

LXXVII.—*Transformation of Ammonium Cyanate into Urea.*

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SINCE Wöhler's memorable observation that ammonium cyanate spontaneously undergoes transformation into urea, the subject, probably from the very magnitude of the result achieved, has been entirely neglected. One or two points of interest, however, occur in connection with this transformation, and it is the object of the present paper to draw attention to them.

Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, **20**, 393) note that whilst the change takes place immediately on boiling the aqueous cyanate solution, it is gradual when the solution is left to evaporate in the air, or is evaporated by the aid of a gentle heat. It thus seemed possible that the course of the reaction might be followed at different temperatures, provided that a method could be found for estimating in a simple fashion the amount of ammonium cyanate or of urea in the solution at any specified time. Such a method was developed by taking advantage of the circumstance that silver nitrate has no action on urea, whereas with ammonium cyanate it yields a silver salt practically insoluble in cold water.

Method of Estimation.

The mode of experiment was as follows. A measured volume of the solution to be investigated was introduced into a small flask containing a known volume of decinormal silver nitrate solution, in excess of the quantity necessary to completely precipitate the cyanate. The contents of the flask were cooled as rapidly as possible

to the ordinary temperature by means of a stream of water, and allowed to remain for a few minutes. The silver cyanate had then, as a rule, collected to an easily-filtered precipitate, the filtrate from it being either quite clear or only slightly opalescent. The contents of the flask were thrown on a 5-cm. filter, the flask rinsed out twice with water, and the precipitate washed three times on the filter. The filtrate was then transferred to a porcelain basin, and the excess of silver in it titrated by Volhard's method with $1/50$ N ammonium thiocyanate solution.

The solubility of silver cyanate in water at the ordinary temperature is so slight as to be within the experimental error of the method. It was found that the amount dissolved by 100 parts of water at 16° is 0.006; that is, 25 c.c. of water dissolve what corresponds to 0.1 c.c. of $1/50$ N thiocyanate solution. As the filtered solution, including wash water, never amounted to more than 50 c.c., the maximum error from this source is 0.2 c.c. of thiocyanate solution; and this amount is never even approximately reached, as the solubility of silver cyanate is greatly diminished by the presence of the silver nitrate in the filtrate. An experiment with centinormal silver nitrate, instead of water, showed that the solubility of silver cyanate in this solvent is so small as not to be detected in the titration.

The error of the method, that is, in the filtration, washing, and titration, may be estimated at 0.1 c.c. of the thiocyanate solution, two determinations with the same sample seldom differing by more than that amount.

Reversibility of the Transformation.

It seems to have hitherto escaped observation, that urea, when heated at 100° with water, is partially retransformed into ammonium cyanate. It is of course well known that silver cyanate is formed when a solution of urea is evaporated down with silver nitrate, but this has been uniformly attributed to a specific action of the silver salt. Urea itself gives no precipitate with silver nitrate, but if a solution of it be kept at 100° for half an hour, then cooled and a silver salt added, it gives a considerable precipitate, which has the characteristic properties of silver cyanate. That this precipitate is formed by the double decomposition of silver nitrate with ammonium cyanate is proved by the fact that the quantity of silver cyanate obtained keeps equal pace with the amount of ammonia found in the solution by Nessler's process. Thus a decinormal solution of urea, which originally gave no coloration with Nessler's solution, yielded the following numbers when heated to 100° . After 10 minutes, the amount of urea transformed, as estimated by the silver nitrate method, was 1.2 per cent., as estimated by Nessler's method 1.3 per

cent. After 25 minutes the corresponding numbers were 3.2 per cent. and 4.0 per cent. respectively. These numbers agree with each other within the experimental error, as the quantities estimated were very small.

Preparation of Ammonium Cyanate Solutions.

The method adopted for the preparation of the solutions of ammonium cyanate was the decomposition of silver cyanate by ammonium chloride. The silver cyanate was prepared by heating a seminormal solution of silver nitrate with 5 equivalents of urea for four hours at 100°, the silver cyanate produced being filtered off twice or thrice in that interval. The silver salt obtained in this way was in the form of fine needles, and required no purification. It was drained on a filter plate, washed thoroughly with water, and dried in an exhausted desiccator. The yield, with the quantities given above, is 88 per cent. of the silver nitrate taken, in accordance with the theoretical number of 90 per cent., the mode of deducing which will be given later.

0.4995 silver cyanate gave 0.3585 Ag. Ag = 71.8. Calculated Ag = 72.0 per cent.

