[Contribution from the American Cyanamid Company]

# THE HYDROLYSIS AND POLYMERIZATION OF CYANAMIDE IN ALKALINE SOLUTIONS

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When calcium cyanamide is added to water, hydrolysis of the normal cyanamide occurs, with production of a solution of calcium acid cyanamide and precipitation of calcium hydroxide.[1]

$$2CaCN_2 + 2H_2O \rightleftharpoons Ca(HCN_2)_2 + Ca(OH)_2 \qquad (1)$$

Following the formation of calcium acid cyanamide, a number of reactions may occur, of which the two most important are hydrolysis of the acid cyanamide with production of urea, as represented by

$$Ca(HCN_2)_2 + 4H_2O \rightleftharpoons 2NH_2CONH_2 + Ca(OH)_2 \qquad (2)$$

and polymerization to produce dicyandiamide, as represented by

$$Ca(HCN_2)_2 + 2H_2O \rightleftharpoons NH_2C{=}NHNHCN + Ca(OH)_2 \qquad (3)$$

Secondary reactions also may occur, dicyandiamide being hydrolyzed to guanylurea or to cyanurea, and urea to ammonium carbonate.

It has long been known that the reactions of cyanamide in alkaline solutions are dependent upon the nature of the base present. The facts have been summarized as follows:[2] "The strong alkalies KOH or NaOH in aqueous solutions produce almost entirely urea with no trace of dicyandiamide; weak alkalies, $NH_4OH$ or MgO, produce dicyandiamide almost exclusively at first, and then ammonia. CaO, however, produces a mixture of urea, dicyandiamide, ammeline, amidodicyanic acid, ammonia and other bodies."

It must be carefully emphasized that the reactions occurring in soil solutions are not necessarily the same as those in ordinary aqueous solutions. In the former such variables as colloids, bacteria and the like have important effects upon the course of the reactions. It remains true, however, that one cannot expect fully to understand the reactions of cyanamide in a system as complex as is the soil unless he first understands its reactions in water alone.

That cyanamide is readily converted to other products was noted long before the development of the modern Cyanamid industry. Cloëz and Cannizzaro[3] observed that a compound of the same empirical formula but with markedly different properties was spontaneously formed when

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[1] Drechsel, *J. prakt. Chem.*, [2] **16**, 210 (1887); Kappen, *Landw. Vers. Sta.*, **68**, 301 (1908); Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, **40**, 613 (1910).

[2] Pranke, "Cyanamid," Chemical Publishing Co., **1913.**

[3] Cloëz and Cannizzaro, *Ann.*, **78,** 228 (1851).

solutions of cyanamide were allowed to evaporate. They named this new product cyanuramin—it was undoubtedly dicyandiamide. The same observers reported that alkalies decomposed cyanamide, although they did not mention the products formed. Other early observers were aware of the formation of polymerized products, variously styled, and of urea.[4]

The first attempt at a quantitative study of the reactions of calcium cyanamide in alkaline solutions was made by Grube and his co-workers.[5] They found that the concentration of the alkali had a marked effect upon the velocity of decomposition of cyanamide, the velocity increasing and then decreasing with increasing alkali concentration. As a result of their work a process for the manufacture of dicyandiamide was worked out, styled by the inventors the "Process of Optimum Lime Concentration."[6] According to their procedure a solution of calcium acid cyanamide was first prepared, and to this solution sulfuric acid was added in varying amounts and at varying time intervals. The additions were to be made in accordance with the theory that there should always be present in the solution four moles of cyanamide for each mole of lime, this ratio being considered the "optimum" for dicyandiamide formation. The mechanism of the reaction, according to these workers, is that dicyandiamide is formed by reaction between an undissociated cyanamide molecule and a cyanamide ion, as represented by the equation

$$(\mathrm{NHCN})^- + \mathrm{H_2NCN} = (\mathrm{NHC{=}NHNHCN})^-$$

Morrel and Burgen[7] also studied the kinetics of the formation of dicyandiamide from cyanamide and arrived at the same conclusion, namely, that the reaction is ionic. This theory, announced almost simultaneously by Grube and Krüger and by Morrell and Burgen, is discussed more fully in a later section of the present paper where we have shown that our own data are consistent with and confirmatory to the ionic theory.

Hetherington and Braham[8] studied the polymerization and hydrolysis of cyanamide in aqueous alkaline solutions. Earlier investigators had assumed that the cyanamide disappearing was completely transformed to dicyandiamide, an assumption which our data show to be true only under special conditions. Hetherington and Braham determined cyanamide disappearing and urea formed. Dicyandiamide formed was arrived at by difference. A summary of their results is shown below.

