# LVIII.—The Polymerisation of Cyanamide.

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As is well known, cyanamide undergoes, according to conditions, more or less rapid polymerisation into dicyanodiamide, yet the kinetics of the reaction, and the precise conditions under which it occurs, do not seem to have been investigated. Since at the present time cyanamide and its salts are of importance as fertilisers, a still greater interest attaches to this subject, and this investigation was undertaken with a view of obtaining quantitative data as to the course of the polymerisation, and the influence of catalysts on it.

The formation of dicyanodiamide during the evaporation of aqueous solutions of cyanamide was first recorded by Beilstein and Geuther (Annalen, 1858, 108, 99; 1862, 123, 241), and later by Dreschel (J. pr. Chem., 1875, [ii], 11, 298), and the influence of ammonia in accelerating the change by Haag (Annalen, 1862, 122, 22). Beilstein and Geuther (loc. cit.) also make the statement that a specimen of cyanamide which had been kept for several months no longer gave the characteristic reactions for this substance. Baumann (Ber., 1873, 6, 1373), studying the formation of carbamide by the action of mineral acids on cyanamide, observed that dicyanodiamide was produced as a by-product, and that the more dilute the acid the greater the proportion of dicyanodiamide obtained. He also made the observation that alkali hydroxides accelerated the polymerisation, as Haag had previously observed in the case of ammonia.

Whilst the present investigation has in the main confirmed the qualitative statements of these early investigators, it has in its quantitative aspect brought out the fact, which from statements in books of reference one would scarcely have expected, that the polymerisation of cyanamide in aqueous solution of even 5N-concentration, and at elevated temperatures, proceeds with considerable sluggishness, and that, on the other hand, an enormous accelerating influence is exerted by acids and alkalis, even if present in extremely minute quantities. It was found, moreover, that in no case did the polymerisation proceed as a bimolecular reaction as expressed by the equation:

## $NH_2 \cdot CN + NH_2 \cdot CN = C_2H_4N_4$ ,

and evidence was forthcoming that the change resulting in the formation of dicyanodiamide is ionic in character, although a single explanation, which will cover the accelerating action of both acids and bases, cannot be put forward.

## The Determination of Cyanamide.

In order to follow quantitatively the course of the polymerisation, it was first of all necessary to find some trustworthy, and at the same time rapid, method of determining the amount of cyanamide present in the solution from time to time. A number of processes are to be found in the literature,\* all involving as their

<sup>\*</sup> The original papers dealing with the methods of determination used in this work are as follows: Perotti, Gazzetta, 1905, 35, ii, 228; Caro, Zeitsch. angew. Chem., 1910, 23, 2407; Monnier, Chem. Zeit., 1911, 35, 601; Stutzer, Chem. Zeit., 1911, 35, 694; and Kappen, Chem. Zeit., 1911. 35, 950.

main principle the precipitation of silver cyanamide by means of an ammoniacal silver solution. With regard, however, to the conditions of precipitation and the method to be adopted for the subsequent determination of the cyanamide, much diversity of opinion exists and conflicting results have been put forward, but it appears certain that concordant results cannot be obtained without strict adherence to specified conditions, owing to the variable composition of the silver cyanamide precipitated in varying circumstances. Α concensus of opinion favours a Kjeldahl determination of the nitrogen in the silver cyanamide precipitate as being, if not absolutely accurate, at least more free from error than titration methods, and uninfluenced by the variability in composition of the precipi-In view of the absence of any definite information as to the tate. magnitude of possible error involved by the much more easily carried out titration methods, comparative experiments have been made with solutions of partly polymerised cyanamide of various strengths to ascertain the conditions necessary for obtaining concordant results, and the degree of accuracy attainable.

