ZnO, %.	*d.*	P_2O_5, %.	ZnO, %.		P_2O_5, %.	ZnO, %.	*d.*	P_2O_5, %.	ZnO, %.	
(*a*) At 25°.											
0·435	0·231	1·003	—	—	A	35·5	16·6	—	35·8	19·7	C
0·489	0·267	1·004	—	—		37·3	15·95	1·63	37·8	25·6	
0·714	0·373	1·007	—	—		39·8	15·91	—	39·7	27·2	
0·935	0·484	1·01	—	—		40·6	15·75	—	40·5	20·0	
1·16	0·586	1·01	—	—		44·9	13·06	1·67	47·1	26·0	D
3·13	1·52	1·04	—	—		49·6	9·03	—	47·7	24·4	
4·07	1·95	1·04	—	—		53·7	7·66	—	48·3	24·2	
4·09	1·95	1·04	—	—		55·3	7·23	1·67	48·2	24·9	
8·72	4·26	1·11	—	—		57·0	7·51	1·72	52·5	17·1	
11·60	5·59	—	19·2	17·7		57·3	7·75	—	57·0	8·92	
14·92	7·28	1·23	—	—		59·1	5·25	—	60·2	12·19	E
17·87	8·63	1·28	—	—	B	60·3	3·72	—	60·9	7·52	
19·38	9·30	1·30	22·1	14·0		62·1	2·45	1·69	62·1	7·56	
21·03	10·13	1·33	24·7	17·5		63·5	1·55	1·69	—	—	
26·4	12·64	—	—	—							
(*b*) At 37°.											
0·467	0·236	1·00	—	—	A	17·04	8·26	1·25	—	—	A
0·907	0·442	1·01	20·8	35·6		18·02	8·76	1·27	—	—	
0·984	0·508	1·01	—	—		18·02	8·70	1·26	25·2	29·4	
4·10	1·85	1·05	12·5	17·6		19·56	9·70	1·30	—	—	B
7·69	3·50	1·10	—	—		21·07	10·68	1·34	—	—	
7·77	3·49	1·09	18·3	24·8		24·13	12·27	1·39	—	—	
13·66	6·49	1·19	25·4	35·6		52·7	11·94	—	47·7	26·2	D
14·49	6·84	1·20	—	—		55·1	10·66	—	—	—	
(*c*) At 50°.											
0·84	0·40	1·001	—	—	A	28·3	14·74	1·45	—	—	A
1·61	0·68	1·01	—	—		29·6	15·60	1·52	—	—	
4·93	2·01	1·05	—	—		30·0	15·97	1·52	30·0	17·1	
6·64	2·78	1·07	20·3	30·7		31·3	16·34	1·54	32·3	24·1	B
7·67	3·22	1·08	—	—		34·4	17·48	1·64	—	—	
10·58	4·62	1·12	—	—		35·3	17·49	1·62	34·1	25·1	
13·86	6·23	1·14	—	—		38·7	17·30	1·65	39·2	36·4	C
17·56	8·27	1·24	21·18	19·52		41·3	17·73	—	—	—	
17·91	8·51	1·26	21·14	19·48		41·4	18·01	—	40·5	30·1	
18·31	8·68	1·27	—	—		43·5	17·34	—	—	—	
22·04	10·98	1·33	—	—		45·9	15·98	—	45·0	20·2	
22·61	11·40	1·36	25·9	30·0		49·3	17·2	—	49·3	18·0	
23·56	11·90	1·37	27·1	30·2		50·9	15·36	—	51·1	15·4	
27·4	14·35	1·46	28·5	25·4		53·4	12·62	—	54·0	14·23	
27·5	14·41	1·46	—	—		56·7	11·93	—	55·4	12·48	
(*d*) At 60°.											
3·98	1·54	1·02	—	—	A	26·6	13·79	1·44	—	—	A
7·93	3·20	1·08	—	—		28·6	15·37	1·49	—	—	
10·43	4·42	1·12	—	—		32·7	16·81	1·58	33·1	24·4	B
16·21	7·52	1·22	—	—		36·2	18·42	1·65	34·4	30·0	
23·10	11·64	1·36	—	—							
(*e*) At 75°.											
1·56	0·58	—	—	—	A	25·7	13·27	—	30·3	48·0	A
7·27	2·68	—	12·8	12·9		26·3	13·78	—	—	—	
7·32	2·66	—	—	—		26·7	13·96	—	—	—	
13·57	5·71	—	—	—		27·2	14·25	—	31·4	49·5	
18·77	8·72	—	30·2	49·0		29·8	16·32	—	31·9	49·5	
24·42	12·33	—	30·9	49·8		31·3	17·49	—	36·7	43·4	C
24·73	12·59	—	—	—		35·7	18·47	—	36·5	26·6	
25·0	12·80	—	30·0	3·89		45·3	25·2	—	—	—	

TABLE I—*continued.*

Solution.			Moist solid.			Solution.			Moist solid.		
P_2O_5, %.	ZnO, %.	*d.*	P_2O_5, %.	ZnO, %.		P_2O_5, %.	ZnO, %.	*d.*	P_2O_5, %.	ZnO, %.	
(*f*) At 86·3°.											
0·77	0·26	0·99	4·50	6·59	A	23·51	11·79	1·32	25·91	25·96	A
1·52	0·50	0·99	6·46	8·90		23·84	11·99	—	26·56	25·71	
7·36	2·61	1·05	12·34	12·83		24·02	12·17	—	—	—	
13·63	5·67	1·16	18·24	18·12		26·4	13·60	—	31·3	49·0	
15·43	6·66	1·19	—	—		29·1	15·65	—	32·9	42·9	
18·06	8·29	1·18	22·45	24·36		32·9	18·20	—	36·8	32·3	C
20·90	10·05	1·26	—	—		38·5	20·09	—	39·2	28·0	
22·83	11·38	1·31	26·37	28·99							
(*g*) At 100°.											
7·37	2·52	—	—	—	A	21·29	10·33	—	26·5	31·3	A
13·94	5·81	—	—	—		21·93	10·88	—	26·9	30·5	
17·82	8·08	—	23·0	24·6							

* Solid phases: A = $Zn_3(PO_4)_2,4H_2O$. B = $ZnHPO_4,3H_2O$. C = $ZnHPO_4,H_2O$.
D = $Zn(H_2PO_4)_2,2H_2O$. E = $Zn(H_2PO_4)_2,2H_3PO_4$.