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[4] Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, **40**, 613 (1910); Haag, *Ann.*, **122**, 23 (1862); Baumann, *Ber.*, **6**, 1371 (1873); Beilstein and Geuther, *Ann.*, **108**, 99 (1858); **123**, 241 (1862).

[5] Grube and Krüger, *Z. physik. Chem.*, **86**, 65 (1913); Grube and Nitsche, *Z. angew. Chem.*, I, **27**, 368 (1914).

[6] Grube and Nitsche, German Patent 279,133, June 5, 1913.

[7] Morrell and Burgen, *J. Chem. Soc.*, **105**, 576 (1914).

[8] Hetherington and Braham, THIS JOURNAL, **45**, 828 (1923).

Cyanamide at start 0.5 *M*. Temperature 50°

| NaOH, moles/l. | After 1 hour, % of total nitrogen present as | | | After 2 hours, % of total nitrogen present as | | |
|---|---|---|---|---|---|---|
| | Cyan. N | Urea N | Dicyan.[a] N | Cyan. N | Urea N | Dicyan.[a] N |
| 0.01 | 92.1 | 2.9 | 5.0 | 90.4 | 3.3 | 6.3 |
| 0.1 | 69.6 | 3.2 | 27.2 | 55.6 | 3.8 | 40.6 |
| 1.0 | 94.0 | 5.0 | 1.0 | 92.3 | 7.0 | 0.7 |

| NaOH, mole/l. | After 3 hours, % of total nitrogen present as | | | After 20 hours % of total nitrogen present as | | |
|---|---|---|---|---|---|---|
| | Cyan. N | Urea N | Dicyan.[a] N | Cyan. N | Urea N | Dicyan.[a] N |
| 0.01 | 85.8 | 3.3 | 10.9 | 47.2 | 4.9 | 47.9 |
| 0.1 | 44.4 | 4.1 | 51.5 | 14.1 | 10.1 | 75.8 |
| 1.0 | 89.3 | 8.3 | 2.4 | 62.7 | 34.4 | 2.9 |

[a] Dicyandiamide obtained by difference.

Hetherington and Braham's results show that in alkaline solution urea is formed as well as dicyandiamide, increased concentrations of alkali resulting in increased urea formation. Hetherington and Braham concluded that their results with respect to dicyandiamide formation could be explained by the theory of Grube and Krüger. The formation of urea was attributed to the catalytic effect of hydroxyl ions.

Although it seems readily apparent that effects such as those reported by the previous investigators are controlled by hydrogen-ion concentration, the problem had not heretofore been studied from this point of view. It therefore became the purpose of the work which is here reported to study the influence of hydrogen-ion concentration upon the fate of cyanamide in alkaline solutions. In the experiments, the details of which are recorded below, the course of cyanamide disappearance and urea and dicyandiamide formation was observed in solutions whose hydrogen-ion concentration was maintained at constant values.

## Dicyandiamide Formation

### Experimental Method

**Cyanamide Solutions.**—Commercial calcium cyanamide was agitated for one hour with three times its weight of water at 30° and filtered. To the filtrate dilute sulfuric acid was added carefully and with vigorous stirring, the temperature being maintained below 30°. The sulfuric acid addition was continued until the solution was just acid to methyl red indicator (about *P*H 5), and the precipitated calcium sulfate was filtered off. Solutions of cyanamide prepared in this way and kept at ordinary room temperature suffer practically no change in cyanamide concentration over a period of several months.

**Buffer Solutions.**—For the measurements at *P*H 6 sodium dihydrogen phosphate and sodium hydroxide were employed as the buffer combination. For *P*H 8 to *P*H 10 sodium hydroxide–boric acid solutions were used. The buffer solutions used were all more concentrated than those usually employed (0.5 molal phosphate or borate instead of 0.2 molal). As will appear from the data the buffering was very good throughout this range. For hydrogen-ion concentrations lower than *P*H 10, sodium hydroxide was used because suitable buffer combinations were not available. Alkalinity control was consequently poor.

**Methods of Analysis.**—Cyanamide was determined by precipitating it as silver cyanamide from an ammoniacal solution, filtering, washing and determining nitrogen in the precipitate by the Kjeldahl method.

Urea was determined by the urease method.