The determinations were first carried out using solutions which varied in cyanamide content from normal to half-normal, and containing more and more dicyanodiamide as the percentage of cyanamide sank. Five c.c. of the solution were measured out, diluted to 50 c.c., and 20 c.c. of this diluted solution used for each determination. Caro's method, namely, precipitation with ammoniacal silver acetate, and determination of nitrogen in the precipitate by Kjeldahl's method, was compared with that finally adopted by Kappen, namely, the addition of a known excess of ammoniacal silver solution and titration of the filtrate, and washings with ammonium thiocyanate. The results are shown in the following table, the figures referring to 20 c.c. of the diluted solution, or 2 c.c. of the original:

			N	/10-Hydrochloric
	N/10-Ammoniacal	N/10-Thiocyanate	N/10-Silver used	acid required
	silver added.	for back titration.	for NH <sub>2</sub> CN.	for Kjeldahl.
1.	40 c.c.	20.9 c.c.	19-1 c.c.	19·2 c.c.
2.	$\begin{cases} 40 & ,, \\ 36 & ,, \end{cases}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	18·7 " 18·2 "	18·7 ,, 18·6 ,,
3.	$\begin{cases} 40 & ,, \\ 34 & ,, \end{cases}$	22·5 ,, 17·0 ,,	17.5 ,, 17.0 ,,	_
4.	$\left\{\begin{matrix}40\\32\end{matrix}\right.,$	29·2 ,, 21·6 ,,	10·8 " 10·4 "	10·8 " 10·7 "

The table shows at once the effect on the titration values of the addition of a greater or less excess of silver, the precipitate produced in the former case containing a larger proportion of silver to cyanamide radicle than in the latter. This, according to Stutzer (*loc. cit.*), is due to the formation of double and basic compounds.

The Kjeldahl values, however, appear to be practically unaffected, and hence more trustworthy. This is in agreement with Caro (*loc. cit.*), who states that although the precipitate may vary in composition, it contains all the nitrogen of the cyanamide, which it yields as ammonia by the Kjeldahl process.

Under the above conditions, then, the titration method admits of considerable error; but it was found by further experiment that if the precipitation was conducted in extremely dilute solution, a variation in the excess of silver within reasonable limits produced scarcely any measurable difference in the titration results. The method finally adopted was therefore as follows: The solution under test was rapidly cooled, 5 c.c. were measured out with a pipette and diluted to 50 c.c., of which 20 c.c. were taken for each determination. Before precipitation, however, it was again diluted with about 100 c.c. of water, and a measured excess of N/10-silver solution, also preferably somewhat diluted, and containing about 2 per cent. of ammonia, was then added. After remaining for about thirty minutes, for the very finely divided precipitate to coagulate, it was filtered through special "barium sulphate" filter paper, and washed first with weak ammonia water, and then with pure water until the washings were free from silver and ammonia. The excess of silver in the acidified filtrate and washings was then determined by titration with standard ammonium thiocyanate. The appended table shows the results obtained by the titrations compared, where necessary, with the Kjeldahl determination on the precipitate:

			N	10-Hydrochlorid
	N/10-Ammoniacal silver added.	N/10-Thiocyanate for back titration.	N/10-Silver used for cyanamide.	acid required for Kjeldahl.
1	$\begin{cases} 40 \text{ c.c.} \\ 30 \text{ ,,} \end{cases}$	20.60 c.c. 10.80 ,,	19·40 c.c. 19·20 ,,	19·30 c.c. 19·30 ,,
2.	$\begin{cases} 40 & ,, \\ 30 & ,, \end{cases}$	21.15 ,, 11.15 ,,	18·85 " 18·85 "	
3	$\begin{cases} 40 & ,, \\ 30 & ,, \end{cases}$	20·75 " 10·80 "	19·25 ,, 19·20 ,,	
4.	$\begin{cases} 40 & ,, \\ 26 & ,, \end{cases}$	24·30 " 10·35 "	15.70 ,, 15.65 ,,	
5.	$\begin{cases} 40 & ,, \\ 40 & ,, \\ 24 & ,, \\ 24 & ,, \\ 24 & ,, \end{cases}$	29.00 ,, 29.10 ,, 13.50 ,, 13.60 ,,	11·00 ,, 10·90 ,, 10·50 ,, 10·40 ,,	10.50 ,, 10.40 ,,
6	$\begin{cases} 40 & ,, \\ 20 & ,, \end{cases}$	30·35 ,, 10·70 ,,	9·65 ,, 9·30 ,,	9·35 ,, 9·20 ,,

From the results of 1, 2, 3, and 4 it is evident that the titration method can be relied on if carried out as above described. Determinations 5 and 6 show, however, that if the excess of silver added is very great, that is, of the order of four times the amount theo-

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retically required for the precipitation, then the results begin to vary; but a determination of nitrogen in the precipitate still gives concordant results, agreeing well with the lower titration reading, where only a moderate excess of silver was employed. Hence, in the experiments about to be described, in every case where the initial and final values of cyanamide were widely divergent, a preliminary series of experiments was made, precipitating throughout with the same volume of silver solution. A second series was then conducted, readings being taken at the same intervals as before, and a volume of silver added which was just about double the amount found to be required for the precipitation in the preliminary series. In this way the addition of an excessive proportion of silver was avoided.

