CCCXCVIII.—*Equilibrium Diagram of the System Thallium–Phosphorus.*

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The system thallium–phosphorus has not hitherto been investigated. Thallium was prepared as previously described by the author (*J. Inst. Metals*, 1922, **28**, 453); its purity was 99·5%, the chief impurity being iron (less than 0·3%). Merck's pure red phosphorus was repeatedly boiled with water and then showed a content of 99·91%.

Preparation of Alloys.—Molten thallium alloyed readily with phosphorus, and the action was more marked above 400°. When more than 2·5% of phosphorus had been added, the alloys separated into two layers, the upper one being dark and brittle, and the lower layer soft. The dark substance was readily oxidised to phosphoric acid on being exposed to the air.

Thermal Analysis.—To avoid oxidation of the mixtures, they were prepared in hard-glass tubes from weighed quantities of thallium or the alloy and not more than 1 g. of free phosphorus at a time. The tubes were then evacuated and sealed and the cooling curves were obtained by applying the hot junction of a nichrome–constantan couple to the outside of the tube, contact being made more intimate by means of fireclay. The tubes were packed in sand in an iron tube about 1½ inches in diameter and 1 foot in length, the whole being heated in an electrical tube furnace. The molten alloy was thoroughly mixed by repeatedly tilting the furnace, and the cooling curves were then taken.

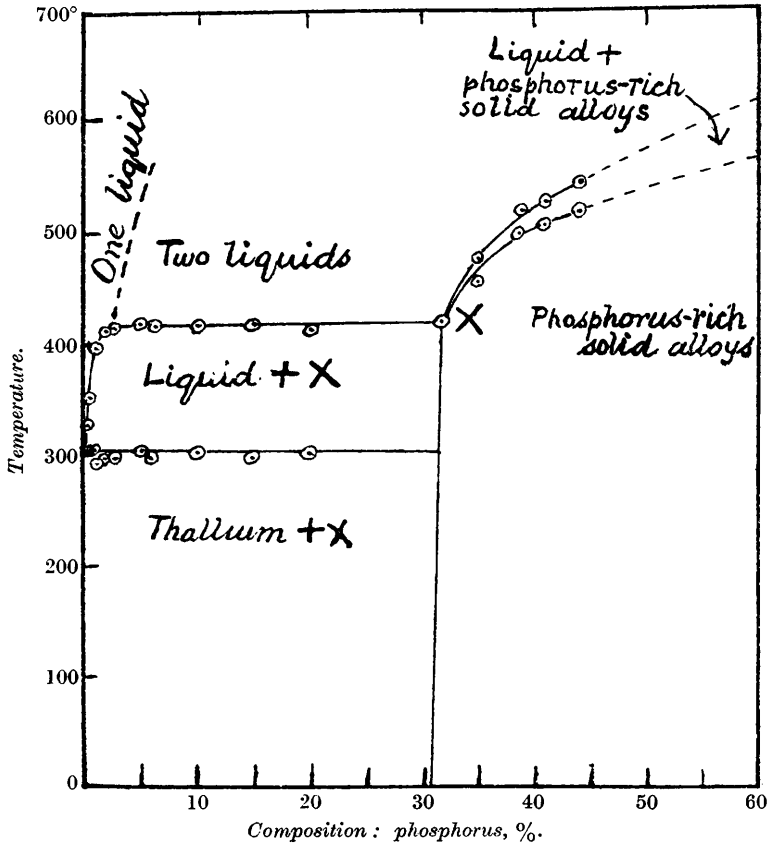
A suspended mirror galvanometer and scale were used for taking temperatures, the rate of cooling being about 8° per minute at high temperatures and about 5° per minute below 300°. Half-minute readings gave the following thermal arrests from which the equilibrium diagram was constructed.

Alloy No.	P, % by weight.	Thermal arrests. 1.	2.	Alloy No.	P, % by weight.	Thermal arrests. 1.	2.
1	0·00	—	303°	9	10·00	416°	303°
2	0·17	328°	302	10	15·00	418	298
3	0·38	352	303	11	20·00	412	300
4	0·87	396	290	12	31·40	420	—
5	2·00	410	296	13	35·00	476	456
6	2·50	412	296	14	38·75	520	500
7	5·00	418	302	15	41·20	528	506
8	6·08	416	296	16	43·90	546	520

Alloys containing from 2·5% to about 27% of phosphorus show two layers, the lower layer being practically pure thallium and

freezing at the melting point of that metal. Thallium, therefore, does not seem to dissolve any of the upper layer at its melting point. The upper layer freezes at about 420°. In alloys containing more than 2·5% of phosphorus, the two layers may dissolve in each other at higher temperatures than 420°. An attempt was made to find at what temperatures the two layers dissolved in each other

FIG. 1.



Equilibrium diagram of the system thallium–phosphorus.

by heating the alloys to definite temperatures above 420° and chilling them, but a considerable pressure was developed and the tubes burst. However, an alloy containing about 0·2% of phosphorus was heated to 350° and chilled; although this burst in water, a small piece was obtained which, on being polished, was found to be uniform, showing that in this alloy the two layers were miscible at about 350°. The solubility of the two layers in each other is there-

fore dependent upon the temperature. A short dotted line has been drawn on the left side of the diagram to indicate this solubility.

Composition of the Alloys.—As most of the alloys were not homogeneous, they were not analysed, but their compositions were deduced from the weights of the constituents in the tubes. The upper dark layer, which was brittle, could be separated by powdering; it contained 31·4—31·5% of phosphorus. The lower layer contained no phosphorus. The thallium was estimated as described by the author (*loc. cit.*), and the quantity of phosphorus was found by difference.

Conclusions.

1. Up to 45% of phosphorus, thallium and phosphorus alloy in all proportions.

2. They form a homogeneous substance, X, containing about 31·4% of phosphorus and melting at about 420°. At this temperature, about 8% of this substance dissolves in thallium, to give an alloy containing 2·5% of phosphorus. Owing to the low solubility of X in thallium, the alloys separate into two layers, the upper layer being X and the lower layer a solution of a small quantity of X in thallium. On cooling, thallium gradually loses all the X dissolved in it and freezes at its melting point.

3. Quantities of phosphorus in excess of 31·4% dissolve in X and form solid solutions, which freeze at temperatures above 420° and over a temperature range. The phosphorus may exist as yellow phosphorus in these alloys, for they take fire when rubbed on emery paper.

4. The substance X tends to dissociate into its constituents at all temperatures, and a high pressure is therefore necessary for its formation; owing to this high pressure, the solubility curve of X in thallium could not be studied.

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