# The Absorption of Hydrocyanic Acid by Solid Sodium Carbonate<sup>1</sup>

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**\IVE** patents give information regarding the reaction:  $Na_2CO_3 + 2HCN = 2NaCN + H_2O + CO_2$ 

In the earliest of these, Roeder and Grünwald<sup>2</sup> state that hydrocyanic acid may be recovered, from reducing gases containing it, by absorbing it in a molecular mixture of sodium and potassium carbonates, and that this absorption may take place under a slight vacuum. In a later patent<sup>3</sup> they state that the most favorable temperature for the absorption of hydrocyanic acid by sodium carbonate is about 700° C. Tcherniac,<sup>4</sup> who worked with a mixture of hydrocyanic acid and oxidizing gases, found that the hydrocyanic acid began to be absorbed by soda ash at below 200° C., and that 450° C. was the most favorable temperature for the reaction. He further states<sup>5</sup> that the reaction given in the above equation is reversible and that the absorption of hydrocyanic acid, from hydrocyanic acid and carbon dioxide mixtures, takes place at from 400° to 500° C. This has been confirmed by Metzger.<sup>6</sup>

In a previous article the writer<sup>7</sup> described the conditions for setting free hydrocyanic acid gas by the action of carbon dioxide upon impure alkaline cyanides while under less than atmospheric pressure. In order to maintain the desirable features of that method experiments were carried out to determine if the hydrocyanic acid could be recovered from such dilute mixtures when the absorption of the hydrocyanic acid was carried out at a similarly reduced pressure.

#### Experimental

For the purpose of obtaining preliminary information in regard to the best temperatures at which to carry out the reaction, the apparatus shown in Figure 1 was used. A smal Pyrex flask, F, equipped with a dropping funnel, D, was connected to a drying tube, C, which in turn led to a special Utube of 8 mm. i. d. Pyrex tubing, U. This tube contained soda ash held in place by a plug of glass wool. It was connected to an absorption bottle, M, containing 0.5 N potassium hydroxide and this bottle was connected to the mercury gage and vacuum pump. For temperatures below 250° C. oil was used in the bath in which the U-tube dipped, but for temperatures above this and up to 400° C. a fused mixture of 55 per cent by weight of potassium nitrate and 45 per cent of sodium nitrate was employed.<sup>8</sup>

At the start of an experiment a gram of sodium carbonate (commercial), the theoretical amount, was placed in the U-tube while a gram of pure sodium cyanide was placed in the Pyrex flask. The apparatus was then evacuated to the desired pressure and the heating bath brought up to temperature. Finally, 40 per cent sulfuric acid was allowed to drop from the funnel slowly upon the sodium cyanide. The duration of each experiment was 10 minutes.

- <sup>2</sup> German Patent 132,999 (July 3, 1902).
- <sup>3</sup> German Patent 134,102 (September 5, 1902).
- 4 German Patent 145,748 (October 28, 1903).
- <sup>5</sup> German Patent 160,637 (Mav 10, 1925)
- <sup>6</sup> U. S. Patent 1,439,909 (December 26, 1922). 7 THIS JOURNAL, 17, 57 (1925)
- <sup>8</sup> Briscoe and Madgin, J. Chem. Soc. (London), **123**, 1608 (1923).

Influence of	of Pressure cyani	Pressure and Temperature upon Absorption of Hydro- cyanic Acid by Sodium Carbonate							
Expt.	HCN Gram	HCN absorbed <sup>a</sup> Per cent	Temp. °C.	Pressure (abs.) Mm.	HCN lost Per cent				
1 .	$0.362 \\ 0.366 \\ 0.240$	13 71	200 300	230 293	None None				
0 4 5	$0.340 \\ 0.354 \\ 0.322$	72 73 59	390 340 300	230 230 710	2 11				

<sup>a</sup> Determined by dividing the weight of HCN absorbed, calculated from the NaCN present in the U-tube, by the sum of this amount and that retained by the KOH in the bottle, *M*.

The figures show that no great gain in efficiency is obtained by working at temperatures much above 300° C., provided that the pressure in the system is kept at about 230 mm. absolute. If, however, the pressure is close to atmospheric the amount of hydrocyanic acid absorbed is markedly reduced.



A few experiments were carried out in this apparatus using pulverized sodium hydroxide as agent for absorbing hydrocyanic acid. The apparatus is not satisfactory for use with caustic soda, for as soon as an appreciable portion of the alkali has been converted to sodium cyanide the melting point of the former is lowered to less than 130° C., and then as the rapid absorption of hydrocyanic acid continues the melt becomes solid and thus shuts off the flow of gas. Enough data were obtained, however, to show that solid caustic soda under an absolute pressure of 50 mm. and at 110° C. will absorb hydrocyanic acid without discoloration, whereas Tcherniac,<sup>5</sup> working at atmospheric pressure, found 200° C. to be the minimum temperature for this result.

## Absorption of Hydrocyanic Acid from Mixtures with Carbon Dioxide by Sodium Carbonate

	HCN	HCN in				
	$+ \dot{C}\dot{O}_2$	$CO_2 + HCN$	HCN	Rate of	Temperature	Pressure
	mixture	mixture	absorbed <sup>a</sup>	CO <sub>2</sub> flow	of Na <sub>2</sub> CO <sub>3</sub>	(abs.)
Expt.	Grams	Per cent	Per cent	Cc./min.	° Č.	Mm.
1	0.994	12.0	27.2	27.2	310	206
2	0.763	26.9	42.0	8.5	310	230
3	0.928	26.2	51.0	9.9	310	230
4	1.116	24.1	50.0	22.1	305	230
5	1.628	14.6	31.8	31.5	306	230
6	1.651	21.5	50.0	22.2	340	508
7	1.865	22.5	50.0	12.2	305	155
8	2.034	22.3	50.1	13.2	340	135
9	1.839	14.2	41.6	24.8	360	155
10	1.704	7.3	39.1	11.0	315	230

<sup>a</sup> Determined as in previous experiment.