## The Polymerisation of Cyanamide in Aqueous Solution.

The figures given refer, as before, to 2 c.c. of the original undiluted solution.

(a) Solution maintained at  $100^{\circ}$  in a boiling-water bath:

Time in hours.	N/10-Silver added.	N/10-Silver precipitated by cyanamide.	$K=1/t\log_c a/a-x.$
0	<b>40 c.c.</b>	19.30 c.c.	
1	40 "	19.20 "	0.002e
4	40 "	18.85 "	0.003e
14	26 ,,	13.00 ,,	0.016e
19	24 "	10.45 "	0·019e

(b) Solution gently boiled over wire-gauze:

Time in hours.	N/10-Silver added.	N/10-Silver precipitated by cyanamide.	$K = 1/t \log_e a/a - x.$
0	40 c.c.	19.40 c.c.	
1	40 ,,	19.20 ,,	0.0045e
2	40 ,,	18.30 "	0-020e
3	40 ,,	17.30 "	0.024e
5	40 ,,	15.35 "	0.026e
9	40 "	12.10 ,,	0-026e
15	40 "	8.60 "	0.024e
23	40 "	5.55 "	0.024e

## (c) Solution gently boiled over wire-gauze:

Time in hours.	N/10-Silver added.	N/10-Silver precipitated by cyanamide.	$K=1/t\log_c a/a-x.$
0	40 c.c.	19.35 c.c.	
2	40	19.00	0.004e
6	40 "	15.50 "	0.022e
10	30 "	12.15 "	0.026e
12	30	10.50 "	0.028e
16	20	9.00 ,,	0.018e
20 <del>1</del>	16 "	7.35 "	0.019e

## (d) Solution maintained at $75^{\circ}$ in a thermostat:

Time in hours.	N/10-Silver precipitated N/10-Silver added. by cyanamide. $K=x/t$ .			
0	160 c.c.	90.60 c.c.		
10	160	81.25 ,,	0.023	
15	160	76.35 ,	0.024	
20	160	71.40 ,	0.025	
25	160 ,	67.40 "	0.020	

An examination of these results brings to light several remarkable facts. At the commencement of the heating, in every case but little effect on the titration value was produced, even after the expiration of from one to two hours, and in the case of series (a), where the solution was not actually boiled, but a water-bath was used to effect the heating, the period of comparative stability continued for some four hours. During the initial stages of the second period, the reaction is characterised by attaining its maximum observed velocity, at which it proceeds almost constant for about ten hours in series (b), (c), and (d), and still longer in series (a). Equal amounts of cyanamide are then polymerised in equal intervals of time, as may be seen at a glance from the second and three following readings in each table, and also from the ascending values of "K," calculated for a unimolecular reaction. A distinct retardation is then observable, but the figures obtained do not agree well with the velocity of a unimolecular reaction, and are certainly in even worse agreement with a bimolecular reaction.

Since the results of each series of experiments are substantially the same, and the method of determination has been shown to be trustworthy, an explanation of the apparently erratic figures must be sought in the complicated nature of the reaction itself. The initial stability of cyanamide in pure water must be conceded as being characteristic of the pure substance. In order firmly to establish this, a further series of experiments was undertaken, using carefully recrystallised cyanamide dissolved in distilled water, and heated at 100° in a water-bath in a flask of hard resistance glass provided with an efficient reflux condenser. The cyanamide was found even at this high temperature to be quite stable in its titration-value during three hours' heating:

Time in hours.	N/10-Silver nitrate required.
0	19·85 c.c.
1	19.85 "
2	19.95 "
3	19-80 "