The ammonium cyanate solution for each day's work was prepared specially, as even at the ordinary temperature the transformation into urea is fairly rapid. To obtain the solution of the requisite strength, a weighed quantity of finely powdered silver cyanate, very slightly in excess of that calculated, was washed into a measuring flask, into which had been introduced a quantity of ammonium chloride, accurately weighed to give the ammonium cyanate solution of the proper strength when the mixture was diluted to the mark. Occasionally a measured quantity of ammonium chloride solution of known concentration was added instead of the weighed solid. After the flask had been filled to the mark with water, the contents were kept continually agitated for an hour, as the action between the practically insoluble silver cyanate and the ammonium chloride is comparatively sluggish. At the end of that time, however, it may be assumed to be complete, for a part of the filtered solution when treated with nitric acid gives no precipitate, either with silver nitrate or with ammonium chloride. Each filtered solution was tested in this way before being used, and rejected if more than a slight opalescence appeared with either of the reagents.

Determination of the Equilibrium Point.

For the calculation of the velocity constant of the reaction, it was necessary to determine the point at which the transformation ceased. This point should be the same, whether approached from the ammo-

nium cyanate end or from the urea end, as it is the point at which the two opposed actions are balanced, as much ammonium cyanate being transformed into urea in a given time as is reproduced from the urea in the same time. As the rate at which the ammonium cyanate is converted into urea is much greater than the rate of the reverse action, it follows that the end-point must lie near the urea end.

Experiments with decinormal urea at 100° gave the following results.

<i>t.</i>	Titre.	Percentage of urea transformed.
0	5.00	0
14	4.40	2.4
60	3.85	4.6
120	3.90	4.4
182	3.90	4.4
0	5.00	0
15	4.60	1.6
32	4.10	3.6
55	3.90	4.4
87	3.95	4.2
107	3.90	4.4

In the first column, the time in minutes from the beginning of the heating is given. In the second column, we have the numbers obtained by adding 5 c.c. of the solution to 1 c.c. of decinormal silver nitrate, filtering, and titrating with 1/50 N ammonium thiocyanate solution. Four times the difference between these numbers and 5.0 gives the percentage of urea transformed. It is apparent that after an hour the end-point is reached, no further change in the titre taking place.

Approaching the end-point from the other side (decinormal ammonium cyanate) we obtained the following results.

<i>t.</i>	Titre.	Percentage of cyanate transformed.
0	0	0
11	18.9	75.6
30	20.9	83.6
60	21.3	85.2
90	22.3	89.2
120	23.2	92.8

Five c.c. of the solution were added to 5 c.c. of decinormal silver nitrate, and the filtrate titrated as usual with 1/50 N thiocyanate. The quantity of urea transformed in no case that we observed

exceeded 93 per cent., the maximum numbers obtained in a considerable number of experiments averaging 91.6 per cent. This number, when added to the number obtained from the urea experiment, should give a sum equal to 100, but, as we see, the sum on the average only reaches 96. This deficit, however, is easily accounted for. Ammonium cyanate, while passing for the most part into urea, undergoes at the same time a subsidiary transformation into ammonium carbonate. Now, 1 mol. of ammonium cyanate is transformed into 1 mol. of ammonium carbonate, but whilst the former fixes one equivalent of silver nitrate, the latter fixes two; so that more silver nitrate is precipitated than would be the case if no such secondary transformation had occurred, and the quantity of silver left for titration in the filtrate is in consequence too small. The formation of ammonium carbonate can be detected by the solution giving a precipitate with calcium nitrate, this precipitate dissolving with effervescence in acetic acid. A quantitative experiment gave the following results.

Forty c.c. of a decinormal ammonium cyanate solution, which had undergone transformation at 69° , were precipitated with calcium nitrate and a little ammonia. The carbonate obtained was converted into calcium sulphate, the weight of which was found to be 0.0221 gram. This corresponds to 10 milligrams of ammonium cyanate, the total quantity in 40 c.c. of a decinormal solution being 0.24 gram. Thus 4 per cent. of the ammonium cyanate had been converted into ammonium carbonate, an amount which exactly accounts for the deficit above noted.

It will be seen from the table that the conversion of ammonium cyanate into urea at 100° proceeds very rapidly, three-fourths of the total amount being transformed in 11 minutes. In every case, a brown turbidity was observed in the solution after 30 minutes at 100° , which was probably due to the reduction of a trace of silver compound in the solution. The silver precipitates, also, obtained from solutions at this temperature, were usually brown, marking a secondary decomposition of the ammonium cyanate.

The true end-point for the equilibrium between ammonium cyanate and urea must lie very close to that obtained with urea solutions, for there the amount of ammonium cyanate, and consequently the amount of secondary decomposition, is throughout at a minimum. No appreciable precipitate with calcium nitrate was obtained with such solutions, and we may thus assume that the theoretical end-point of the transformation of ammonium cyanate into urea, were there no secondary decomposition, would, at 100° , lie at 95 per cent. with a possible error of 0.5 per cent.

It was of both theoretical and practical importance to determine

the displacement of the end-point by variation of temperature, and experiments were made with this object.