By studying the corresponding manganous phosphate system at 25° and 55°, Grube and Staesche (*Z. physikal. Chem.*, 1927, **130**, 572) covered a wider temperature range. Their work indicated that all the solid phases occurring in this sytem possessed positive temperature coefficients of solubility. However, their results for the system at 25° were not in agreement with those previously published by Amadori (*Atti R. Ist. Veneto*, 1921—2, **81**, 603), and the compounds which, according to them, separated from solution differed from the manganous phosphates described by earlier workers, such as Erlenmeyer and Heinrich (*Annalen*, 1878, **190**, 191). In particular, they reported that they obtained the tertiary phosphate from dilute solution in an anhydrous form, whereas other workers have always found it to be hydrated.

The work of Travers and Perron (*Ann. Chim.*, 1924, **1**, 298) on the dissociation of zinc primary phosphate in solution and the corresponding investigation by Viard (*Compt. rend.*, 1899, **129**, 412; *Bull. Soc. chim.*, 1899, **21**, 807) of the manganous primary phosphate supplemented the evidence provided by the phase-diagram studies. [Data published by Sokolovsky and Koulagina for manganous phosphates at 100° (*J. Appl. Chem. U.S.S.R.*, 1945, **18**, 412) seem to be identical with those given by Viard.] Both primary phosphates were shown to be partly dissociated in solution [*e.g.*, $3Zn(H_2PO_4)_2 \rightleftharpoons Zn_3(PO_4)_2 + 4H_3PO_4$)] and in the more dilute solutions this occurred to a greater extent at 100° than at room temperature. In the case of the zinc phosphate, this result was in accord with the decreasing solubility of the tertiary phosphate established by Eberly, Gross, and Crowell (*loc. cit.*). To reconcile the results of Viard's work on manganous phosphates with those of Grube and Staesche, however, it would be necessary to postulate that a reverse in the solubility coefficient of the phase in equilibrium with dilute solutions took place between 55° and 100°. The possibility was one to be taken into account, because a change in the solid phase apparently also occurred within this range. A secondary–tertiary phosphate was found by Viard at 100° in approximately the same range of concentration as Grube and Staesche had given for the stability of the anhydrous tertiary phosphate.

It was evident that more complete information was needed on the behaviour of both systems with variation of temperature. A study was accordingly made at several temperatures between 25° and 100° and a summary of the results is given below.

Within the chosen range of temperature, five compounds occurred as stable solid phases in the zinc phosphate system. They were: (*a*) A diacid primary phosphate, $Zn(H_2PO_4)_2,2H_3PO_4$; (*b*) a primary phosphate dihydrate, $Zn(H_2PO_4)_2,2H_2O$; (*c*) a secondary phosphate monohydrate, $ZnHPO_4,H_2O$; (*d*) a secondary phosphate trihydrate, $ZnHPO_4,3H_2O$; (*e*) a tertiary phosphate tetrahydrate, $Zn_3(PO_4)_2,4H_2O$.

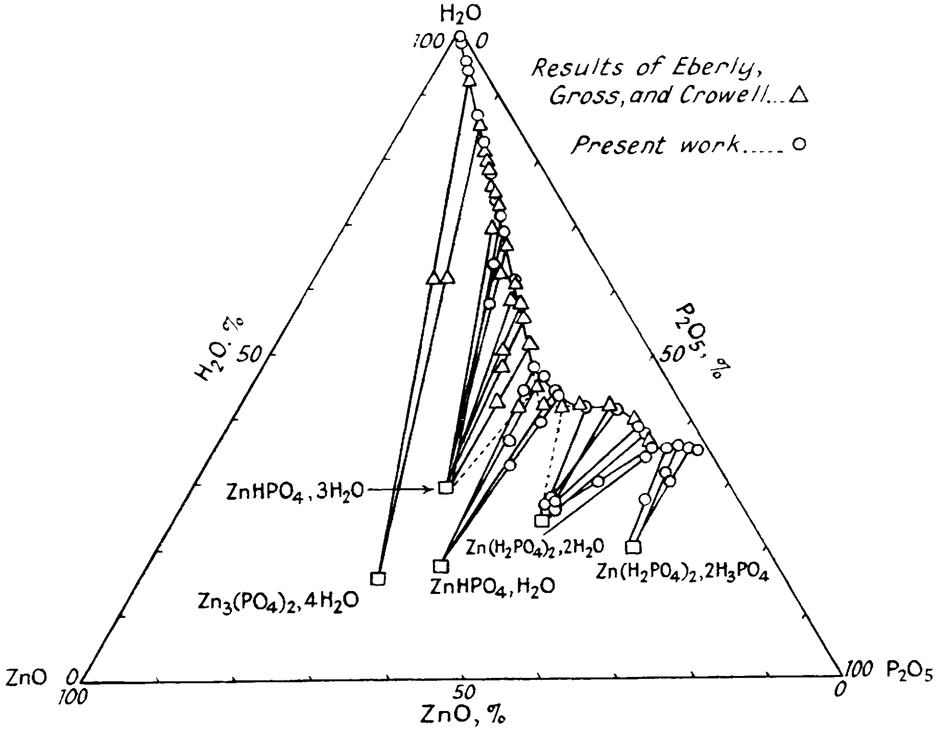
All of these compounds had been described by Eberly, Gross, and Crowell, except the first. This diacid primary phosphate is an unstable compound and it has not been isolated. It was found to be stable in contact with the most concentrated solutions at 25° (Fig. 1), but would not crystallise at higher temperatures.

Above 37°, the primary phosphate would not crystallise but formed syrupy supersaturated solutions. Consequently, it was not possible to add to the information already published by Eberly, Gross, and Crowell.