The subsequent acceleration in the rate of polymerisation suggests, in the light of our knowledge regarding the accelerating influence of bases, the gradual contamination of the solution with

basic constituents dissolved out of the glass. Such contamination would naturally be more rapid in solutions which were actually boiled, but the maximum of contamination would eventually be the same in every case at the same temperature. The experiments have confirmed this, for in series (b) and (c) the period of stability is shorter than in series (a). Yet the final velocity-constants attained are all of the same order, series (a) gradually rising to 0.019 after nineteen hours, (b) and (c) being at that time 0.024 and 0.019 respectively. This, furthermore, suggests a reason why the observed rate of polymerisation in the first stages does not decrease, the loss in reacting substances being accidentally just compensated by the additional small quantity of catalyst still entering the solution at that stage. The linear character of certain periods of the reaction would on this hypothesis be explained away, but the absence of the expected bimolecular reaction,

 $NH_2 \cdot CN + NH_2 \cdot CN = C_2H_4N_4$ 

and the general indication of a unimolecular reaction, still demands explanation.

An ionic theory of the polymerisation suggests itself as feasible, an ion maintained in the solution in constant concentration reacting with some other constituent to form dicyanodiamide or dicyanodiamide ion. Further information on the catalytic action of bases was now found to be necessary in order to put a theory of this nature to the test. First of all, however, a series of experiments was made to demonstrate the influence of the solvent. If one or both the reacting substances were ions, either derived from the dissociation of cyanamide as an acid, or generated by the presence of a base, then the use of a less powerfully ionising solvent, such as ethyl alcohol, would be expected to depress the rate of polymerisation. This expectation was borne out by experiment, as the following table shows:

### Polymerisation in Alcoholic Solution.

Approximately 5N-alcoholic solution maintained at  $75^{\circ}$  in a thermostat:

Time in hours.	N/10-Silver nitrate required for 0.5 c.c.
0	22.50 c.c.
5	22.45 "
10	22.35 "
15	22.15 "
20	22.15 "
25	22.15 "

A comparison of this series with series (d) above, which was carried out in aqueous solution of about the same strength under otherwise absolutely similar conditions, shows that whereas in alcohol the cyanamide was almost stable for twenty-five hours, in aqueous solution it had polymerised in the same period to the extent of 25 per cent. Only two explanations appear to be possible, both are in accord with the ionic theory of the reaction, and both are probably factors in producing the final result. First, the hot alcohol has probably extracted less catalytic matter from the glass than the hot water, and, secondly, that which has been extracted has generated fewer ions in alcoholic solution from cyanamide, less cyanamidion, that is, than the same amount in aqueous solution.

## Polymerisation in the Presence of Bases.

In the first series of experiments the accelerating action of ammonia was studied and found to be exceedingly pronounced, even when added in minute quantities. So, for example, in the experiments given in the first table below, where cyanamide was heated at  $100^{\circ}$  in N/70-ammonia; the 50 c.c. of solution used contained only one drop of concentrated solution of ammonia, but yet at the end of four hours 20 per cent. of the cyanamide had polymerised, whereas in pure aqueous solution the amount changed in that time was inappreciable.

When an ammonia solution of ten times the above strength was employed, polymerisation was almost complete in one and a-half hours, and a qualitative test made after three hours entirely failed to give the reaction of cyanamide at all, showing, therefore, that no condition of equilibrium is attained, but that the formation of dicyanodiamide proceeds to completion.

(a) Cyanamide heated in a water-bath at  $100^{\circ}$  in N/70-ammonia:

	N/10-Silver nitrate pre-	
	cipitated by 2 c.c.	
Time in hours.	of solution.	$K=1/t\log_e a/a-x.$
0.0	17.5 e.e.	,
0.5	16.0 "	0.078e
1.0	14.9 "	0.062e
1.5	14.0 "	0.054e
2.5	12.6 "	0.046e
4.5	10.6 "	0.038e
8.5	8.4 "	0.025e

(b) Cyanamide heated in a water-bath at  $100^{\circ}$  in N/7-ammonia:

Time in hours.	N 10-Silver nitrate precipitated by 2 c.c. of solution.
0.0	18·30 c.c.
0.5	6.75 ,,
1.0	3.65 "
1.5	1.40 "
3.0	0.00 ",

