

DECOMPOSITION OF POTASSIUM CYANIDE.

BY J. F. WILKES.

Entomologists frequently find it convenient in killing insects to use a bottle containing moistened potassium cyanide over which plaster of Paris is spread. The insect usually dies in a few minutes after enclosure in the bottle, the mixture assumes a brownish tint and the odor of hydrocyanic acid can easily be detected. As no explanation of this reaction could be found, some experiments were undertaken with a view to deciding the effect of the plaster of Paris and how far it is necessary for the reaction.

To determine the nature of the gas given off, about one grain of pure potassium cyanide (only the chemically pure was used throughout these experiments) was placed in a test-tube, moistened with water and covered with a layer of plaster. Through an accurately-fitting cork two bits of tubing entered this test-tube, one extending nearly to the surface of the mixed substances and having its other end connected with a washing flask containing a strong solution of sodium hydroxide; the other just entered the cork and was connected with a calcium chloride tube to which was joined a tube, 300 m. m. long, filled with mercuric oxide. A smaller tube from the end of this dipped beneath a solution of potassium hydroxide. By means of an aspirator, air was drawn through this system of tubes slowly and at regular intervals for about two days. At the end of this time the potassium hydroxide was tested with the ferroso-ferric solution and no trace of prussian blue could be detected. The calcium chloride and mercuric oxide tubes were then removed and air once more drawn through into a solution of potassium hydroxide. On testing this the reaction for hydrocyanic acid with the ferroso-ferric solution was very clearly given. Here then was proof that hydrocyanic acid and no cyanogen was formed during the reaction. As a confirmatory test, however, hydrochloric acid was added to a portion of the potassium hydroxide through which the gas had been drawn, then sodium hydroxide, and it was heated to boiling. No ammonia could be detected. There was therefore no potassium cyanate present and hence no cyanogen had entered the liquid.

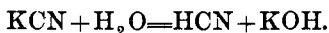
The aqueous solution of potassium cyanide can be kept unaltered in closed vessels at ordinary temperatures according to Pelouze and Geiger (Gmelin's Hand-book, vii, 415), but when boiled it is resolved into ammonia and potassium formiate. It is well known that a strong

smell of ammonia can be detected on opening a bottle containing moist cyanide, but we have seen no mention of the formation of hydrocyanic acid from the cyanide by simple decomposition without the aid of carbon dioxide or any strong acid. It was noticed during these experiments that when moistened potassium cyanide was enclosed in a test-tube and air aspirated over it for several days a slight but distinct prussian blue test was given by the solution of potassium hydroxide through which the air after leaving the tube was drawn. Of course every precaution was taken to free the air from all traces of carbon dioxide or acid. It was made to pass through a wash bottle containing a concentrated solution of sodium hydroxide, then through two U tubes filled with small lumps of solid hydroxide, and lastly, to have proof of the absence of carbon dioxide, through a small tube containing lime water, passing thence into the tube containing the cyanide. This experiment was repeated at various temperatures ranging from 12° — 18° C. and always with the same result. If the amount of moisture was small, the depth of color gotten in the ferroso-ferric test was slight. If about 1 c.c. of water was used to 1 gram of the cyanide a clear deep green was gotten. With calcium carbonate, ordinary hydrated calcium sulphate or barium sulphate, the cyanide when mixed in about equal parts and moistened gave off apparently about the same amount of hydrocyanic acid as when alone, judging from the depth of color in the ferroso-ferric test. With the anhydrous sulphate a distinct blue was gotten, showing a decidedly increased decomposition, and in this case the mixture left in the tube had a purplish brown color which was not observed with the others.

Since other sulphates and other calcium compounds failed to act on the potassium cyanide and no change in the anhydrous sulphate itself could be detected, it seemed probable that its action was due in some way to its power of combining with a portion of the water present to form the hydrated sulphate. When an excess of water, 3–5 c.c., was added to the mixture of the cyanide and the anhydrous sulphate, the test showed very little, if any, more hydrocyanic acid to be given off than when the hydrated sulphate or the cyanide alone was used and no discoloration was produced. When barely moistened the evolution of hydrocyanic acid was considerable. If porous, partially dehydrated calcium chloride was added to the cyanide in the place of the sulphate the amount of acid

evolved was still greater and the color of the mixture almost black. Anhydrous sodium carbonate had the same effect, though in a lesser degree. Again, when the cyanide and the plaster had both been carefully dried the air was drawn over them for four days and no hydrocyanic test could be gotten in the final tube of potassium hydroxide.

The mixture of potassium cyanide and anhydrous calcium sulphate left after two or three days of aspirating was examined and found to contain potassium hydroxide. The reaction then is probably



It has been shown by Karsted (Poggendorff's Annalen, 115,348) and Storer (Amer. Chem. Journal v. 69) that where air alone comes in contact with corks and organic connectors carbon dioxide is formed. This would probably account for decomposition when potassium cyanide and water alone were used, but the greatly increased depth of test when plaster of Paris is added shows a decided action on the part of that body.

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RATE OF REVERSION IN SUPERPHOSPHATES PREPARED FROM RED NAVASSA ROCK.

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The manufacture of a high grade superphosphate from Red Navassa rock is one of those problems which, appearing easy of answer, yet present great difficulties. How great these difficulties are, only the manufacturer knows. Working formulæ which on other natural phosphates give entire satisfaction, on red Navassa give curious and rather discouraging results. In this rock we have to deal with a mixture of the phosphates of calcium, iron, and aluminium, and the oxides of iron, and aluminium. The superphosphate made from it is consequently of a more complicated structure than that made almost entirely of tri-calcium phosphate, i. e., from bone, or Apatite, or Charleston Rock.

In the superphosphate itself, the rapidity with which reversion takes place is largely dependent upon the content of iron and