Some light has been thrown on the conditions under which the two hydrates of zinc secondary phosphate are stable. The monohydrate has proved to be more soluble as the temperature increases, in spite of the implication to the contrary in the work of Eberly, Gross, and Crowell. It forms a stable phase in the system at 25°, although these authors were unable to crystallise it at that temperature. Both sets of results are shown in Fig. 1, from which it can be seen that good agreement was obtained except in the range where this secondary phosphate monohydrate is the stable solid phase. Neither of the hydrates of the secondary phosphate crystallised well (they formed woolly masses of crystals) and neither was stable except in contact with its mother-liquor.

The solubility of the tertiary phosphate was found to decrease with rise of temperature up to 100°.

FIG. 1.—ZnO–P_2O_5–H_2O *at* 25°.



Within the same range of temperature, the manganous phosphates which were stable in contact with saturated solutions were: (*a*) A mono-acid primary phosphate, $Mn(H_2PO_4)_2,H_3PO_4$; (*b*) an anhydrous primary phosphate, $Mn(H_2PO_4)_2$; (*c*) a hydrated primary phosphate, $Mn(H_2PO_4)_2,2\frac{1}{2}H_2O$; (*d*) a secondary phosphate trihydrate, $MnHPO_4,3H_2O$; (*e*) a secondary–tertiary phosphate pentahydrate, $Mn_3(PO_4)_2,2MnHPO_4,5H_2O$.

The second of these does not seem to have been described before. It forms a stable phase in the system at 75°, but not at 50° or lower temperatures. At 75°, it is stable only in contact with its mother-liquor (Fig. 4).

All the other compounds were reported by Erlenmeyer and Heinrich or by Amadori. The mono-acid compound was shown by Amadori to crystallise from the most acid solutions at 25°. It has been established that it forms a stable phase up to 50° (Fig. 3) (also Table II, *b* and *c*). Above that temperature its field is replaced by that of the anhydrous primary phosphate.

The hydrated primary phosphate was regarded by Amadori and also by Erlenmeyer and Heinrich as being a dihydrate, whereas Grube and Staesche considered it to be a trihydrate. The results of the present work, however, suggest that, in fact, it may crystallise with $2\frac{1}{2}$ molecules of water.

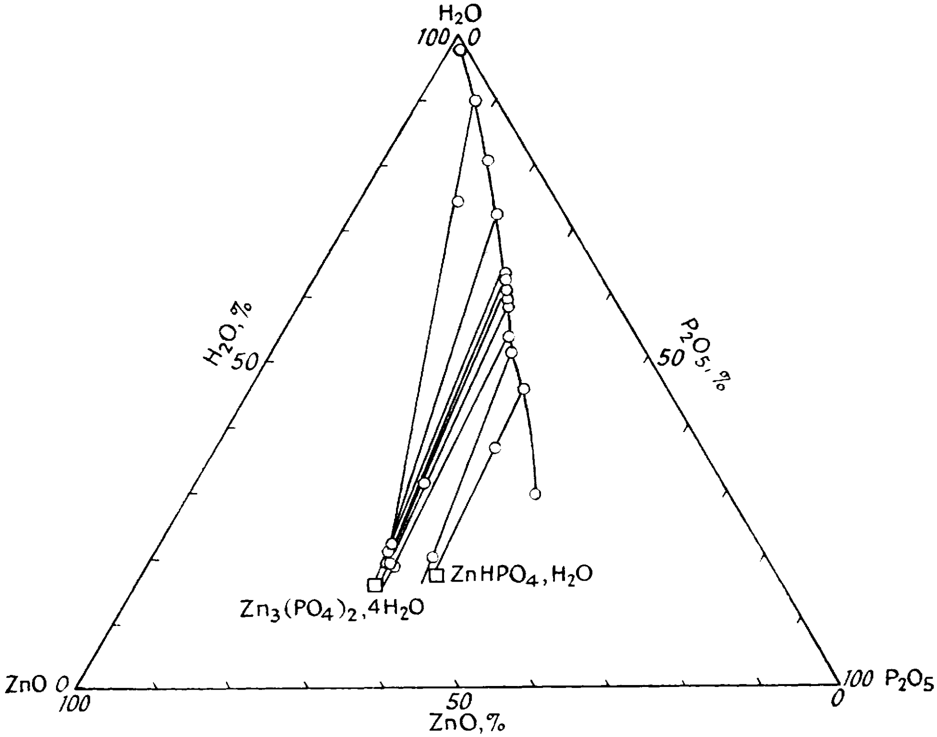
The conditions under which the secondary phosphate forms a stable phase at 25° were described by Amadori. It is stable over practically the same range of concentration at 37° but it does not appear in the system at 50° or above (Figs. 3 and 4).

The secondary–tertiary phosphate which replaced the secondary phosphate at 50° and above (Fig. 4) was the pentahydrate described by Amadori and not the tetrahydrate discovered by Erlenmeyer and Heinrich and reported also by Bassett and Bedwell (*J.*, 1933, 877). The conditions necessary for the crystallisation of this tetrahydrate have not been established.

At no temperature was the tertiary phosphate evident as a stable phase in the system, although the possibility that it possesses an extremely narrow field in the region of very dilute solutions is not precluded.

On the whole, Amadori's results for the system at 25° have been confirmed. No such agreement can be registered with any of the results of Grube and Staesche except for their solubility data at 25°, and they accord with those of Amadori.

FIG. 2.—ZnO–P_2O_5–H_2O *at* 75°.



The results now obtained for the two systems are presented in Tables I and II, respectively. Figs. 1 and 2 show the system zinc oxide–phosphoric oxide–water at 25° and 75°, respectively, and Figs. 3 and 4 the corresponding manganous oxide system at 37° and 75°.

Decrease in solubility with rise of temperature occurred among the zinc phosphates only in the tertiary compound, which separated from the more dilute solutions. The compositions of saturated solutions in equilibrium with this phosphate at different temperatures are shown in Fig. 5. This fall in solubility meant that as the temperature was increased its field on the phase diagram encroached on that of the secondary phosphate trihydrate, which gave evidence of a fairly marked increase in solubility with rise of temperature. Because the solubility of the secondary phosphate monohydrate increased but little with temperature, its field likewise encroached on that of the trihydrate. As a result the trihydrate did not appear in the system at 75° (Fig. 2).