Ammonia is undoubtedly lost during the prolonged heating involved in these experiments. The rate of reaction, therefore,

diminishes more rapidly than it would if the ammonia content could be kept constant throughout, and K, which has been calculated for series (a) on the unimolecular formula, eventually sinks to a value 0.025e, of the same order as that obtained with pure aqueous solutions of cyanamide. These results led us to study the action of a non-volatile alkali, and for this purpose sodium hydroxide was selected. Cyanamide was dissolved in solutions of the base of widely varying strengths, from N/800 (1 in 20,000) to 2N (1 in 12.5), heated at  $100^{\circ}$ , and determinations made in the usual way, with the following results:

(c) Cyanamide heated in N/800-sodium hydroxide solution (1 in 20,000) at 100° in a water-bath:

	N/10-Silver nitrate pre-	
	cipitated by 2 c.c.	
Time in hours.	of solution.	$K=1/t\log_e a/a-x.$
0	28.30 c.c.	
1	25.00 ,,	0.054e
2	22.30 ,,	0.049e
3	20.10 ,,	0.045e
4	18.40 "	0.038e
5	16.90 "	0·037e
6	15.65 "	0-033e

(d) Cyanamide heated in N/400-sodium hydroxide solution (1 in 10,000) at 100° in a water-bath:

Time in hours.	N/10-Silver nitrate added.	$K = 1/t \log_e a/a - x.$	
0	20 c.c.	9·25 c.c.	
1	18 "	7.10 ,,	0·115e
2	16 "	5.70 ,,	0.095e
3	14 "	4.80 "	0-075e
4	12 "	4.25 "	0·053e

(e) Cyanamide heated in N/70-sodium hydroxide solution (1 in 1750) at 100°.

(1) Preliminary experiment precipitating throughout with 40 c.c. of N/10-ammoniacal silver nitrate:

Time in minutes.	N/10-Silver nitrate precipitate tes. by 2 c.c. of solution.	
0	19.95 c.c.	
15	14.50 ,,	
30	10.80 "	
60	6.30 "	

(2) Confirmatory experiment precipitating with decreasing quantities of silver nitrate proportional to the amount of unchanged cyanamide present, as explained in the section on the "Determination of Cyanamide":

Time in minutes.	N/10-Silver nitrate precipitated.	$K = 1/t \log_e a/a - x.$
0	18.3 c.c.	
15	12.8 ,	0-621e
30	9.1 "	0·593e
45	6.6	0:558e
60	5.0 ,,	0·482e

(f) Cyanamide heated in N/4-sodium hydroxide solution at 100°. The solution at the commencement was approximately normal with respect to cyanamide.

(1) Preliminary experiment as above.

Time in minutes.	N/10-Silver nitrate precipitated. 18-3 c.c.	
0		
15	8.3 "	
30	6.1 "	
45	4.7 "	
60	3.7 "	

(2) Confirmatory experiment as above.

Time in minutes.	N/10-Silver nitrate precipitated.	$K = 1/t \log_a a/a - x$
0	18.25 c.c.	
15	6.70	1.736e
30	4.75	0.603e
45	3.70 "	0.434e
60	3.00 ,,	0·364e

(g) Cyanamide (approximately normal solution) heated in N/2-sodium hydroxide solution at 100°. (Approximately the compound NaHN·CN.)

(1) Preliminary experiment.

Time in minutes.	N/10-Silver nitrate precipitated.
0	18.7 c.c.
15	13.0 "
30	9.3 "
60	5.2 "

# (2) Confirmatory experiment.

Time in minutes.	N/10-Silver nitrate precipitated.	$K = 1/t \log_e a/a - x.$
0	18·4 c.c.	
15	12.1	0.728e
30	8.5	0-614e
45	6.1 "	0·576e
60	4.5 "	0.528e

(h) Cyanamide (approximately normal solution) heated in N-sodium hydroxide solution at 100°.

### (1) Preliminary experiment.

Time in minute <b>s.</b>	N/10-Silver nitrate precipitated
0	18.95 c.c.
15	13.60
30	10.10
60	6.20 ,

### (2) Confirmatory experiment.

Time in minutes.	N/10-Silver nitrate precipitated.	$K = 1/t \log_e a/a - x.$
0	18.40 c.c.	
15	13.60 "	0.525e
30	9.90 ,,	0.551e
45	7.25 ,,	0.541e
60	5.25 ,,	0.560e

From the above six series of experiments several important facts are at once obvious. Using equivalent quantities of ammonia and sodium hydroxide (series a and e), the velocity is vastly greater in the latter case than in the former. On the ionic theory of the reaction, this follows at once from the fact that the stronger base generates a greater concentration of cyanamidion than the equivalent amount of the weaker base ammonia.