Dicyandiamide was determined by hydrolyzing to guanylurea under carefully controlled conditions, precipitating guanylurea picrate by the addition of picric acid and weighing. Details of the method are as follows. A 10-cc. sample is pipetted into a 150-cc. beaker and 25 cc. of hydrochloric acid solution (one volume of sp. gr. 1.18 mixed with two volumes of water) added. The beaker is suspended over a gently boiling water-bath so that the bottom of the beaker almost touches the water and is held there for fifteen minutes. The solution is then cooled, made slightly alkaline to phenolphthalein with 10% sodium hydroxide solution, and made up to 100 cc. in a volumetric flask. To a 25-cc. aliquot of this solution, 5 cc. of an alcoholic solution of picric acid (6 g. of picric acid in 100 cc. of 95% ethyl alcohol) is added. The solution is allowed to stand for one hour with occasional stirring and is then filtered through a tared Gooch crucible. A saturated solution of guanylurea picrate is used for washing. The precipitate is dried at 105° for one hour. A solubility correction of 0.0044 g. is added to the weight of the precipitate. The factor for conversion of the weight of guanylurea picrate to dicyandiamide nitrogen is 0.169. The quantity of picric acid recommended is sufficient for about 0.2 g. of guanylurea picrate.

Melamine, guanylurea and guanidine were tested for by means of picric acid with negative results in all of the experiments.

**Measurement of the Hydrogen-Ion Concentration.**—Hydrogen-ion concentrations were determined by potentiometer measurements with a hydrogen electrode immersed in the solution. A saturated potassium chloride calomel cell was used as the other electrode. The chain was at 50°. The value of the chain

$$\text{Hg–HgCl} - \text{satd. KCl} - \text{satd. KCl} - 0.1\ M\ \text{HCl} - \text{H}_2\text{(Pt)}$$

was checked at intervals and found to agree with the value reported by Fales and Mudge for 50°.[9] The hydrogen-ion concentration was calculated from the e.m.f. measurement by means of the Nernst equation, which for this temperature and chain is

$$P_{\text{H}^+} = 15.60E - 3.61$$

**Procedure.**—In a water-bath at 50 ± 0.1° were placed bottles containing the necessary buffer solutions, a wash bottle containing distilled water and, in a standard 200-cc. flask, exactly enough cyanamide solution to contain 2.80 g. of cyanamide nitrogen. When all had reached the temperature of the bath, the proper amounts of buffer solutions were pipetted into the cyanamide solutions, distilled water was added to make the volume up to 200 cc. (0.5 molal) and the contents of the flasks were mixed as quickly as possible. The initial time was taken at the moment when the additions of buffer solutions had been completed. Samples were withdrawn immediately for analysis and subsequently at various time intervals as indicated in the tables. Immediately after samples were withdrawn, they were made neutral to methyl red to prevent further reaction.

In the tables the velocity constants, $k_\text{D}$, for the polymerization of cyanamide to dicyandiamide are calculated by means of the formula for a reaction of the second order

$$k_\text{D} = \frac{1}{t}\frac{x}{c(c - x)}$$

where $c$ is the initial concentration of cyanamide, in grams of nitrogen

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[9] Fales and Mudge, This Journal, **42**, 2434 (1920).

per 100 cc., and $x$ is the change in concentration occurring in the time interval, $t$, in hours.

For the hydrolysis to urea and for the decomposition of dicyandiamide the velocity constants $k_{\text{U}}$ and $k_{\text{D}}1$ are calculated for a reaction of the first order

$$k = \frac{1}{t} \log \frac{c}{c - x}$$

Table I summarizes the results of this study over the range *P*H 6 to *P*H 12. The relation between the velocity constants and the hydrogen-ion concentrations is shown graphically in Fig. 1.