In the manganous phosphate system a complication is introduced by the transition, at just below 50°, from the secondary phosphate to the secondary–tertiary phosphate as the stable phase in the region of more dilute solutions. The compositions of saturated solutions in this range at different temperatures are plotted in Fig. 6, from which it is apparent that the solubilty falls with rise of temperature. The compounds separating from the more concentrated solutions, on the other hand, showed an increasing solubility with rise of temperature.

It is apparent that in both systems the fall in solubility with rise of temperature is restricted to solutions containing 30% of phosphoric oxide or less, and these may for this purpose be described as " dilute " solutions. The inference is that dilute phosphoric acid solutions are less

TABLE II.

Manganous phosphate solutions.

Solution.			Moist solid.*			Solution.			Moist solid.*		
P_2O_5, %.	MnO, %.	*d*.	P_2O_5, %.	MnO, %.		P_2O_5, %.	MnO, %.	*d*.	P_2O_5, %.	MnO, %.	
(*a*) At 25°.											
0·764	0·375	1·007	—	—	A	49·3	1·93	1·50	48·9	24·1	B
18·44	7·83	1·26	—	—		57·7	1·30	1·59	—	—	
25·12	10·29	—	26·12	12·95		61·2	0·65	—	60·9	4·27	C
29·1	9·13	1·40	—	—	B	64·1	0·16	1·66	63·8	3·67	
37·3	5·09	1·41	—	—							
(*b*) At 37°.											
1·260	0·619	1·011	29·9	30·4	A	43·1	3·92	—	47·0	19·17	B
3·206	1·475	—	26·7	26·5		48·0	2·88	—	48·6	19·37	
5·96	2·58	1·058	33·8	34·1		50·9	2·35	—	48·9	17·73	
10·57	4·56	—	28·4	27·3		52·4	2·04	—	50·0	14·26	
14·26	6·05	—	28·4	26·4		56·9	1·69	—	51·4	16·02	
19·67	8·13	1·26	33·4	32·5		59·6	1·94	—	49·7	21·57	
22·66	9·50	—	31·1	27·4		60·6	1·19	—	60·8	5·12	C
28·2	11·70	—	43·9	23·4	B	61·7	0·71	—	60·8	6·03	
29·3	10·98	—	46·6	23·7		62·1	0·78	—	62·4	5·36	
33·6	8·20	—	48·8	24·4		63·0	0·31	—	63·6	4·45	
38·3	5·84	—	46·6	22·06		63·5	0·52	—	63·6	5·30	
39·0	5·39	—	47·3	21·94		64·0	0·29	—	64·0	3·36	
40·0	4·86	—	—	—		64·4	0·28	—	63·9	5·62	
41·9	4·43	—	47·1	20·46		65·0	0·25	—	64·5	3·79	
(*c*) At 50°.											
1·25	0·57	1·005	30·1	36·1	D	33·4	9·98	—	—	—	B
2·95	1·21	1·027	30·5	38·4		33·5	9·36	—	44·8	20·86	
4·40	1·76	1·046	32·4	40·5		34·1	8·87	—	47·3	23·84	
4·73	1·85	—	39·4	48·8		41·4	5·70	—	47·0	21·04	
6·89	2·94	—	—	—		42·7	5·25	—	45·3	18·2	
7·81	3·05	1·082	37·8	47·4		51·1	3·24	—	49·9	16·7	
9·28	3·56	1·10	36·1	45·1		53·5	2·73	—	52·0	9·27	
10·50	4·04	1·12	36·8	45·7		55·4	2·54	—	53·3	8·93	
20·20	7·99	1·27	36·9	44·7		56·8	2·24	—	52·0	15·9	
21·04	8·28	—	31·9	32·8		60·2	2·26	—	55·8	21·4	C
24·2	9·41	—	38·1 †	48·0†		61·0	2·08	—	58·0	20·60	
25·3	9·65	—	33·1	32·0		62·8	0·99	—	62·3	6·82	
28·7	11·44	—	32·4	23·07		63·4	0·87	—	63·6	6·36	
(*d*) At 75°.											
4·29	1·46	—	—	—	D	46·1	6·63	—	46·1	14·47	B
4·41	1·49	—	38·2	47·8		47·7	5·73	—	—	—	
8·25	2·58	—	28·9	33·4		52·6	5·35	—	—	—	
14·29	5·16	—	38·6	48·0		57·6	3·86	—	53·3	15·94	
16·91	5·95	—	36·9	45·3		58·6	3·33	—	55·7	21·3	E
21·1	7·58	—	27·1	21·2		59·8	2·98	—	56·5	11·4	
27·8	10·17	—	32·1	23·43		60·2	2·53	—	57·2	19·61	
30·4	11·04	—	—	—		60·9	2·21	—	59·2	12·4	
34·5	13·02	—	—	—		61·6	2·20	—	60·1	8·15	
35·5	12·45	—	—	—		62·2	1·65	—	58·5	17·8	
35·7	12·89	—	36·0	18·38		63·6	1·58	—	62·8	4·30	
						63·9	1·70	—	58·2	19·98	
(*e*) At 85°.											
2·58	0·78	—	34·2	42·3	D	11·56	3·48	—	32·8	39·1	D
3·46	1·02	—	36·6	45·9		22·22	7·18	—	32·2	32·4	
5·92	1·82	—	33·1	40·2		27·32	9·68	—	—	—	

† Solid washed and left to dry in the air before analysis.

* Solid phases : A = $MnHPO_4,3H_2O$. B = $Mn(H_2PO_4)_2,2\frac{1}{2}H_2O$. C = $Mn(H_2PO_4)_2,H_3PO_4$. D = $Mn_3(PO_4)_2,2MnHPO_4,5H_2O$. E = $Mn(H_2PO_4)_2$.