Approximately normal solutions of cyanamide being taken in every case, the accelerating influence of the base has increased as its concentration rose from N/800 to N/4, and, moreover, the increase in the more dilute solutions has been roughly proportional to the amount of base present. This will be seen by a comparison of the initial velocity-constants:

Concentration of sodium hydroxide.	Velocity constant.
1 in 20,000	0.054e
1 ,, 10,000	0-115e
1 " 1,750	0.621e

The increase in concentration of cyanamidion in dilute sodium hydroxide solution will also be approximately proportional to the increase in concentration of hydroxide, according to the equilibria

$$\begin{array}{l} \mathbf{H}_{2}\mathbf{N}\cdot\mathbf{C}\mathbf{N}+\mathbf{N}\mathbf{a}\mathbf{O}\mathbf{H} \end{array} \rightleftharpoons \begin{array}{l} \mathbf{N}\mathbf{a}\mathbf{H}\mathbf{N}\cdot\mathbf{C}\mathbf{N}+\mathbf{H}_{2}\mathbf{O} \\ & \downarrow \uparrow \\ \mathbf{N}\mathbf{a}\cdot\mathbf{H}'\mathbf{N}\cdot\mathbf{C}\mathbf{N} \end{array}$$

Then, with regard to the actual courses of the reactions, it will be seen that although in the three cases just mentioned "K" on the unimolecular formula is not constant, but gradually decreases, yet the values approximate much more closely on this formula than on the bimolecular equation. For a purely unimolecular reaction we should have

$$H_2N \cdot CN + H'N \cdot CN = C_2N_4H'_3$$

the ion H'N.CN being assumed of constant concentration. In actual fact, however, cyanamidion is not present in quite constant concentration, because although the small amount of sodium hydroxide is constant, yet as the reaction proceeds more and more of this base is shared by the dicyanodiamide produced. The ion H/N·CN does not, however, decrease at anything like the same rate as does cyanamide; if it did, the reaction should appear bimolecular. Apart altogether from the minor question of differences in the degree of hydrolysis of sodium cyanamide and sodium dicyanodiamide, it is obvious that since the molecular concentration of dicyanodiamide is only one-half that of the molecular concentration of the cyanamide from which it was produced, and since both are dissociated primarily as monobasic acids, a larger proportion of sodium hydroxide will be available for the generation of cyanamidion than if each dicyanodiamide molecule had demanded as much as did the two molecules of cyanamide of which it is com-Hence the net result is a reaction the rate of which posed. decreases more rapidly than a unimolecular, and more slowly than a bimolecular, reaction, which condition is fulfilled by the figures obtained.

The next feature to be considered is the remarkable fact that when the concentration of sodium hydroxide has been increased to N/4, the reaction has its maximum observed velocity, the further increase in concentration producing a retarding effect. At this concentration half the cyanamide will have been converted into its sodium compound, which for simplicity's sake we may imagine as being completely dissociated into Na' and NH' CN. The other half of the cyanamide will remain undissociated, and this is precisely the conditions, according to the theory, for the maximum velocity, each of the reacting masses at the initial stage having equal concentrations,

# $NH_2 \cdot CN + NH' \cdot CN = C_2 N_4 H'_3.$

This, of course, can only momentarily be the condition, for as the reaction proceeds more and more base is set free to react with nonionised cyanamide, until in the final stages there should be nearly sufficient sodium hydroxide to ionise both the dicyanodiamide formed and the small amount of cyanamide remaining. This removal of undissociated substance corresponds with the rapid fall in velocity shown in series (f).