At low temperatures, the transformation of urea proceeds so slowly that the end-point might only be reached after weeks or even months. Solutions were therefore made up containing both urea and ammonium cyanate in such proportions that the composition approximated to that of the solution in equilibrium at 100° . A decinormal solution with 5 per cent. of cyanate and 95 per cent. of urea did not change in titre on remaining for 43 hours at 39° . A similar solution, containing 2 per cent. of cyanate and 98 per cent. of urea, showed a diminution of 0.25 c.c., or 0.5 per cent. under the same conditions. Some of the urea had therefore been converted into ammonium cyanate, so that we must conclude that temperature influences the end-point but little, since at 100° it stands at 95 per cent., and at 39° lies between that figure and 97.5 per cent. at the utmost, being, in all probability, much nearer the former than the latter.

As the velocity experiments were all made with ammonium cyanate solutions, the "practical" end-point, as recorded by the maximum titre at 100° , was taken instead of the real end-point, which does not allow for the secondary decomposition of the cyanate. Thus, with decinormal solutions, the calculations were performed with the end-point 91.6 per cent., or 22.9 c.c. of the titrating solution, except in the case of the experiments at 25° and 39° , where the secondary decomposition, as judged by the amount of precipitate with calcium nitrate, was much smaller. For these temperatures, the end-points 94 and 92.8 were taken, but the value of the velocity constant is thereby very little affected.

Calculation of the Velocity Constant.

The decinormal solution of ammonium cyanate was heated to the temperature of observation as soon as possible after its preparation. As will be seen later, its rate of transformation rises very rapidly with the temperature, so that in order to get a zero-time from which the intervals could be calculated, the heating had to be quickly performed. The solution, usually about 70 c.c., was placed in a 4-oz. flask and heated with the naked flame to the temperature of the thermostat in which it was to be placed. This process occupied little more than a minute at most, so that the error in calculating the time is comparatively small, even at the higher temperatures, and the influence of initial disturbances slight. At suitable intervals, 5 c.c. of the solution were removed from the well-corked flask, added to 5 c.c. of decinormal silver solution, cooled, filtered, and titrated.

The following numbers were obtained at 50.1° . In the table, t indicates the interval in minutes from the time at which the solution

acquired the temperature of observation, x is the titre, and A the end-point, expressed in c.c. of the 1/50 N thiocyanate solution.

Decinormal Cyanate at 50.1°. $A = 22.9$.

t .	x .	$A - x$.	$\frac{1}{t} \log \frac{A}{A-x}$.	$\frac{1}{t} \cdot \frac{x}{A-x}$.
45	4.4	18.5	0.00206	0.00528
72	6.5	16.4	0.00201	0.00549
107	8.3	14.6	0.00183	0.00529
157	10.1	12.8	0.00161	0.00502
230	12.3	10.6	0.00145	0.00505
312	14.2	8.7	0.00134	0.00524
600	17.2	5.7	0.00101	0.00502

Before Guldberg and Waage had formulated and applied in all directions the law of mass action, it had been shown by Wilhelmy and by Harcourt and Esson that when one molecule was transformed into another or others, the rate at which this transformation occurred was expressed by a logarithmic formula, which is deduced from the general law as follows. Let A be the original active mass of the substance undergoing transformation, and let x have been transformed at the time t , then the rate of transformation, $\frac{dx}{dt}$, at that time will be

$$\frac{dx}{dt} = C(A - x),$$

that is, proportional to the active mass, $A - x$, of the substance then untransformed. The constant, C , is the velocity constant of the reaction. Bearing in mind that when $t = 0$, $x = 0$, we obtain, on integration,

$$\log_e \frac{A}{A-x} = Ct;$$

or, if we use the decadic instead of the natural logarithms,

$$\frac{1}{t} \log \frac{A}{A-x} = 0.4343 C.$$

Now both magnitudes on the right hand side of the equation are constant, therefore if the action is a simple transformation of 1 mol. of ammonium cyanate into 1 mol. of urea, the expression $\frac{1}{t} \log \frac{A}{A-x}$ should be constant. A glance at the table shows that this expression, instead of being constant, sinks steadily to half its original value. It is true that instead of the real active mass of the cyanate at the beginning of the action, namely, 25 c.c. in our arbitrary units, we

have employed the number 22.9, the practical end-point. But it is capable of a simple mathematical proof that in a unimolecular reversible reaction this mode of procedure is permissible, the logarithmic expression given above being constant as well as the more complicated expression which involves the real active mass and takes account of the opposed reaction, that is, the simultaneous transformation of urea into ammonium cyanate.

We are thus forced to conclude that the production of urea from ammonium cyanate does not proceed in so simple a way as we might be disposed to imagine.