TABLE II—*continued.*

	Solution.		Solid.†		
No.	P_2O_5, %.	MnO, %.	P_2O_5, %.	MnO, %.	H_2O, %.
(*f*) At boiling temperature.					
1	—	—	38·4	48·2	—
2	1·27	0·33	38·9	48·1	—
Calc. for $Mn_3(PO_4)_2,2MnHPO_4,5H_2O$			38·04	47·49	14·47
,, $Mn_3(PO_4)_2,2MnHPO_4,4H_2O$			38·98	48·66	12·36

† The solids which separated from these solutions were washed and left to dry in the air before analysis.

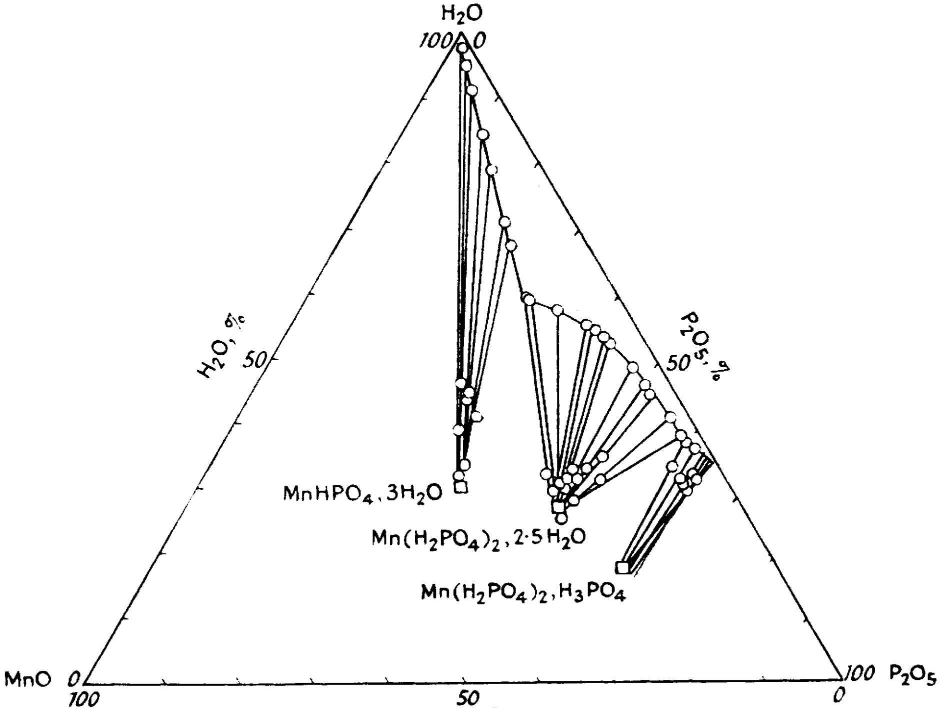
Solution 1 made from 3·50 g. of primary phosphate and 100 ml. of water.
Solution 2 made from 3·00 g. of primary phosphate and 100 ml. of water.

TABLE III.

Ferrous phosphate solutions at 25°.

Solution	P_2O_5, %	9·15	12·27	14·40	17·19
	FeO, %	4·20	5·51	7·57	7·49

FIG. 3.—$MnO–P_2O_5–H_2O$ *at* 37°.



able to retain heavy-metal phosphates in solution as the temperature increases. Otherwise stated, as the temperature rises, the reaction

$$3M(H_2PO_4)_2 \rightleftharpoons M_3(PO_4)_2 + 4H_3PO_4$$

is displaced to the right. Now the equation may be rewritten as

$$3M^{++} + 6H_2PO_4^- \rightleftharpoons M_3(PO_4)_2 + 4H^+ + 4H_2PO_4^-$$

which implies that the reaction will go to the right if the hydrogen and phosphate ions are removed in the form of un-ionised molecules or possibly ion pairs. For such a reaction to account for the behaviour of the phosphates there must be a reduction in the degree of ionisation of phosphoric acid as the temperature increases. It has been assumed that only the first stage of ionisation of phosphoric acid need be considered, and support for this is provided by the low value of K_2 for the acid.

Fig. 4.—MnO–P_2O_5–H_2O *at* 75.