Passing on to the final series, (h), with N-sodium hydroxide, it will be seen that the reaction now gives almost constant values for K on the unimolecular formula, and, moreover, that it is an almost exactly similar reaction to series (e), where N/70-sodium hydroxide was used. The velocity-constants are almost identical

in value, and if the curves are plotted they run almost exactly parallel to one another throughout their length. The conditions here are much more complicated than when very dilute sodium hydroxide was used. The solution during the reaction contains ever-varying amounts of sodium cyanamide, sodium dicyanodiamide, and free sodium hydroxide, and, as the dilution is not great, the nature and extent of dissociation and hydrolysis must also be factors in the case. Comparing with series (e), it is probable that here matters are reversed, cyanamidion present initially in large amount corresponding with undissociated cyanamide in that experiment, and undissociated sodium cyanamide, or cyanamide produced by hydrolysis, present in very small amount, and by compensating influences held at fairly constant concentration, corresponding with the cyanamidion in series (e).

## Polymerisation in Presence of Acids.

An ionic theory appears to explain the accelerating influence of bases, but it is difficult to see how the equally powerful accelerating effect of acids can be brought into harmony with the same theory. The addition of a strong acid to cyanamide solutions would result in the practical removal of even the small amount of cyanamidion originally present. Yet this undissociated substance in the presence of dilute sulphuric acid rapidly polymerises, when warmed, to dicyanodiamide. Hydrolytic side reactions are, however, in this case possible, the more concentrated the acid the greater the amount of carbamide produced (Baumann, loc. cit.), and in all circumstances the dicyanodiamide is also hydrolysed to dicyanodiamidine (compare Lidholm, Ber., 1913, 46, 156). This latter substance is a fairly strong base, so that when only a small quantity of acid was used the solution became after a time quite neutral, and the accelerating influence of the free acid on the polymerisation thereby ceased. When a larger quantity of sulphuric acid was employed (N/10-solution) the velocity of polymerisation became so much greater than that of the subsequent hydrolysis that at the end of half an hour the solution was still acid, and gave but the slighest reaction for cyanamide with ammoniacal silver nitrate.

Cyanamide heated in N/70-sulphuric acid at  $100^{\circ}$ :

Time in minutes.	N/10-Silver nitrate precipitated by 2 c.c.		
0	19.00 c c.		
15	16.45 "		
30	15.10 "		
60	14.40 "		
120	12.65 "		

At the expiration of 120 minutes the solution had become neutral to litmus paper.

# Experiments on the Stability of Cyanamide at the Ordinary Temperature.

Accurate data as to the keeping powers of cyanamide at the ordinary temperature do not seem to be available in the previous literature. There is only the statement of Beilstein and Geuther (loc. cit.), who assert that a sample kept for several months failed to give the reactions of cyanamide. Experiments were therefore made with two 10 per cent. solutions, one kept in the dark, and the other in ordinary diffused daylight at summer temperatures, and also with a sample of the pure solid substance kept for the complete exclusion of moisture in a desiccator. The analytical results obtained showed that the admission or exclusion of light had no appreciable influence on the polymerisation; that the solid was more stable than the dissolved substance, but that the stability of both was of an order quite at variance with Beilstein and Geuther's observation. After keeping for six months, in fact, only 8.9 per cent. of the solid was found to have changed, whilst in 10 per cent. solution nearly 35 per cent. of the dissolved cyan-The actual figures were as follows: amide had disappeared.

N/10-Ammoniacal silver nitrate required

	For 0.5 c.c.	For 0.5 c.c.	For 0.1 gram
	of solution	of solution	of solid
Time in months.	in daylight.	in the dark.	substance.
0	41.0 c.c.	40·8 c.c.	47·0 c.c.
1	40.1 ,,	39.8 ,,	46.5 "
6	26.9 "	27.0 "	42.8 "

The stability of the sodium salt at the ordinary temperature has not been accurately investigated, but it has been noticed during the preparation of cyanamide from the commercial sodium cyanamide, supplied by Kahlbaum, that very different yields have consistently been obtained from different samples, 50 grams of the commercial product yielding in the poorest samples as little as 5 grams of cyanamide, and as much as 14 grams from the best. This variation is quite possibly due to the greater or less facilities for polymerisation which have been allowed during the process of manufacture, for since the sodium salt in solution polymerises much more rapidly than the free cyanamide itself, any undue heat applied during the concentration of the mother liquors must inevitably result in an extensive amount of polymerisation.

Note.—Since the above paper was read a communication by Grube and Krüger (Zeitsch. physikal. Chem., 1913, 86, 65) has appeared, which confirms from a somewhat different point of view some of the results arrived at in this investigation.

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