Let us now proceed on the assumption that the interaction of two molecules is necessary for the production of urea. If, as before, we represent the active mass of each kind of molecule (supposed to be present in equivalent quantities) by A , and the quantity transformed at the time t by x , we have, for the rate of transformation,

$$\frac{dx}{dt} = C(A - x)(A - x),$$

this rate being proportional to the active mass of each kind of molecule. The expression obtained on integration is $\frac{x}{A - x} = ACt$, or $\frac{1}{t} \cdot \frac{x}{A - x} = AC$, a constant quantity.

Neglecting, as in the previous case, the slow reverse action by taking the value of the practical end-point as the original active mass, we find that the expression $\frac{1}{t} \cdot \frac{x}{A - x}$ is now indeed constant.

Reference to the table will show that the constancy is not absolute, but, from beginning to end, the constant fluctuates about the mean value, exhibiting no steady increase or decrease like the logarithmic expression. The maximum variation from the mean is only 6 per cent., and this will be deemed satisfactory when we consider that one-tenth of a degree difference in temperature causes a variation of 1.5 per cent. Here, then, is distinct evidence that for the production of urea the interaction of two molecules is necessary, and that these must always be present in the ammonium cyanate solution in equivalent proportions. The first assumption to make is that the two molecules are two molecules of ammonium cyanate, but it will be proved in the sequel that this assumption is erroneous. In the meantime, we proceed to give the results of experiments performed at different temperatures in order to ascertain the temperature-

coefficient of the expression $\frac{1}{t} \cdot \frac{x}{A - x}$.

Temperature Experiments.

The thermostat employed was a water-bath with windmill and stirrer as described by Ostwald, *Physico-chemical Measurements*, p. 64, and a vapour-pressure thermo-regulator (Benoit's modification of Andreae's, *loc. cit.*, p. 59). The liquids used for filling the various regulators were ether, acetone, methylic alcohol, and ethylic alcohol.

The results obtained are exhibited in the following tables, the symbols being as before.

Decinormal Cyanate at 25.0°. A = 23.5.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
1325	5.6	17.9	0.000236
1970	7.0	16.5	0.000214
2725	9.0	14.5	0.000228
5640	13.3	10.2	0.000231
			Mean = 0.000227

Decinormal Cyanate at 39.0°. A = 23.2.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
228	6.1	17.1	0.00156
373	8.2	15.0	0.00147
591	9.9	13.3	0.00126
1266	14.6	8.6	0.00134
1577	16.1	7.1	0.00143
			Mean = 0.00141

Decinormal Cyanate at 59.7°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
15	4.3	18.6	0.0154
30	6.7	16.2	0.0138
50	9.5	13.4	0.0142
80	12.1	10.8	0.0140
140	15.4	7.5	0.0147
			Mean = 0.0144

Decinormal Cyanate at 64.5°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A - x}$.
20	7.0	15.9	0.0220
37	10.3	12.6	0.0221
50	12.1	10.8	0.0224
65	13.8	9.1	0.0233
95	16.0	6.9	0.0244
150	17.7	5.2	0.0227
			Mean = 0.0228

Decinormal Cyanate at 69.2°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A - x}$.
10	6.7	16.2	0.041
15	8.7	14.2	0.041
20	9.9	13.0	0.038
30	12.2	10.7	0.038
45	15.0	7.9	0.042
			Mean = 0.040

Decinormal Cyanate at 74.7°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A - x}$.
15.5	11.3	11.6	0.063
37.0	15.7	7.2	0.059
60.0	17.9	5.0	0.060
124.0	20.4	2.5	0.066
			Mean = 0.062

Decinormal Cyanate at 75.0°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A - x}$.
12	9.7	13.2	0.061
27	14.7	8.2	0.066
45	17.0	5.9	0.064
65	18.3	4.6	0.061
			Mean = 0.063

Decinormal Cyanate at 80.0°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
14	13.3	9.6	0.099
26	16.3	6.6	0.095
44	18.5	4.4	0.096
64	20.1	2.8	0.112
			Mean = 0.100

Decinormal Cyanate at 80.1°. A = 22.9.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
7	9.0	13.9	0.093
17	14.6	8.3	0.103
37	17.9	5.0	0.097
57	19.5	3.4	0.101
97	20.9	2.0	0.108
			Mean = 0.100

These numbers will suffice to show that the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ remains substantially constant at each of the temperatures studied. The determinations at the higher temperatures are difficult on account of the rapidity of the transformation. In the case of the two highest, duplicate experiments are given, which show that although the individual values vary considerably, the mean is sensibly the same.

The temperature, as is usual in such cases, has an enormous influence on the rate of the action. Whilst at 80° half of the ammonium cyanate has been transformed in 10 or 12 minutes, at 25° three days are required to produce the same effect.