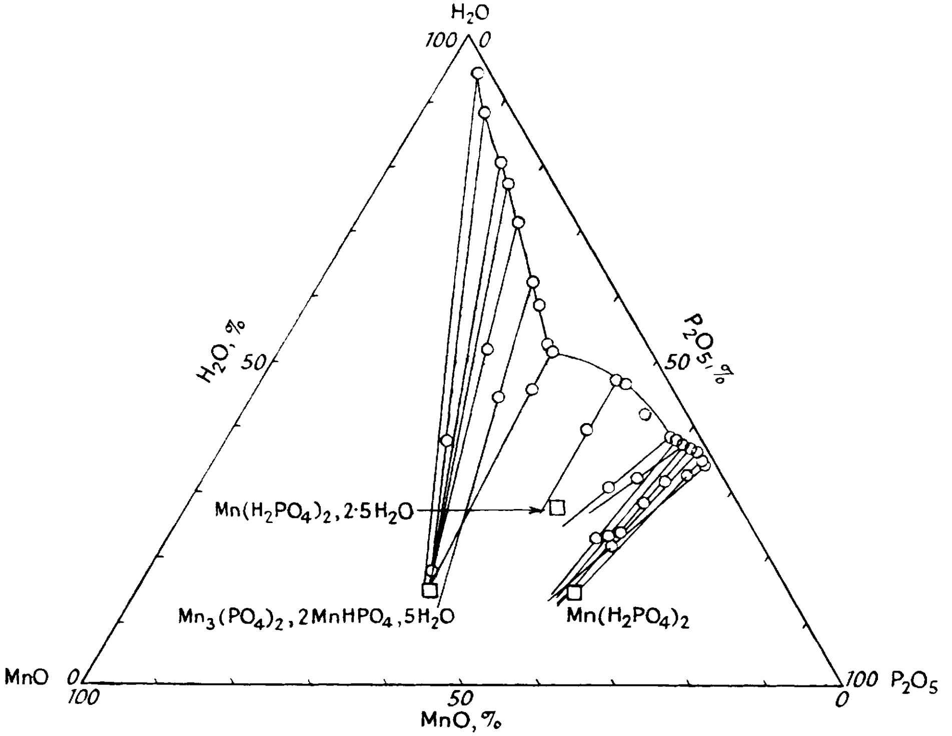
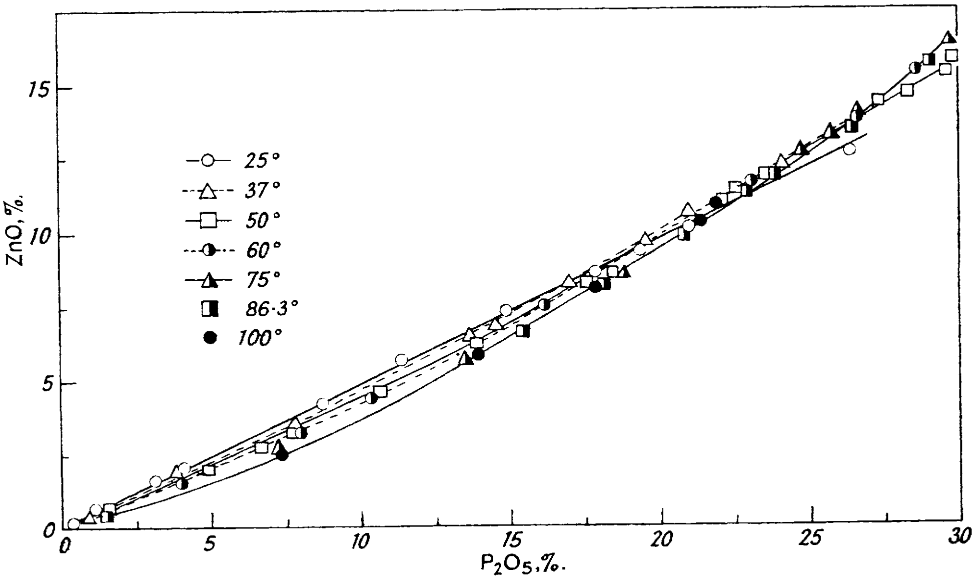


Fig. 5.

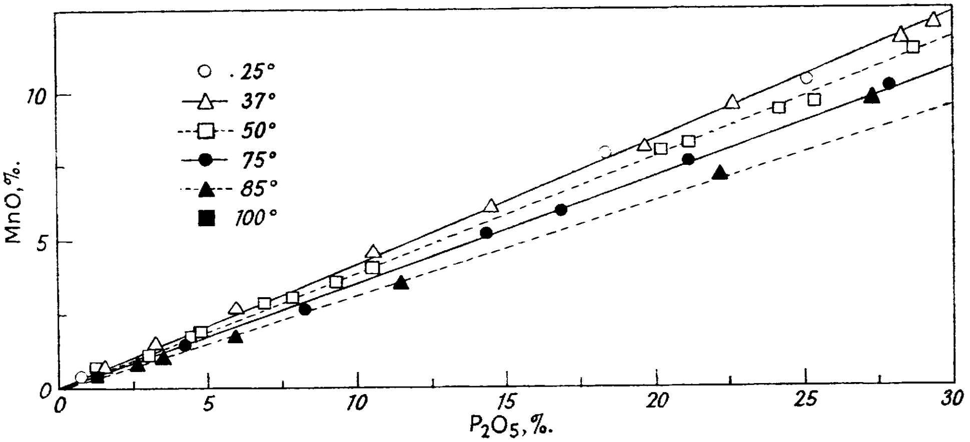


Evidence for a decrease in ionisation with rise of temperature comes from several sources. Noyes and Eastman (*Carnegie Inst. Publ.*, 1907, No. 63, 239—284) measured the conductivity of phosphoric acid solutions containing from 0·5 to 100 milliformula-weights/litre between 18° and 156° They found that the value of 100 Λ/Λ_0 fell continuously with increasing temperature, and this may be taken to indicate a decrease in the degree of dissociation of the acid. Harned and Embree (*J. Amer. Chem. Soc.*, 1934, **56**, 1050) observed that the ionisation constants of weak acids pass through a maximum value with variation of temperature and conform to the equation

$$\log (K/K_{\text{max.}}) = -5{\cdot}0 \times 10^{-5}(t - \theta)^2$$

where t is the temperature (c.) and θ is the temperature corresponding to the value $K_{\text{max.}}$.

FIG. 6.



Nims (*ibid.*, p. 1110) determined the values of the first dissociation constant, K_1, of phosphoric acid between 0·3° and 50°. He obtained his results from e.m.f. measurements on cells without liquid junction, using the Debye–Hückel limiting equation to evaluate mean ionic activities. The variation of the first dissociation constant could, he found, be expressed by Harned and Embree's equation in the form

$$\log K_1 + 2{\cdot}0304 = -5 \times 10^{-5}(t + 18)^2$$

Thus the theoretical maximum value of K_1 would occur at − 18° and, above this, the ionisation would decrease with rise of temperature. Nims had earlier (*ibid.*, 1933, **55**, 1946) obtained values for the second dissociation constant between 20° and 50° and had discovered that this also passed through a maximum value—in this case at about 43°—so that above this temperature any effect related to the second stage of dissociation would in fact reinforce that due to the first stage.

If the decrease of solubility of the phosphates of zinc and manganese in dilute solutions is due to this decrease in the degree of ionisation of the acid, the same behaviour should be observed with the phosphates which separate from the more dilute solutions in the systems of other metals. The compositions of some saturated solutions in the ferrous phosphate system at 25° were determined, and in Fig. 7 there is a comparison with the data for the same system at 70° as given by Carter and Hartshorne (*J.*, 1926, 363). A decrease in solubility is again indicated. That the behaviour is not peculiar to the phosphates of bivalent metals is clear from the work of Carter and Hartshorne on the system ferric oxide–phosphoric oxide–water (*ibid.*, 1923, **123**, 2223). They found that the tertiary phosphate, $FePO_4,2\frac{1}{2}H_2O$, was much less soluble, and had a much greater range of stability, at 70° than at 25°.

