# An Improved Method for the Generation of Hydrocyanic Acid[1]

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IN 1876, Nandin and de Montholon[2] described a method for setting free hydrocyanic acid by the action of moist carbon dioxide upon alkali metal cyanides, whereby, in time, one could completely displace the combined hydrocyanic acid, thus:

$$2\,KCN + H_2O + CO_2 = K_2CO_3 + 2\,HCN$$

**The action of carbon dioxide at less than atmospheric pressure upon moist sodium cyanide or crude calcium cyanide has been investigated, with the result that a new method is now proposed for the commercial recovery of hydrocyanic acid from these cyanides. The preliminary studies have indicated that excellent yields of hydrocyanic acid coupled with a high degree of safety to the plant operators are thereby possible.**

The statements of Tcherniac[3] also have a bearing upon this subject, but he gives the data necessary for the formation of cyanides from hydrocyanic acid and soda, and shows that the reaction is reversible.

More recently Metzger[4] described the conditions which he has found best suited for the formation of hydrocyanic acid from alkali metal cyanides. According to the method of the first patent he regulates the temperature and carries out the reaction at 0° C. or at above 100° C. In the other case he increases the rate of flow of the carbon dioxide over the reaction mass, thereby avoiding polymerization of the hydrocyanic acid liberated. The apparatus described and illustrated shows that he works with a pressure slightly above atmospheric.

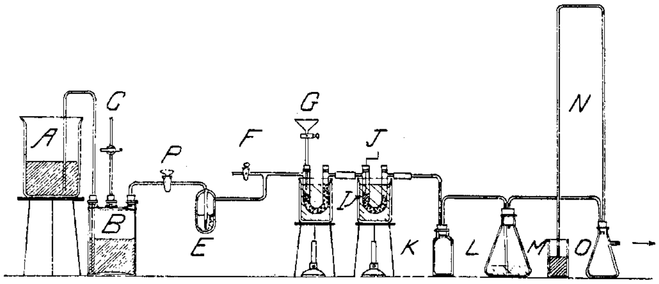
The writer had studied these methods of hydrocyanic acid formation with the primary purpose of finding an economical way to work up the cyanide material formed when one heats together at 800° C. a nitride, a carbide, and an alkali metal carbonate.[5] The sintered material so obtained is quite basic and therefore the cost of a sulfuric acid treatment was prohibitive. The method of Nandin and de Montholon[2] also proved to be nonapplicable, even with the modifications recommended by Metzger,[4] as the moist carbon dioxide employed combined with such avidity with the cyanide-containing material that much tar-like substance was formed. In an attempt to eliminate this formation of tar, which represented a loss of hydrocyanic acid, a study was made of the reaction of carbon dioxide upon the cyanide material at less than atmospheric pressure. The excellence of the yields obtained thereby was so surprising that the investigation was extended to cover the use of sodium cyanide and calcium cyanide.[6]

### Experiments Using Sodium Cyanide

At the start of an experiment the oil which completely filled the Woulfe bottle, *B*, was displaced by carbon dioxide, obtained from a cylinder of the commercial gas, and forced up into the reservoir, *A*. A weighed quantity of sodium cyanide, commercial grade, was then placed in the right-hand U tube, *J*, upon the asbestos pad, *I*. The rubber stopper and stirrer were then replaced and the joint was coated with shellac; when this had hardened the water bath was brought up to the desired temperature and the vacuum pump started. When the column in the mercury gage, *N*, had risen to the desired height, the vacuum cock, *P*, connecting the carbon dioxide holder with the water-filled bubble gage, *E*, was slowly opened until the correct rate of flow, as judged by the rate at which the bubbles formed and by the flow of oil back into the Woulfe bottle, had been obtained. The rate of water addition to the bead-filled saturator tube, *G*, was also adjusted to the required time per drop. A water-operated filter pump was used to obtain the reduced pressure, which by this means could be held to ±10 mm. With this apparatus it was possible to study the reaction under variable conditions as to gas flow, temperature of reaction, temperature of saturated gas, rate of water addition and pressure, and by an analysis of the sodium hydroxide solution in the absorber, *L*, and also of the residual cake, the amount of carbon dioxide used, the hydrocyanic acid recovery, etc., could be readily obtained.