Van't Hoff (*Etudes*, p. 114) and Arrhenius (*Zeit. physikal. Chem.*, 4, 227) have shown that the formula

$$C_1 = C_0 e^{A(T_1 - T_0)/T_0 T_1}$$

is capable of representing the influence of temperature on a velocity constant with great accuracy, and have endeavoured to assign its theoretical significance. In the expression, C_0 is the velocity constant at the temperature t_0 , C_1 the constant at t_1 ; e is the base of the natural logarithms, T_0 and T_1 are the temperatures t_0 and t_1 when measured in the absolute scale; A , finally, is a numerical constant. Using this formula, and taking the lowest temperature as t_0 , we obtain the following table.

$$t_0 = 25^\circ, C_0 = 0.000227, A = 11700.$$

<i>t.</i>	C (obs.).	C (calc.).
25.0	0.000227	(0.000227)
39.0	0.00141	0.00133
50.1	0.00520	0.00480
59.7	0.0144	0.0137
64.5	0.0228	0.0227
69.2	0.040	0.0365
74.7	0.062	0.0623
80.0	0.100	0.105

In view of the fact that in the range examined, the constant increases more than four hundred fold, the accordance between the calculated and observed numbers may be looked upon as satisfactory.

Influence of Dilution.

In unimolecular reactions, the concentration of the substance which is being transformed has no effect on the course of the action. If at a certain temperature and a certain concentration half of the substance has undergone transformation in a certain time, the same time will be occupied in producing the half-transformation whether we dilute the original solution, or whether we concentrate it. The velocity constant is here independent of the degree of dilution. This is easily comprehensible from the mechanical point of view, for each molecule is transformed independently of all the rest, so that it is a matter of indifference whether the individual molecules of the substance are closely packed together, or not. The case is different in a bimolecular reaction. Here two molecules must meet before transformation can take place, and their chances of meeting are reduced as we dilute the solution, so that the proportion transformed in a given time will be less the more dilute the solution becomes. The effect on the expression $\frac{1}{t} \cdot \frac{x}{A-x}$, will be seen on reference to the integrated equation .

$$\frac{1}{t} \cdot \frac{x}{A-x} = AC.$$

If we reduce the value of *A* to one-half by halving the concentration, the right-hand side of the equation is halved, for *C* is a constant independent of the dilution, being in fact the rate at which the action progresses when the reacting substances are present (and maintained) at *unit* concentration. The left-hand side of the equation must also therefore be halved, so that by taking twentieth-normal ammonium cyanate, the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ should be reduced to one-

half its value for a decinormal solution. It will be observed that in calculating this expression, any unit may be used for A and x , since we are only concerned with the ratio $x/(A - x)$.

0.05-normal Cyanate at 49.8° . $A = 22.9$.

t .	x .	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
120	6.0	16.9	0.00282
180	7.8	15.1	0.00287
240	9.5	13.4	0.00295
400	12.4	10.5	0.00295
533	13.9	9.0	0.00288

Mean = 0.00289

The value of the constant at 50.1° for the decinormal solution is 0.00520. If we double 0.00289, we obtain 0.00578, which is greater than the theoretical value, and is further augmented by applying the correction for the difference in temperature.

0.2-normal Cyanate at 60.1° . $A = 22.5$.

t .	x .	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
10.0	4.65	17.85	0.0260
25.0	8.6	13.9	0.0247
40.3	11.3	11.2	0.0252
60.0	13.8	8.7	0.0264
127.0	17.2	5.3	0.0256

Mean = 0.0255

The end-point 22.5 was determined by a special experiment.

0.05-normal Cyanate at 60.1° . $A = 22.9$.

t .	x .	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
28	4.4	18.5	0.0085
50	6.8	16.1	0.0085
76	9.0	13.9	0.0085
120	10.8	12.1	0.0074
200	14.2	8.7	0.0082

Mean = 0.0082

We have thus the series

0.05	0.1	0.2-normal.
Const. 0.0082	0.0144	0.0255

Here the fifth-normal solution which should have a constant four times as great as the twentieth-normal solution has in fact a constant only little more than three times as great. The transformation, then, although it preserves the characteristic constant of a bimolecular reaction at various dilutions, is influenced in some secondary way by the dilution, the tendency being to give too great a constant as the dilution is increased. An explanation of this secondary action will be given in the next section.

Influence of Neutral Salts.

We have now to consider the reason why the transformation of ammonium cyanate into urea is a bimolecular reaction, and not a unimolecular reaction as might *à priori* be expected. The two reacting substances must be present in the ammonium cyanate solution in equivalent proportions, otherwise the expression $\frac{1}{t} \cdot \frac{x}{A-x}$, would not remain constant. The assumptions which might account for this are, 1st, that two molecules of ammonium cyanate meet to form urea; 2nd, that the ammonium cyanate is dissociated by the water wholly or largely into ammonia and cyanic acid, and 3rd, that the ammonium cyanate is electrolytically dissociated into ammonium ions and cyanic ions. A means of ascertaining which of these assumptions is correct is to be found in the influence exercised by various substances on the constant. A perfectly indifferent salt has in general little influence; it may slightly alter the numerical value of the constant but no more. The following experiment was made with potassium sulphate added in equivalent proportion to the solution of ammonium cyanate.