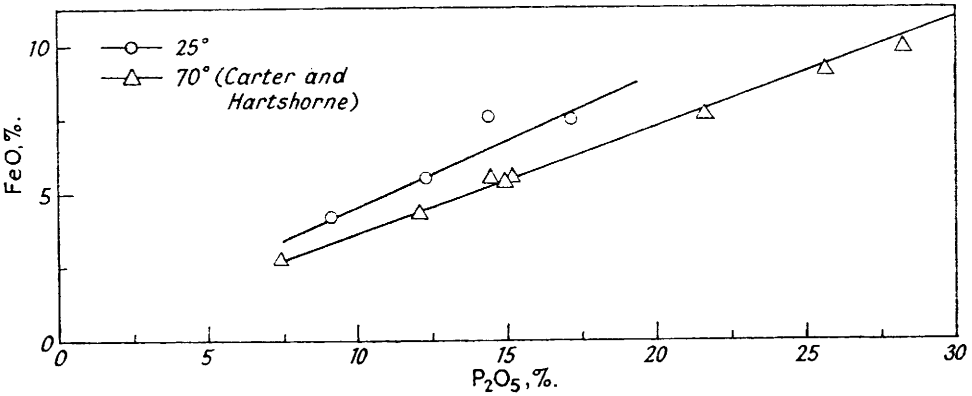
Additional evidence comes from the system calcium oxide–phosphoric oxide–water, investigated by Bassett (*Z. anorg. Chem.*, 1908, **59**, 1) and later by Elmore and Farr (*Ind. Eng. Chem.*, 1940, **32**, 580). They established that the secondary phosphate, $CaHPO_4$, which is the stable phase in contact with saturated solutions containing between 2% and about 20% of phosphoric oxide at 25°, shows a decrease in solubility as the temperature is increased to 100°. An increase in range of stability accompanies the solubility decrease.

Apparently few other systems have been fully examined, but the results quoted show that the effect has been observed with both bivalent and tervalent metals and also with secondary, secondary–tertiary, and tertiary phosphates. The only feature common to these phosphates is that they are the phases which separate from dilute solutions in their respective systems.

It is difficult to decide how far it is permissible to apply dissociation constants determined by the application of the Debye–Hückel limiting equation in explanation of effects observed in solutions of the concentration concerned in phase-diagram studies. The results of Noyes and Bray (*loc. cit.*) demonstrate that the decrease of ionisation with rise of temperature is still observable in M/10-phosphoric acid. It may occur in even more concentrated solutions although, if it does, the actual values of the dissociation constants will differ from those for dilute solutions.

Reference to Figs. 5 and 6 reveals that the solubilities in the zinc and the manganous systems do not fall proportionately to the rise of temperature. In each case, the solubility at 37° is only very slightly less than at 25° (in fact, the solubility of manganous secondary phosphate appears not to vary between these two temperatures), whereas between 37° and 50° there is a distinct fall in the solubility. The values of K_1, calculated from the equation already given, however, vary evenly with change of temperature between 25° and 100°. This difference may be due to the fact that the equilibrium concerned has been represented as involving only simple ions, an assumption which may not be justified. The primary phosphate in solution may be in equilibrium with more complex ions. With the manganous secondary phosphate there is the further complication that it is slightly soluble in water.

FIG. 7.



When discussing the results obtained by his method of "acidimetric precipitation," Rathje (*Ber.*, 1941, **74**, 342, 357, 546) attributed the separation of secondary phosphates from cold solutions and of tertiary phosphates from hot solutions, which his experiments indicated, to the slow rate of crystallisation of tertiary phosphates. He realised that bismuth tertiary phosphate must provide an exception, for it separates rapidly even from cold solutions, a fact utilised in the determination of phosphates. The chief weakness of his theory lies, however, in its inability to explain the decrease in solubility of such compounds as zinc tertiary phosphate, ferric tertiary phosphate, and calcium secondary phosphate which have been observed to separate from both hot and cold solutions. The present explanation seems to accord more closely with the known facts.

EXPERIMENTAL.

Preparation of Solutions for Phase-diagram Studies.—The various methods used were: (*a*) Dissolving the tertiary phosphate in the least possible quantity of phosphoric acid solution—at a temperature below the equilibrium temperature for the more dilute solutions or above it for the more concentrated solutions. (*b*) Dissolving the primary phosphate in water: in dilute solutions a clear metastable solution is first formed from which a more basic phosphate separates only on standing or on warming. (*c*) Dissolving zinc oxide in strong phosphoric acid (about 7M.) at temperatures between 50° and 100° to obtain a saturated solution and then diluting it: this method was not used with the manganous phosphates.

Although the solubility of manganous secondary phosphate varies only slightly with temperature, it is possible to use method (*a*) to prepare solutions in the region of the diagram where it forms the stable solid phase. The reason for this is that freshly diluted phosphoric acid will dissolve more manganous tertiary phosphate than it can retain in solution at room temperature or above.

None of these methods was suitable to obtain ferrous phosphate solutions. These were made from electrolytic iron (in slight excess) and phosphoric acid solution in an atmosphere of nitrogen.

Preparation of Tertiary Phosphates.—The tertiary phosphates were prepared from the metal sulphate according to the equation

$$3MSO_4,xH_2O + 2H_3PO_4 + 6NaOH = M_3(PO_4)_2,yH_2O + 3Na_2SO_4 + (6 + 3x - y)H_2O$$

About 100 g. of the sulphate, together with a slight excess of phosphoric acid, were dissolved in water and diluted to 600 ml. Vigorous stirring accompanied the dropwise addition of sodium hydroxide (1—2N.) until the solution was neutral to methyl-orange or only just faintly acid to litmus paper.

At room temperature this reaction gave either zinc tertiary phosphate tetrahydrate in the form of irregular prisms or a pinkish powder of hydrated manganous tertiary phosphate—the degree of hydration apparently depending on the concentration and on the temperature. At about 80°, the zinc tertiary phosphate appeared in the form of irregular plates, but, in the case of the manganous phosphate, the secondary–tertiary phosphate was precipitated instead of the tertiary compound.