Table I

Results of Experiments

| | | Found, g. of nitrogen per 100 cc. | | | | Formed, g. of nitrogen per 100 cc. | | |
|---|---|---|---|---|---|---|---|---|
| Time, hours | *P*H | Cyanamide | Dicyandiamide | Urea | Sum | Dicyandiamide | Urea | Velocity constant, $k_{\text{D}}$ |
| 0.0 | 6.0 | 1.25 | 0.30 | 0.02 | 1.57 | 0.00 | 0.00 | |
| .5 | .. | 1.23 | .32 | .. | | .02 | .. | |
| 1.5 | .. | 1.31 | .34 | .. | | .04 | .. | |
| 5.5 | .. | 1.23 | .32 | .. | | .. | .. | |
| 143.5 | .. | 1.16 | .35 | .03 | 1.54 | .05 | .. | |
| 0.0 | 8.4 | 1.31 | .23 | .12 | 1.66 | .00 | .00 | ........ |
| 1.0 | .. | 1.21 | .31 | .. | | .08 | .. | ........ |
| 2.0 | .. | 1.07 | .47 | .. | | .24 | .. | $8.6 \times 10^{-2}$ |
| 4.0 | .. | 0.96 | .60 | .. | | .37 | .. | $7.2 \times 10^{-2}$ |
| 6.0 | 8.4 | .85 | .72 | .. | | .49 | .. | $7.3 \times 10^{-2}$ |
| 24.0 | .. | .. | .. | .16 | | .. | .04 | ........ |
| 72.0 | .. | .00 | 1.31 | .. | | 1.08 | .. | ........ |
| | | | | | | Average for *P*H 8.4, | | $7.7 \times 10^{-2}$ |
| 0.0 | 8.9 | 1.31 | 0.23 | .12 | 1.66 | 0.00 | .00 | ........ |
| 1.0 | .. | 0.96 | .49 | .. | | .26 | .. | $21 \times 10^{-2}$ |
| 2.0 | .. | .75 | .70 | .. | | .47 | .. | $24 \times 10^{-2}$ |
| 4.0 | .. | .65 | .95 | .. | | .72 | .. | $21 \times 10^{-2}$ |
| 6.0 | 9.1 | .53 | 1.09 | .. | | .86 | .. | $21 \times 10^{-2}$ |
| 24.0 | .. | .13 | 1.35 | .18 | 1.66 | 1.12 | .06 | ........ |
| 72.0 | .. | .00 | 1.39 | .. | | 1.16 | .. | ........ |
| | | | | | | Average for *P*H 9.0, | | $22 \times 10^{-2}$ |
| 0.0 | 9.3 | 1.32 | 0.19 | .07 | 1.58 | 0.00 | .00 | ........ |
| 1.0 | 9.4 | 0.94 | .58 | .. | | .39 | .. | $31 \times 10^{-2}$ |
| 2.0 | 9.5 | .69 | .77 | .. | | .58 | .. | $32 \times 10^{-2}$ |
| 4.0 | 9.6 | .47 | 1.03 | .. | | .84 | .. | $34 \times 10^{-2}$ |
| 6.0 | 9.6 | .34 | 1.14 | .. | | .95 | .. | $37 \times 10^{-2}$ |
| 24.0 | 9.8 | .12 | 1.36 | .. | | 1.17 | .. | $31 \times 10^{-2}$ |
| 72.0 | 9.9 | .05 | 1.36 | .10 | 1.51 | 1.17 | .03 | ........ |
| | | | | | | Average for *P*H 9.6, | | $33 \times 10^{-2}$ |
| 0.0 | 10.3 | 1.39 | 0.20 | .07 | 1.66 | 0.00 | .00 | ........ |
| 1.0 | .. | 1.02 | .50 | .. | | .30 | .. | $21 \times 10^{-2}$ |
| 2.0 | 10.7 | 0.83 | .68 | .. | | .48 | .. | $21 \times 10^{-2}$ |
| 4.0 | .. | .69 | .83 | .. | | .63 | .. | $16 \times 10^{-2}$ |

TABLE I (*Concluded*)

| | | Found, g. of nitrogen per 100 cc. | | | | Formed, g. of nitrogen per 100 cc. | | |
|---|---|---|---|---|---|---|---|---|
| Time, hours | *P*H | Cyanamide | Dicyandiamide | Urea | Sum | Dicyandiamide | Urea | Velocity constant, $k_D$ |
| 6.0 | . . | 0.62 | 0.93 | . . | | 0.73 | . . | $14 \times 10^{-2}$ |
| 24.0 | . . | .30 | 1.05 | .12 | 1.47 | .85 | .05 | ........ |
| 48.0 | 11.3 | . . | 1.07 | . . | | .87 | . . | ........ |
| | | | | | | Average for *P*H 10.5, | | $21 \times 10^{-2}$ |
| 0.0 | 11.4 | 1.39 | 0.20 | .07 | 1.66 | 0.00 | .00 | ........ |
| 1.0 | . . | 1.32 | .26 | . . | | .06 | . . | ........ |
| 2.0 | . . | 1.28 | .28 | . . | | .08 | . . | $3.1 \times 10^{-2}$ |
| 4.0 | . . | 1.19 | .32 | . . | | .12 | . . | $3.0 \times 10^{-2}$ |
| 6.0 | . . | 1.06 | .35 | . . | | .15 | . . | $2.3 \times 10^{-2}$ |
| 24.0 | 12.1 | 0.72 | .37 | .15 | | .17 | .08 | $2.8 \times 10^{-2}$ |
| 48.0 | . . | .49 | .26 | .23 | 0.98 | .06 | .16 | $2.8 \times 10^{-2}$ |
| | | | | | | Average for *P*H 11.4, | | $3.1 \times 10^{-2}$ |

