Tetramethylammonium Tri- and Tetrachloro-iodides.—Weltzien[1] describes the preparation of the di-, tri- and tetrachloro-iodides of tetramethylammonium. No polyhalides of ammonium or the alkali metals corresponding to tetramethylammonium trichloro-iodide, $N(CH_3)_4ICl_3$, are known; it was, therefore, thought desirable to repeat Weltzien's work.

Analysis of the solid obtained by the method which Weltzien supposed to yield the trichloride gave results which were low and variable, so that the existence of this compound does not appear to be satisfactorily established; probably it is a mixture of the di- and tetrachloro-iodides produced by the partial decomposition of the latter substance.

Weltzien's analysis of the tetrachloro-iodide showed that his product was partly decomposed. A solid more closely approaching the composition of tetramethylammonium tetrachloro-iodide, $N(CH_3)_4ICl_4$, is obtained by the long continued action of dry chlorine gas on tetramethylammonium iodide at 28°. The solid was weighed in a small glass-stoppered weighing bottle, with glass inlet and outlet tubes also fitted with ground glass stoppers. A slow, continuous stream of chlorine was conveniently obtained by the electrolysis of a concd. solution of hydrochloric acid, the gas was passed through water and concd. sulfuric acid and then into the bottle containing the iodide; the latter first turned brown, then black and finally was completely converted into an orange-colored solid. The bottle was weighed from time to time with the following results:

Expt. 1. 0.5173 g. of iodide used		Expt. 2. 0.6030 g. of iodide used	
Time: days	Gain: G.	Time: days	Gain: G.
2	0.0898	38	0.3522
14	0.1874	51	0.3779
29	0.2739	77	0.3820
52 (constant)	0.3616	99 (constant)	0.4244
Total gain 69.9%		70.4%	

The formation of $N(CH_3)_4ICl_4$ requires a gain of 70.6% in weight The substance formed in Expt. 1 was analyzed; 0.8484 g. required 140.48 cc. of 0.0694 *N* arsenite equivalent to 0.3457 g. of chlorine or a gain in weight of 68.8 %.

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Received December 14, 1922
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Some Solidification Curves of Binary Systems.—In a series of papers on the solidification points of binary systems of various nitro derivatives of toluenes by Professor Bell,[1] I am erroneously attributed with having in my prior researches[2] taken as the temperature of solidification of binary

[1] Weltzien, *Ann.*, 99, 1 (1856).

[1] Bell, *J. Ind. Eng. Chem.*, **11,** 1124 (1919).

[2] Giua, *Ber.*, **47,** 1718 (1914). *Gazz. chim. ital.*, **45,** 339 (1915).

mixtures the minimum obtained as the effect of supercooling. Since this opinion is repeated by C. A. Taylor and W. H. Rinkenbach,[3] in order that the American reader may not gain the impression that I am ignorant of the most elementary rules for the determination of the point of solidification (though my book, "Chemical Combinations between the Metals," should be sufficient to demonstrate the contrary) I have replied to Professor Bell in the *Gazzetta chimica Italiana*[4] and to Messrs. Taylor and Rinkenbach in the *Giornale di chimica industriale ed applicata.*[5]

I have to state that in the solidification curve, Fig. 1, as described by Professor Bell, I have taken the point C and not the point B as the temperature of solidification. The discrepancy between my results and those of Professor Bell are due to his having taken the point C' as the solidification point. While my results are *experimental*, Professor Bell's are *extrapolated.* That my results are correct can be deduced also from the excellent investigation of A. L. Macleod, M. C. Pfund and M. L. Kil-

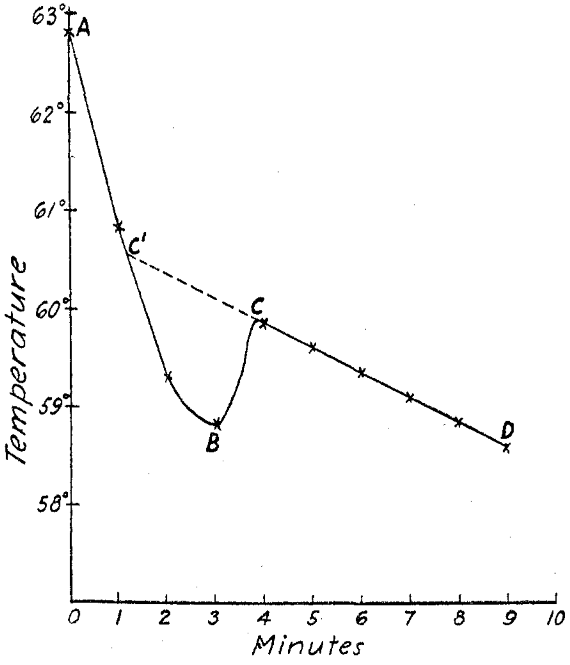

Fig. 1

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[3] Taylor and Rinkenbach, THIS JOURNAL, **45**, 44 (1923). *Ind. Eng. Chem.*, **15**, 73 (1923).

[4] Vol. II, p. 101, 1923.

[5] February, 1923.

patrick[6] who refer directly to my researches and demonstrate that Professor Bell's correction is unnecessary.

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Received March 26, 1923

In the preceding note Professor Giua states that in his experimental data he has taken the point C of the diagram as representing the freezing point of a binary mixture. In his Italian and German articles to which reference has been made he labels the recorded temperatures as "beginning of crystallization." The beginning of crystallization obviously comes at the point B, and the rise in temperature from B to C is a result of crystallization which has followed supercooling. The confusion which has arisen comes, therefore, from the misnaming of temperatures which should have been called "maximum temperatures after crystallization" and not "temperatures of the beginning of crystallization."

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Received April 21, 1923

An Intercepted Hydrolysis.—In one of a series of experiments designed to bring about the formation of phosphonium cyanide, potassium cyanide was heated with stick phosphorus and a little water, in an atmosphere of hydrogen. The free caustic potash in the solution of potassium cyanide was expected to react with the phosphorus to give phosphine, the corresponding amount of liberated hydrogen cyanide providing an opportunity for combination. The gases evolved were passed over warm phosphorus pentoxide, and a white, crystalline product was collected in a cooled receiver. On analysis, this substance proved to be a very pure sample of ammonium cyanide, containing no phosphorus whatever.

The history of the reaction must be as follows. At ordinary temperatures, in a closed vessel, we have the equilibrium, $KCN + H_2O \rightleftharpoons KOH + HCN$. At higher temperatures, this equilibrium is destroyed by the disappearance, through further hydrolysis, of the hydrogen cyanide, $HCN + 2H_2O = NH_4OOCH$, which is a *complete* action, the ammonium formate being destroyed by the equivalent potassium hydroxide formed: $KOH + NH_4OOCH = NH_3 + HCOOK + H_2O$. In sum, $KCN + 2H_2O = NH_3 + HCOOK$, and when potassium cyanide is boiled with water, nearly all of the gas evolved is ammonia.

When phosphorus is present the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide

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[6] Macleod, Pfund and Kilpatrick, THIS JOURNAL, **44**, 2260 (1922).