In an experiment lasting an hour, during which time 1550 cc. of carbon dioxide and 2 cc. of water were allowed to react upon 1.0 gram of commercial grade sodium cyanide placed upon the asbestos pad *I* in the tube *J*, 97.6 per cent of the hydrocyanic acid was recovered. The pressure in the system was 280 mm., while the temperature of both water baths was 75° C.

In a second test 1200 cc. of carbon dioxide and 2 cc. of water were passed over another gram sample of sodium cyanide, in 65 minutes, while the temperature of the baths was at 40° C., and the pressure 50 mm. A yield of 97.6 per cent of hydrocyanic acid was again obtained. The residue in the tube *J* after these trials had but a very slight pink color.



APPARATUS FOR GENERATION OF HYDROCYANIC ACID

It is to be noted that in these experiments the temperature of the saturator bath was but very little above the boiling point of water, at the pressure employed, and in this way the warm sodium cyanide was kept slightly moist. The rate of carbon dioxide flow was such that from two to three times the theory passed over the moist sodium cyanide in 45 minutes, under which conditions the sodium cyanide was converted almost entirely into sodium bicarbonate.

These observations lead one to believe that the action, under less than atmospheric pressure, is not the simple one

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[1] Received May 29, 1924.

[2] *Ber.*, **9**, 1433 (1876).

[3] D. R. P. 160,637 (May 10, 1905).

[4] U. S. Patents 1,385,335 and 1,385,336 (July 19, 1921).

[5] *Chem. Met. Eng.*, **29**, 1098 (1923).

[6] U. S. Patent 1,492,871 (May 6, 1924).

indicated by Nandin and de Montholon,[2] for since water must be present in the liquid phase in order to obtain good yields, this water most probably first hydrolyzed some of the sodium cyanide to hydrocyanic acid and sodium hydroxide. The sodium hydroxide is then removed from the sphere of reaction by being converted into a much less soluble compound, sodium bicarbonate, and thus the liberation of hydrocyanic acid goes to completion.

When operating under these conditions but employing a pressure above atmospheric, the yield of hydrocyanic acid is 90 per cent or below and the residual cake is blackish brown and contains considerable carbonate. With hydrocyanic acid selling at from 40 to 60 cents per pound it is evident that a saving of even 5 per cent of the acid is well worth while.

At higher temperature the beneficial effect of a pressure less than atmospheric is not so marked for when sodium bicarbonate and sodium cyanide are heated together to 150° C., only about 20 per cent of the theoretical quantity of hydrocyanic acid, as based upon the following equation, is set free:

$$2\ NaHCO_3 + 2\ NaCN \rightarrow 2\ Na_2CO_3 + 2\ HCN$$

or expressed in another way and in steps:

$$2\ NaHCO_3 \rightleftharpoons Na_2CO_3 + (H_2O + CO_2)$$
$$(H_2O + CO_2) + 2\ NaCN \rightleftharpoons Na_2CO_3 + 2\ HCN$$

By using an excess of bicarbonate the yield of hydrocyanic acid can be increased, but not enough to make the method of commercial value.

### Experiments Using Calcium Cyanide

As to the action of carbon dioxide upon calcium cyanide no quantitative data could be found in the literature. However, in a French patent[7] a similar reaction is worked out for barium cyanide, wherein moist barium cyanide is systematically treated with carbon dioxide. Unfortunately this method is not satisfactory for calcium cyanide, since strong solutions of this substance are very unstable[8] and the treatment of a sufficiently dilute solution (15 per cent) involves apparatus of too great size.

Because of the successful use of less than atmospheric pressure in the case of sodium cyanide, it was believed it would be advantageous here. Nevertheless, the solution of this problem of hydrocyanic acid recovery from crude calcium cyanide was most troublesome, but a theoretical yield of hydrocyanic acid, as based upon the calcium cyanide content of the material employed, was finally obtained. The secret of success lay in the correct moistening of the cyanide.