<sup>&</sup>lt;sup>1</sup> Received March 30, 1925.

This same apparatus was employed for studying the absorption of hydrocyanic acid from the mixtures of that gas with carbon dioxide obtained, as described in the previous article, by passing carbon dioxide over moistened sodium cyanide. For this purpose the flask F was removed and a U-tube, equipped with stirrer and containing sodium cyanide, was connected in its place.

#### Conclusion

As a result of these and former experiments, it is seen that it is practicable to decompose impure sodium or calcium cyanide and by working in a closed cycle to obtain thereby high-grade sodium cyanide with a high degree of safety and with very low temperature requirements.

# Graphical Rectifying Column Calculations<sup>1</sup>

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Graphical methods of making rectifying column calculations for binary mixtures in both plate and packed columns based on material transfer equations have been outlined and examples given of their use.

Methods of calculation for packed columns when more than two components are present have been discussed.

• ECTIFYING columns may in general be separated into two classes-plate columns and packed columns. In the former the rectification may be conceived as occurring in a series of finite steps, whereas in the latter the rectification is continuous. As the phenomena are somewhat different in the two cases, they will be considered separately.

#### A-Plate Columns

The discussion of plate columns will be limited to binary mixtures and the column will be assumed to be isothermal. This assumption may be made when the mols of vapor condensed for heating are small compared with the total mols of vapor. In this case average quantities of liquor and vapor should be used and the temperature should be taken as the column average. It will also be assumed that an artificial molecular weight has been assigned to one of the components so that the molal heats of vaporization are equal. The mols of vapor going up the column, the mols of overflow above the feed plate, and the number of mols of overflow below the feed plate are therefore constant. One mol of product will be used as the basis of calculation.

#### Nomenclature

- O =mols of overflow above feed plate per mol of product Ň = O + 1 =mols of vapor per mol of product
- F = mols of feed per mol of product O' = O + F = mols of of everflow per mol of product belowfeed plate  $W = O' - V = \mathbf{n}$
- = mols of waste per mol of product
- $x_n = \text{mol fraction of component } A$  in liquor on  $n^{\text{th}}$  plate
- $y_n = \text{mol fraction of component } A \text{ in vapor above } n^{\text{th}} \text{ plate}$
- $x_c = \text{mol fraction of component } A \text{ in product}$
- = mol fraction of component A in waste
- $x_w = \text{mol fraction of component } A$  in waste  $y_n^* = \text{mol fraction of component } A$  in vapor which is in equilibrium with the liquor on the  $n^{\text{th}}$  plate
- $x_0 = \text{mol fraction of component } A$  in liquor at bottom of packed column
- = mol fraction of component A in vapor at bottom of γo packed column
- $x_1 = \text{mol}$  fraction of component A in liquor at point of introduction of feed
- $C_{Ln}$  = concentration of component A in liquor on  $n^{\text{th}}$  plate  $C_G$  = concentration of component A in liquor which is in equilibrium with vapor
- P = total pressure at any height L in column  $K_{\sigma}$  = over-all conductivity coefficient for component Awhen driving force is partial pressure difference

<sup>1</sup> Received June 1, 1925.

 $K_c$  = over-all conductivity for component A when driving force is concentration difference

- L = height of any point in packed column
- $L_1$  = height of point at which feed is introduced  $L_i$  = total height of column
- = area of contact per mol of vapor at any height L in
- packed column v = linear velocity of vapor at point L in column
- M, M', R, and R' are constants determined from column tests

In a previous article<sup>2</sup> the author has shown that under the above conditions, when the driving force of the material may be represented as a partial pressure difference, that

$$y_n = y_n^* - M (y_n^* - y_{n-1}) \tag{1}$$

When the driving force of the material transfer is represented by a concentration difference, the relation between  $y_n$  and  $y_{n-1}$  is given by

$$\int \frac{\mathcal{Y}_n}{\frac{dy}{C_{Ln} - C_o}} = R \tag{2}$$

For cases where it is possible to make approximate integrations by means of straight line relationships between y and C, the above equation becomes

$$y_n = y_n^* - e^{-S_n R} (y_n^* - y_{n-1})$$
(3)

where  $S_n$  is the slope of the straight line relating y and C used for the  $n^{\text{th}}$  plate.

Thiele and McCabe<sup>3</sup> have recently shown how graphical methods may be used in calculations involving the rectification of binary mixtures under isothermal conditions when the concept of the theoretical plate is used. Their method may be readily modified to agree with Equations 1, 2, or 3, instead of using the concept of the theoretical plate.

Consider the sketch in Figure 1. By equating input to output in the dotted section above the feed plate the following equation is obtained:

$$y_n = \frac{x_{n+1}O + x_c}{V} \tag{4}$$

Similarly, for the dotted section below the feed plate:

$$y_m = \frac{x_{m+1} O^1 - x_w W}{V}$$
(5)

On substituting the analogous equations for  $y_{n-1}$  and  $y_{m-1}$ in (1), the results are, respectively:

$$y_n = (1 - M) y_n^* + \frac{M}{V} (x_n O + x_c)$$
 (6)

<sup>2</sup> THIS JOURNAL, 17, 747 (1925).

<sup>3</sup> Ibid., 17, 605 (1925).