Decinormal Ammonium Cyanate in Presence of Decinormal Potassium Sulphate at 74.7°. A = 22.0 by experiment.

<i>t.</i>	<i>x.</i>	<i>A - x.</i>	$\frac{1}{t} \cdot \frac{x}{A-x}$
9	7.4	14.6	0.056
23	12.7	9.3	0.059
47	16.0	6.0	0.057
70	17.3	4.7	0.053
103	18.7	3.3	0.055

Mean = 0.056

The effect of the potassium sulphate is to reduce the constant from 0.062 to 0.056. This might well be in accordance with any of the above assumptions, the influence being comparatively slight. On

the third assumption, a slight diminution of the constant might be predicted, for the number of active molecules, that is NH_4 and CNO , is diminished by the addition of another salt. If, instead of potassium sulphate, we add an equivalent of ammonium sulphate the effect is wholly different. The action is greatly accelerated and the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ is no longer constant, increasing rapidly, especially towards the end of the reaction.

Decinormal Ammonium Cyanate in Presence of Decinormal Ammonium Sulphate at 74.7°. $A = 24.7$ by experiment.

t .	x .	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A-x}$.
8	10.8	13.9	0.097
20	17.5	7.2	0.122
40	21.9	2.8	0.195

Here in 10 minutes the transformation has proceeded half way. In presence of potassium sulphate nearly 20 minutes elapse before the solution has reached the same condition. It will be seen too that the end-point practically corresponds to complete transformation into urea. This is a natural result of the great acceleration of the forward action towards the end, the reverse transformation remaining constant. The lowest value of $\frac{1}{t} \cdot \frac{x}{A-x}$ is 50 per cent.

greater than the value 0.062 for ammonium cyanate alone, and the highest one 200 per cent. The acceleration is, therefore, of quite a different order from the influence exerted by potassium sulphate.

The only reasonable explanation of this acceleration is that the quantity of one or more of the active substances present has been largely increased by the addition of ammonium sulphate. On the first assumption that the active substances are ammonium cyanate molecules, this increase is impossible, so this assumption may be dropped. Unless we assume that ammonium sulphate is to a great extent dissociated into ammonia and sulphuric acid when dissolved in water, an assumption which few will grant, the second supposition must also be set aside: independent evidence of its inadequacy will be given later. There remains then the third assumption that the reacting molecules are ammonium ions, NH_4 , and cyanic ions, CNO , produced by the electrolytic dissociation of the ammonium cyanate. On the dissociation hypothesis, ammonium sulphate is also decomposed electrolytically when dissolved in water, the ions being NH_4 and SO_4 . On adding ammonium sulphate to the solution, then, we increase the active mass of one of the reacting substances,

namely the ammonium ion, and consequently the action proceeds faster, especially towards the end, for then the added ammonium ions bear a greater proportion to the total than they do at the beginning. The experimental result is thus in harmony with the theory of electrolytic dissociation.

An increase in the quantity of the other reacting substance, the cyanic ion, ought also to have an accelerating effect on the action. According to the dissociation theory, potassium cyanate like other potassium salts of monobasic acids, is almost completely dissociated into its ions K and CNO in dilute aqueous solution, so the addition of potassium cyanate should hasten the action considerably. This we find to be the case.

Decinormal Ammonium Cyanate in Presence of Decinormal Potassium Cyanate at 74.7°.

<i>t.</i>	<i>x.</i>
10	13.2
20	16.8
35	20.2
50	21.2
70	21.8

The accelerating effect is of the same order as in the case of the addition of ammonium sulphate. Unfortunately a direct comparison and calculation of the "constant," is impossible, owing to the comparatively great decomposition of cyanate into carbonate which takes place simultaneously with the transformation into urea. After the solution had been heated for an hour, it gave a dense precipitate with calcium nitrate.

As the action at 75° proceeded too rapidly in presence of accelerating agents for accurate calculations, some experiments were performed at 50° in order to obtain more trustworthy data.