The reaction runs smoothly when carried out at room temperature (20° C.) under an absolute pressure of 150 mm. of mercury and with the temperature of the saturator bath, during the first part of the run, at 50° C. The rate of flow of carbon dioxide was adjusted so that 500 cc. of the moist gas passed over the material—which in this case consisted of 0.5 gram ground calcium cyanide mixed with 1.5 grams of 60-mesh calcite to increase the volume of the mass—in half an hour. The temperature of the saturator bath was then slowly raised so that when 750 cc. of carbon dioxide were estimated to have passed over the cyanide, the water in the saturator U tube had reached the boiling point, whereupon the resulting steam went over into the reaction tube and condensed upon the cyanide-containing mass. This mass was then stirred, while enough water was being admitted to the saturator by means of the dropping funnel to keep the calcite–calcium cyanide mixture to the consistency of a thick mesh. In this case 1.5 cc. of water were needed. At the end of 75 minutes, when 2 liters of carbon dioxide had passed through the apparatus, it was swept clear of hydrocyanic acid and carbon dioxide by the admission of $CO_2$-free air through the stopcock *F*, placed just ahead of the bubble gage. This admission of the air also served to break the vacuum. An analysis of the sodium hydroxide solution in the absorber showed that all the hydrocyanic acid had been retained therein.

It is evident that such a process is exceptionally safe to operate, since with the apparatus under less than atmospheric pressure no outward leakage of the intensely poisonous hydrocyanic acid is possible.

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[7] French Patent 387,144 (July 1, 1908).

[8] Williams, "Cyanogen Compounds," **1915**, p. 41. P. Blakiston Son & Co.

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# Modification of Scales' Method for Determination of Nitrates[1]

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Several students in this laboratory obtained low and erratic results in the determination of nitrate nitrogen by the Scales method.[2] A study of the method by the writer indicated that the trouble was caused by too great alkalinity of the electrolyte, a mixture of magnesium oxide and sodium chloride, so that insufficient nascent hydrogen to reduce the nitrate was given off from the copper-zinc couple. Different lots of so-called chemically pure magnesium oxide were found to contain from 4 to 12 per cent sodium carbonate, besides some sodium chloride. When a comparatively pure magnesium oxide was used in the Scales method, the results were good, as was also the case when the excessive alkalinity of the impure magnesium oxide was neutralized by an acid.

About 80 grams of scrap zinc are placed in a 500-cc. Kjeldahl flask and washed with 1 per cent sulfuric acid to produce a fresh surface. The acid is poured off and a 0.5 per cent solution of copper sulfate in 0.3 per cent sulfuric acid is added to coat the zinc with copper. After a few minutes the solution is poured off, the zinc washed once with water and the nitrate solution added. The mixture of 1 gram magnesium oxide and 5 grams sodium chloride is then added, followed by the necessary amount of dilute hydrochloric acid to neutralize excessive alkalinity. Water to make a total volume of 250 cc. is added and the mixture distilled for about 45 minutes until nearly dry, the ammonia generated being collected in standard acid as usual. To find the amount of acid required to neutralize the excessive alkalinity of the magnesium oxide, 1 gram of the oxide is placed in a small flask with 25 cc. of water and some methyl orange as indicator. Dilute hydrochloric acid (1:4) is added rather rapidly till the red color persists for a fourth of a second. Thus the sodium carbonate or hydroxide is neutralized and a little magnesium chloride is formed. It is necessary to make this test with each lot of magnesium chloride.

During the course of this investigation it was found that the Devarda method was generally more reliable than the Scales method, and that presence of soluble phosphates in the solution did not cause difficulties in the use of the Devarda method as they did with the Scales method.

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[1] Received September 22, 1924.

[2] *J. Biol. Chem.*, **27**, 327 (1916); Harrison, *Ibid.*, **46**, 53 (1920).