Some typical analyses of zinc tertiary phosphate obtained by this method were :

	Temperature		Analysis.		
Sample.	of prepn.	of drying.	ZnO, %.	P_2O_5, %.	H_2O, %.
1	room	room	53·4	30·8	—
2	,,	40°	53·2	30·9	—
3	,,	40—45	53·1	30·4	15·91
4	,,	45—50	52·8	30·6	—
5	,,	50—55	52·9	30·4	
6	70—90°	room	53·1	30·5	—
Calc. for $Zn_3(PO_4)_2,4H_2O$			53·28	30·99	15·74

The following results were obtained for the manganous phosphates :

	Temperature		Analysis.		
Sample.	of prepn.	of drying.	MnO, %.	P_2O_5, %.	H_2O, %.
1	room	about 100°	51·0	33·8	—
2	,,	,,	50·3	34·7	—
Calc. for $Mn_3(PO_4)_2,3\frac{1}{2}H_2O$			50·91	33·99	15·09
3	room	room	45·0	29·2	26·28
4	,,	,,	44·5	29·0	—
5	,,	,,	44·2	29·0	—
Calc. for $Mn_3(PO_4)_2,7H_2O$			44·24	29·53	26·23
6	room	room	24·4	16·0	59·1
Calc. for $Mn_3(PO_4)_2,28H_2O$			24·76	16·53	58·71
7	70—80°	room	46·9	37·5	14·46
Calc. for $Mn_3(PO_4)_2,2MnHPO_4,5H_2O$			47·49	38·04	14·47

Sample (6) was prepared by the same method as the other samples but from solutions which were slightly more dilute.

Preparation of the Primary Phosphates.—A solution obtained by diluting 80 ml. of concentrated phosphoric acid with 20 ml. of water was saturated at room temperature with either zinc oxide or manganous tertiary phosphate. A slight excess of the oxide or phosphate was then added and dissolved by warming. On standing, crystals of the primary phosphate separated. They were carefully drained and were dried by pressing between filter paper.

Analysis of samples of zinc primary phosphate.

	ZnO, %.	P_2O_5, %.		ZnO, %.	P_2O_5, %.
Sample 1......................	26·9	47·1	Sample 2......................	26·5	47·3
Calc. for $Zn(H_2PO_4)_2,2H_2O$	27·5	48·1			

Analysis of samples of manganous primary phosphate.

	MnO, %.	P_2O_5, %.		MnO, %.	P_2O_5, %.
Sample 1......................	23·9	48·6	Sample 2......................	24·1	48·3
Calc. for $Mn(H_2PO_4)_2,2\frac{1}{2}H_2O$	24·12	48·31			

Materials.—All compounds and solutions were prepared from analytical grade materials. The tertiary phosphates obtained in the manner described were free from sodium.

Apparatus and Procedure.—The containers used were Monax boiling-tubes or flasks closed with rubber bungs. They were placed in a thermostat which was kept to within 0·1° of the chosen temperature. Normally they were shaken once a day. The most satisfactory method of detecting the attainment of equilibrium in the solutions proved to be repeated analysis. Changes in the conductivities and pH values of the solutions were observed to accompany crystallisation, but these did not provide a reliable enough indication. In practice it was necessary to make only one determination of the time required to reach equilibrium in a given range of concentration at a given temperature. It could be applied to other solutions of the same order of concentration. If the analysis was not constant after 60 days, the experiment was abandoned.

The method of removal of successive samples was impracticable with ferrous phosphate solutions because they oxidise so rapidly in air. The solutions were given much longer to reach equilibrium than was known to be taken by the corresponding zinc and manganous phosphates and one analysis only was made—at the end of the period.

Solutions were left undisturbed for one or two days before removal of a sample. The solid phase had by then had time to sink to the bottom and to leave a completely clear supernatant liquor. Samples were taken by pipette (which gave an approximate value for the density) and were transferred to weighing bottles which were immediately stoppered. When it was certain that equilibrium had been reached, a sample of the moist solid phase was also analysed, if enough had crystallised out.

Analytical Methods.—Zinc was determined by titration with potassium ferrocyanide solution (approximately M/20)—the method used by Eberly, Gross, and Crowell. Neither the presence of phosphate nor that of perchloric acid (used in the phosphate determination) interfered with the procedure. It was found that, as recommended by Frost (*Analyst*, 1943, **68**, 51), *o*-dianisidine was a better indicator than diphenylamine for this titration.

Manganese was determined by potentiometric titration according to the method of Lingane and Karplus (*Ind. Eng. Chem. Anal.*, 1946, **18**, 191). It was found that the presence of orthophosphate did not interfere, neither did that, in small amounts, of perchloric acid.

Iron was determined by titration with standard potassium dichromate solution (approximately N/20). Since, after a short exposure to the air, the samples were partly oxidised, they were first reduced with stannous chloride in the usual manner.

Phosphate was determined by titration with standard bismuth oxyperchlorate solution (approximtely M/20). The method, which was developed by M. Hyams (unpublished work), depends on the precipitation of the phosphoric acid as bismuth phosphate. Bismuth oxyperchlorate solution is added to the phosphate solution, and the first excess of bismuth solution above that required to precipitate all the phosphoric acid is detected by means of thiourea (a yellow colour is produced). This procedure is similar to that described by Rathje (*Angew. Chem.*, 1938, **51**, 256) in which potassium iodide was employed as the indicator, but has the advantage that the titration may be carried out at slightly above room temperature instead of at the boiling temperature as with potassium iodide. Acids other than perchloric acid interfere with the titration, so that solid samples are first dissolved in that acid. The acid concentration is kept as low as possible. It was found that the presence of zinc and manganese in the amounts contained by the samples did not interfere. The titration could not, however, be carried out in the presence of iron and this had first to be removed by percolating the solution through a column of Permutit Zeo-Karb 215 ion exchange material.

The water present in the tertiary phosphates and in the manganous secondary–tertiary phosphate was determined by the loss on heating to constant weight, at dull red heat.

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William Ramsay Laboratory of Inorganic and
Physical Chemistry, University College, London, W.C.1.

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