When the reacting substances are not present in the solution in equivalent proportion, the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ no longer remains constant and another must be substituted for it. Let the original concentration of the one substance be *A*, and of the other *B*, then the rate at any time is expressed by the equation

$$\frac{dx}{dt} = C(A-x)(B-x),$$

which, on integration, becomes

$$\frac{1}{t} \log \frac{(A-x)B}{(B-x)A} = 0.4343(A-B)C.$$

All the magnitudes on the right hand side of the equation are

constant, so that the left hand side must also be constant. On adding ammonium sulphate in equivalent proportion to a solution of ammonium cyanate, we do not double the number of ammonium ions in the solution, for the sulphate, according to the electrical conductivity, is less dissociated than the cyanate, and each diminishes the dissociation of the other from the value it would have were it dissolved separately in the same volume of water as is used to dissolve both. Using the conductivity numbers of Kohlrausch and others, we find that the ammonium ions in the mixed solution should be to those in the pure cyanate solution in the ratio of 5 : 3 approximately, the number of cyanic ions being very slightly diminished. Taking A for the cyanic ions equal to its former value, we have approximately B for the ammonium ions equal to 1.61 A . Substituting this value for B in the above equation and re-arranging, we obtain

$$\frac{1}{t} \log \frac{A - 0.62x}{A - x} = 0.61 \times 0.4343 C,$$

C having the same numerical value as it had when the ammonium cyanate was alone in the solution.

Decinormal Ammonium Cyanate in presence of Decinormal Ammonium Sulphate at 49.8°.

t .	x .	$A - x$.	$A - 0.62x$.	$\frac{1}{t} \log \frac{A - 0.62x}{A - x}$.
33	5.4	19.3	21.3	0.00129
62	8.0	16.7	19.8	0.00119
99	10.6	14.1	18.1	0.00110
162	14.2	10.5	16.0	0.00117
226	16.6	8.1	14.4	0.00110

$$\text{Mean} = 0.00117$$

The value of $A = 24.7$ was obtained by direct experiment. It will be seen that the constant is fairly good, and from it we can calculate C by means of the equation

$$0.00117 = 0.61 \times 0.4343 C.$$

This gives us $C = 0.00443$, and when we allow for 0.3° difference in temperature at 15 per cent. per degree, we obtain 0.00463, which is a fair approximation to the value of $C = 0.0052$ in the pure cyanate solution at 50.1°.

An experiment was made with a solution decinormal with respect to ammonium cyanate, and 1/20 N. with respect to the ammonium sulphate. Here the amount of ammonium ions is not increased by one-half, but only by a quarter, as a consideration of the conduc-

tivities will show, the chief diminution being due to the effect of the cyanate on the less dissociated sulphate. We have therefore $B = 1.25 A$, and the formula becomes

$$\frac{1}{t} \log \frac{A - 0.8x}{A - x} = 0.25 \times 0.4343 C.$$

For A we have the value 24.4 determined by an end-point experiment.

Decinormal Ammonium Cyanate in presence of 0.05-normal Ammonium Sulphate at 49.9°.

t .	x .	$A - x$.	$A - 0.8x$.	$\frac{1}{t} \log \frac{A - 0.8x}{A - x}$.
43	5.2	19.2	20.2	0.00051
71	7.8	16.6	18.2	0.00056
113	9.9	14.5	16.5	0.00050
170	12.4	12.0	14.5	0.00048
235	14.6	9.8	12.7	0.00048
395	18.4	6.0	9.7	0.00053

$$\text{Mean} = 0.00051$$

From the mean 0.00051 we obtain C by the equation

$$0.00051 = 0.4343 \times 0.25 C.$$

This gives us $C = 0.0047$, from which, if we add 3 per cent. as the temperature correction, we get the value $C = 0.00484$ for the constant at 50.1°, in close approximation to the observed value, 0.0052.

Considering the slight uncertainty that attaches to the calculation of the exact degree of dissociation from the conductivities as tabulated in Ostwald's *Lehrbuch*, vol. II, pt. 1, the constancy of these numbers and the values they give for C must be held as strong evidence in favour of the application of the dissociation theory to the matter in hand.

In the last section, it was found that the influence of dilution on the speed of the action was disturbed by some secondary action, which, at low concentrations, tended to give a greater constant than theory predicted. If we take the degree of dissociation at the various dilutions into account, however, the discrepancy disappears. At low concentrations, the degree of dissociation, as indicated by the conductivities, is greater than at higher concentrations, so that in the more dilute solutions there are relatively more of the active ions than in the more concentrated solutions. At the dilution $\frac{1}{5}$ N., the value of $\frac{1}{t} \cdot \frac{x}{A - x}$ was found to be 0.0255; at the dilution $\frac{1}{20}$ N., it

was 0.0082. If there were four times as many ions at the dilution $\frac{1}{5}$ N. as at $\frac{1}{20}$ N., the value for the former should be 0.0328 instead of 0.0255; but the conductivities show that there are only 3.3 times as many ions, so we obtain $0.0082 \times 3.3 = 0.0270$, not far removed from the observed value, 0.0255.