The data of Table I may be summarized as follows: (1) At constant hydrogen-ion concentration the polymerization of cyanamide to dicyandiamide proceeds as a reaction of the second order. (2) The velocity of the reaction is a function of the hydrogen-ion concentration. (3) The velocity of formation of dicyandiamide is at a maximum at *P*H 9.6 and decreases rapidly at hydrogen-ion concentrations above or below this point. (4) Urea formation is negligible throughout this range of hydrogen-ion concentration. (5) Cyanamide disappearing is quantitatively accounted for by dicyandiamide produced up to about *P*H 10. Above *P*H 10, nitrogen accounted for as dicyandiamide and urea is significantly less than the cyanamide disappearing. That this is due to dicyandiamide destruction is shown in a later section of this paper.

It is of interest to attempt a correlation of the velocity constants of dicyandiamide formation shown in our table with the theory of Grube and Krüger,[5] which, it will be recalled, states that dicyandiamide is formed by reaction between a cyanamide molecule and a cyanamide ion.

$$(\mathrm{NHCN})^- + \mathrm{H_2CN_2} \rightleftharpoons (\mathrm{NHCNHNHCN})^-$$

According to this theory

$$\frac{dx}{dt} = g(\mathrm{H\ Cy})(\mathrm{Cy}^-) \qquad (1)$$

where $g$ is the velocity constant of the reaction.

The ionization constant, $K$, of cyanamide is given by

$$\frac{\mathrm{H}^+ \times \mathrm{Cy}^-}{\mathrm{H\ Cy}} = K \quad \text{or} \qquad (2)$$

$$\frac{\mathrm{Cy}^-}{\mathrm{H\ Cy}} = \frac{K}{\mathrm{H}^+} \qquad (3)$$

Adding one (1) to both sides of this equation, we have

$$\frac{\mathrm{Cy}^- + \mathrm{H\ Cy}}{\mathrm{H\ Cy}} = \frac{K + \mathrm{H}^+}{\mathrm{H}^+} \qquad (4)$$

Since

$$Cy^- + H\,Cy = (c - x) \tag{5}$$

$$H\,Cy = (c - x)\frac{H^+}{K + H^+} \tag{6}$$

In a similar manner it can be shown that

$$Cy^- = (c - x)\frac{K}{K + H^+} \tag{7}$$

On substitution of values given by (6) and (7), Equation 1 becomes

$$\frac{dx}{dt} = (c - x)^2 g\frac{K\,H^+}{(K + H^+)^2} \tag{8}$$

Our experimental work has shown that

$$\frac{dx}{dt} = k_D(c - x)^2 \tag{9}$$

where $k_D$ is a function of $H^+$

Therefore

$$k_D = g\frac{K\,H^+}{(K + H^+)^2} \tag{10}$$

The ionization constant, $K$, of cyanamide is given by Kamayama[10] as $20.1 \times 10^{-11}$ at 50°. Thus

$$K = 20.1 \times 10^{-11} = 10^{-9.7} \tag{11}$$

Using this value of $K$ in (10) we have the equation giving $k_D$ as a function of H

$$k_D = g\frac{10^{-9.7}\,H^+}{(10^{-9.7} + H^+)^2} \tag{12}$$

From Equation 12 it may be seen that, knowing the value of $k_D$ for any value of $H^+$, we may calculate the constant $g$. Then knowing $g$, we may calculate $k_D$ for any value of $H^+$. In other words, if we know the velocity constant at any one hydrogen-ion concentration, it is possible to calculate it for any other hydrogen-ion concentration. In the following table we have taken the value of $k_D$ for *P*H 8.4, and from it have calculated the velocity constants for the hydrogen-ion concentrations at which our experiments were conducted.

TABLE II

OBSERVED AND CALCULATED CONSTANTS

| *P*H$^+$ | 8.4 | 9.0 | 9.6 | 10.5 | 11.4 |
|---|---|---|---|---|---|
| $k_D$ observed | $7.7 \times 10^{-2}$ | $21 \times 10^{-2}$ | $33 \times 10^{-2}$ | $21 \times 10^{-2}$ | $3.1 \times 10^{-2}$ |
| $k_D$ calculated | ........ | $21 \times 10^{-2}$ | $38 \times 10^{-2}$ | $21 \times 10^{-2}$ | $3.1 \times 10^{-2}$ |

**Formation of Urea in Highly Alkaline Solutions.**—We have seen from the data already presented that dicyandiamide is practically the only product obtained from solutions of cyanamide up to about *P*H 10. Above *P*H 10 the rate of dicyandiamide formation became slower and at the highest *P*H studied, *P*H 12, small amounts of urea were being formed. This

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[10] Kamayama, *Trans. Am. Electrochem. Soc.*, **40**, 131 (1921).

suggested a few experiments on the fate of cyanamide in highly alkaline solutions. The data of this work are shown in Table III.

