

patrick<sup>6</sup> who refer directly to my researches and demonstrate that Professor Bell's correction is unnecessary.

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MICHELE GIUA

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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**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,  $\text{KCN} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{HCN}$ . At higher temperatures, this equilibrium is destroyed by the disappearance, through further hydrolysis, of the hydrogen cyanide,  $\text{HCN} + 2\text{H}_2\text{O} = \text{NH}_4\text{OOCH}$ , which is a *complete* action, the ammonium formate being destroyed by the equivalent potassium hydroxide formed:  $\text{KOH} + \text{NH}_4\text{OOCH} = \text{NH}_3 + \text{HCOOK} + \text{H}_2\text{O}$ . In sum,  $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCOOK}$ , and when potassium cyanide is boiled with water, nearly all of the gas evolved is ammonia.

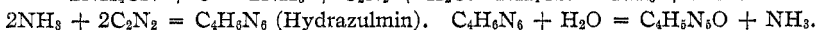
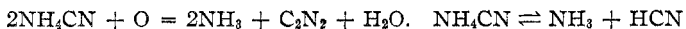
When phosphorus is present the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide

<sup>6</sup> Macleod, Pfund and Kilpatrick, *THIS JOURNAL*, **44**, 2260 (1922).

present, an equivalent amount of hydrogen cyanide being liberated. With a large excess of water, we should probably have  $3\text{KCN} + 4\text{P} + 12\text{H}_2\text{O} = 3\text{KH}_2\text{PO}_2 + \text{PH}_3 + 3\text{HCOONH}_4$ , but this excess is not present, and after a small amount of ammonium formate has formed, we reach equilibrium and hydrogen cyanide is liberally evolved.

There is, thus, a main reaction,  $\text{KCN} + 2\text{H}_2\text{O} = \text{NH}_3 + \text{HCOOK}$ , and a subsidiary reaction,  $3\text{KCN} + 4\text{P} + 6\text{H}_2\text{O} = 3\text{KH}_2\text{PO}_2 + \text{PH}_3 + 3\text{HCN}$ . We refer to them in this manner because the ammonia evolved was always in excess over the hydrogen cyanide.

The experiment was repeated with other non-volatile substances, reactive with potassium hydroxide. Aluminum powder, in place of phosphorus, also produced ammonium cyanide of great purity. A greatly superior yield, however, was obtained by using a suitable proportion of sulfuric acid. Attention was called in this case to the great readiness with which ammonium cyanide is oxidized. In the first trials of the sulfuric acid method, hydrogen was neither formed in the reaction (as in the case of aluminum) nor flushed through the apparatus (as in the case of phosphorus). The product was ochreous in appearance, and was sublimed only with difficulty. The cause of this proved to be the formation of a matrix of azulmic acid, produced, we think, as follows.



It has often been remarked that while ammonia is effectively administered in cases of prussic acid poisoning, ammonium cyanide is powerfully poisonous. As, however, this substance cannot exist at the temperature of the body, its effects are probably due to the formation of cyanogen, as shown above, through a damp oxidation. Ammonium cyanide is most readily ignited, burning with a pale, fawn-colored flame. It immediately decolorizes neutral potassium permanganate solution: when the latter is added drop by drop until the decolorization is *slow*, a vivid yellow solution is formed, and this does not become brown nor deposit hydroxides until after standing exposed to the air for many hours.

Similarly, ammonium cyanide is reactive with sulfur. When it is dissolved in a chloroform solution of sulfur, thin leaves of ammonium thiocyanate separate on partial evaporation.

CONTRIBUTION FROM THE  
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