TABLE III

RESULTS OF EXPERIMENTS

| Time, hrs. | Normality of NaOH | *P*H | $N_2$ per 100 cc., g. Cyanamide | Dicyandiamide | Urea | Velocity constant, $k_U$ |
|---|---|---|---|---|---|---|
| 0 | 0.49 | 12.6 | 1.40 | 0.00 | 0.00 | ......... |
| 21 | .. | | 0.88 | .00 | .41 | $0.96 \times 10^{-2}$ |
| 41 | .. | | .57 | .00 | .63 | $.95 \times 10^{-2}$ |
| 89 | .. | | .28 | .00 | .98 | $.79 \times 10^{-2}$ |
| 113 | .. | | .20 | .00 | 1.11 | $.74 \times 10^{-2}$ |
| 168 | .. | 13.4 | .10 | .00 | 1.26 | ......... |
| 0 | 0.68 | 12.9 | 1.40 | .00 | 0.00 | ......... |
| 21 | .. | | 0.93 | .00 | .44 | $.85 \times 10^{-2}$ |
| 69 | .. | | .42 | .00 | .88 | $.76 \times 10^{-2}$ |
| 93 | .. | | .28 | .00 | 1.04 | $.83 \times 10^{-2}$ |
| 168 | .. | 13.5 | .10 | .00 | 1.24 | ......... |
| 0 | 1.00 | 13.4 | 1.40 | .00 | 0.00 | ......... |
| 21 | .. | | .. | .00 | .38 | ......... |
| 69 | .. | | 0.42 | .00 | .86 | $.76 \times 10^{-2}$ |
| 93 | .. | | .28 | .00 | 1.05 | $.83 \times 10^{-2}$ |
| 168 | .. | 13.6 | .11 | .00 | 1.23 | ......... |

The conclusions which may be derived from these data are as follows. (1) Cyanamide disappearing is quantitatively accounted for by urea formed. (2) The hydrolysis of cyanamide to urea in alkaline solutions is a reaction of the first order. (3) In the range studied the reaction velocity is independent of the alkali concentration.

We conclude from the data of Tables III and I that the hydrolysis of cyanamide in alkaline solutions is a reaction of cyanamide ion, and that the velocity of the hydrolysis is proportional to the concentration of this ion. When sufficient alkali is present to convert all the cyanamide into the salt, further addition of alkali has no further effect on the rate of hydrolysis.

**Dicyandiamide Destruction.**—The data of Table I show that at the higher alkalinities the cyanamide disappearing cannot be accounted for by urea and dicyandiamide produced. That this is in part at least due to destruction of dicyandiamide is indicated by the dicyandiamide analyses of the solution maintained at *P*H 11, where it was found that the dicyandiamide content of the solution was reduced by one-half between the twenty-fourth and the forty-eighth hours.

This led to an investigation of the stability of dicyandiamide at various hydrogen-ion concentrations. The methods were the same as those employed in the previous work. Pure dicyandiamide was dissolved in the buffered solutions and its concentration determined after various intervals of time. The data are shown in Table IV and graphically in Fig. 1.

TABLE IV

EXPERIMENTAL DATA

| Time, hours | *P*H+ | $N_2$ per 100 cc., g. Dicyandiamide found | Dicyandiamide destroyed | Velocity constant, $k_{D1}$ |
|---|---|---|---|---|
| 0.0 | 9.3 | 1.057 | ... | |
| 24.0 | | 1.035 | ... | |
| 72.0 | | 1.057 | 0.000 | |
| 168.0 | | 1.058 | .000 | 0 |
| 0.0 | 9.8 | 1.009 | ... | |
| 24.0 | | 1.000 | .009 | |
| 72.0 | | 0.998 | .011 | |
| 168.0 | | .985 | .024 | $6.9 \times 10^{-5}$ |
| 0.0 | 10.3 | 1.020 | ... | |
| 24.0 | | 1.018 | .002 | |
| ... | | ... | ... | |
| 168.0 | | 0.950 | .070 | $1.23 \times 10^{-4}$ |
| 0.0 | 11.0 | .939 | .. | |
| 24.0 | | .901 | .028 | |
| 72.0 | | .890 | .049 | |
| 168.0 | | .827 | .112 | $3.23 \times 10^{-4}$ |
| 0.0 | 11.4 | 1.047 | ... | |
| 24.0 | | 0.940 | .107 | |
| 72.0 | | .835 | .212 | $1.36 \times 10^{-3}$ |

It will be seen that dicyandiamide is relatively stable up to *P*H 10. Above *P*H 10 dicyandiamide is destroyed, the rate increasing with increasing *P*H. The nature of the products thus formed was not studied; cyanurea is known to be formed under these conditions.[11]

**Effect of Temperature on Hydrogen-Ion Concentration Optimum for Polymerization.**—On page 196 we considered the Optimum Lime Process of Grube, which was based upon the maintenance of equal concentrations of cyanamide ions and undissociated cyanamide. That this condition necessitates maintenance of the hydrogen-ion concentration at a constant value is proved as follows. In any solution containing cyanamide

$$\frac{H^+ (Cy)^-}{H\,Cy} = K$$

$$\text{If } (Cy)^- = H\,Cy \text{ then } H^+ = K$$

This relation may also be derived from Equation 10.

The value of $K$ at 50°, as was noted above, was found by Kamayama to be $10^{-9.7}$, which our work has shown to be the optimum hydrogen-ion concentration for the polymerization of cyanamide to dicyandiamide. This relationship between $H^+$ and $K$ holds regardless of the temperature. Since Kamayama has reported the ionization constants for cyanamide at various temperatures, we may adopt his values as the optimum hydro-

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[11] Hallwachs, *Ann.*, **153**, 295 (1870); Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, **40**, 613 (1910).

gen-ion concentration for the temperatures in question. His values are given in Table V.

TABLE V

VALUES OF KAMAYAMA

| Temp., °C. | 0 | 25 | 50 | 80 | 100 |
|---|---|---|---|---|---|
| $K \times 10^{11}$ | 1.15 | 5.42 | 20.1 | 75.6 | 163 |
| *P*H | 10.4 | 10.3 | 9.7 | 9.1 | 8.8 |

**Reactions of Cyanamide in the Soil.**—In view of the fact that the *P*H of soil solutions in humid regions is usually less than 7, it will be evident from the data which we have presented that dicyandiamide cannot normally be formed when calcium cyanamide is applied to the soil. Even at 50° our results show negligible dicyandiamide formation at this *P*H, while at lower temperatures not only is the reaction velocity greatly reduced but the limiting *P*H for dicyandiamide formation is raised.

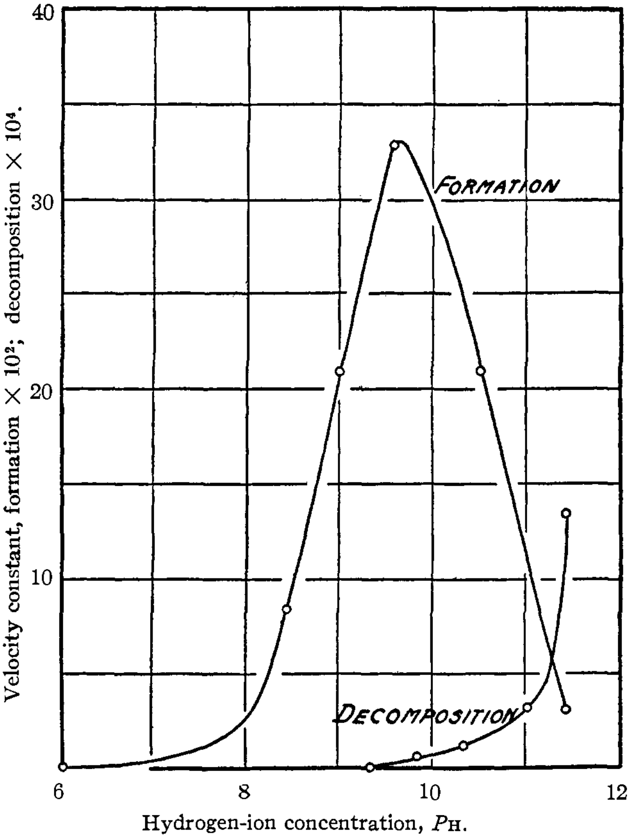

Fig. 1.—Effect of *P*H on velocities of formation and decomposition of dicyandiamide.

The occasional finding of dicyandiamide reported by some investigators is clearly attributable to improper conditions of application. Calcium cyanamide is an alkaline material and should be applied is such a manner that its alkalinity does not exceed the buffering capacity of the soil. This necessitates proper distribution so that local high concentrations of alkalinity are avoided and suggests special care when calcium cyanamide is applied to sandy soils deficient in humus and other colloidal materials.

Many studies of the fate of calcium cyanamide in the soil are reported in the literature and the conclusion reached that cyanamide is converted to urea.[12] In our experiments urea formation was negligible in solutions of low *P*H. This difference between ordinary aqueous solutions and soil solutions is to be ascribed to the catalytic effect of the soil colloids. That the conversion of cyanamide to urea is catalyzed by such substances has been shown by many investigators. Kappen in particular in his elaborate "Dissertation" (Die Katalyse des Cyanamids und ihre Bedeutung für die Landwirtschaft) has called attention to the catalytic action of soil colloids, metallic oxides and hydroxides, and has, in fact, obtained a long series of patents on the production of urea from calcium cyanamide by agitating it with water in the presence of such catalytic materials.[13]

**Addendum.**—Subsequent to the preparation of the above paper, our attention was called to an article by Cochet on the polymerization of cyanamide to dicyandiamide as a function of hydrogen-ion concentration.[14] Cochet did not buffer his solutions and very marked changes in hydrogen-ion concentration occurred during the course of the experiments, a fact to which attention is called by the author. His results are in entire accord with our own, when the increasing *P*H observed in his experiments is taken into account. Cochet concludes that the polymerization reaction reaches an equilibrium at the end of 165 hours. We are of the opinion that the equilibrium is only an apparent one and that the reaction velocity has been reduced by the rise in the *P*H.

Cochet reports that cyanamide in the soil is rapidly transformed into urea.

The authors wish to express their thanks to Mr. P. W. Griffith for valuable assistance.

## Summary

1. The influence of hydrogen-ion concentration on the reactions of cyanamide in aqueous solution has been studied from *P*H 6 to *P*H 13 at 50°.

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[12] Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, **40**, 613 (1910); Seelhorst, *J. Landw.*, **53**, 323 (1905); Stutzer and Reis, *ibid.*, **58**, 65 (1910); Kappen, "Die Katalyse des Cyanamids und ihre Bedeutung für die Landwirtschaft," Dissertation, Jena, **1913**.

[13] Immendorf and Kappen, U. S. Patent 1,048,699; British Patents 17,018, 20,611; German Patents 254,474; 256,524; 256,525; 257,642; 257,643 and 267,206.

[14] Cochet, Congrès des Engrais Azotés de Synthèse, May, **1927**, p. 34.

2. Polymerization to dicyandiamide takes place quantitatively in alkaline solution up to *P*H 10.
3. The velocity of dicyandiamide formation is a function of the hydrogen-ion concentration. It reaches a maximum at *P*H 9.6 and decreases rapidly below or above this *P*H.
4. Above *P*H 12 cyanamide is hydrolyzed quantitatively to urea.
5. The rate of hydrolysis is independent of alkalinity in the range studied.

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# THE POLARITIES AND THE ORIENTING INFLUENCES OF SUBSTITUTES IN THE BENZENE RING

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More than fifty years ago it was observed that certain groups, when substituted for hydrogen in benzene, direct the next entering group to the meta position and that other groups direct to the ortho and para positions. There have been many attempts to classify atoms and groups on the basis of this behavior.[1] The most successful theory (proposed by Lapworth[2] and Stieglitz[3] and supported and amplified by many others) assumes alternate polarities in the carbon atoms of the benzene ring, induced by the electronegative or electropositive character of the first substituted group. The theory is based upon arbitrary qualitative estimates of polarity.

We wish to present in this paper a system which gives at least a semiquantitative basis for determining polarity and which may, therefore, serve as a means of classifying groups exerting different orienting influences.

Our plan is to estimate, from considerations of electronic configurations, the residual charge on the atom attached to the ring. When a pair of electrons is shared between two atoms, we assume, except in the case of hydrogen, that the electrons are quantized in respect to the field between the atoms and that the effect of their charges is distributed between the atoms in the ratio of the positive charges on the two kernels. Thus we consider a pair of electrons between carbon and nitrogen as contributing $2 \times 4/9$ electron charges to the carbon atom and $2 \times 5/9$ electron charges to the nitrogen.

The bond between hydrogen and another atom cannot be so treated, as

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[1] The following are important references to the earlier literature: (a) Hübner, *Ber.*, **8**, 873 (1875); (b) Noelting, *ibid.*, **9**, 1797 (1876); (c) Armstrong, *J. Chem. Soc.*, **51**, 258 (1887); (d) Crum-Brown and Gibson, *ibid.*, **61**, 367 (1892); (e) Flürscheim, *J. prakt. Chem.*, **66**, 32 (1902); (f) Fry, This Journal, **38**, 1323 (1916).

[2] Lapworth, *J. Chem. Soc.*, **121**, 1391 (1922).

[3] Stieglitz, This Journal, **44**, 1299 (1922).