To apply a final test to the validity of the theory of electrolytic dissociation in this connection, an experiment was made with ammonium cyanate in presence of ammonia. If the dissociation caused by the water is a dissociation into ammonia and cyanic acid, and into ammonia and sulphuric acid, we should have ammonia solution producing at least the same effect as an equivalent solution of ammonium sulphate. On the other hand, if we consider the conductivities of ammonia solutions, the dissociation theory predicts that ammonia should behave towards ammonium cyanate as an indifferent substance like potassium sulphate. The conductivities obtained by Bredig (*Zeit. physikal. Chem.*, 1894, **13**, 294) show that in decinormal solution, ammonia is dissociated only to the extent of 1.5 per cent. into its ions. This amount of dissociation is diminished to the vanishing point in presence of the highly dissociated ammonium cyanate, so that as the ammonia contributes no ammonium ions to the solution, it will behave as an indifferent substance. The following are the results obtained.

Decinormal Ammonium Cyanate in Presence of Decinormal Ammonia at 49.4°. A = 22.9.

t .	x .	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
71	5.6	17.3	0.00456
110	7.4	15.5	0.00434
155	9.2	13.7	0.00433
215	11.2	11.7	0.00445

Mean = 0.00442

In performing this experiment, the silver nitrate into which the measured quantity of solution was poured, was mixed with a quantity of nitric acid exactly sufficient to neutralise the free ammonia, in order that the solubility of the silver cyanate might not be increased.

The expression $\frac{1}{t} \cdot \frac{x}{A - x}$ remains constant, as if no active substance had been added, and its value, 0.0049, when corrected for temperature, is very near the value 0.0052, obtained with ammonium cyanate alone at 50.1°. Ammonia then behaves towards ammonium cyanate in precisely the same way as potassium sulphate does, in harmony with the requirements of the dissociation theory.

We find, then, that the consistent application of the theory of electrolytic dissociation accounts for the bimolecular nature of the transformation of ammonium cyanate into urea, the quantitative influence on it of dilution, and of the presence of potassium sulphate, potassium cyanate, ammonium sulphate, and ammonia. On no other theory, as it appears to us, can even a qualitative explanation of our results be given.

Interaction of Urea and Silver Nitrate.

As we have already stated, the silver cyanate used in these experiments was prepared by heating semi-normal silver nitrate solution at 100° with five equivalents of urea. The yield of silver cyanate was in no case greater than 88 per cent. of that theoretically possible, continued heating causing no further precipitation beyond this quantity. The silver cyanate is, of course, produced by the interaction of the silver nitrate and the ammonium cyanate formed from the urea. As the ammonium cyanate is removed from the solution as fast as it is formed, it might, at first sight, be expected that, since a great excess of urea is present, the action would go on until practically all the silver is precipitated, unless the silver cyanate were comparatively soluble in water at 100° . The solubility, however, is not great, 100 c.c. of a saturated aqueous solution of silver cyanate at 100° containing only 0.12 gram of the salt, that is, the solution is 0.008 normal. In the actual solution this solubility is much diminished by the presence of undecomposed silver nitrate, yet it is the minute quantity of silver cyanate dissolved which determines the stoppage of the action at a point so much short of the possible yield.

The point of equilibrium may be easily calculated on the dissociation theory as follows. We found that at 100° , 5 per cent. of a decinormal solution of urea was transformed into ammonium cyanate. Assuming, for simplicity's sake, that the ammonium cyanate is entirely dissociated, which is very nearly the case, we have the following equation to express the equilibrium between the urea and the cyanate.

$$0.005 \times 0.005 = K \times 0.095.$$

The magnitudes on the left-hand side are the active masses of the ammonium and cyanic ions in terms of a normal solution; on the right-hand side K is the ratio of the velocity constants (which remains unaltered so long as the temperature is the same) and 0.095 is the active mass of the urea. From this equation we obtain

$$K = 0.000263,$$

which determines the equilibrium between the urea and the ammonium and cyanic ions.

Now, when silver nitrate is added, the cyanic ions can only come from the unprecipitated silver cyanate, so that their number is determined by the solubility of the silver cyanate. According to the theory developed by Nernst, and experimentally verified by him and by Noyes, the solution equilibrium is of such a kind that the concentration of the *undissociated* silver cyanate in solution remains constant. But for the equilibrium between dissociated and undissociated silver cyanate we have the equation

$$\text{Act. mass Ag} \times \text{act. mass CNO} = K' \times \text{act. mass AgCNO.}$$

As K' is a constant, and the active mass, that is, the concentration, of the undissociated silver cyanate remains constant, the right-hand side of the equation is constant, and is very nearly equal to 0.000064; for the concentration of the saturated solution of silver cyanate at 100° is 0.008, and this may be taken as the active mass of each ion, the cyanate being almost entirely dissociated, so that the left-hand side is $0.008 \times 0.008 = 0.000064$. We are now in possession of the two constants which enable us to calculate the equilibrium. The solubility of the silver cyanate determines the number of cyanic ions, which again determines the number of ammonium ions required to produce equilibrium with the urea. But the number of ammonium ions corresponds to the number of silver ions which have disappeared, and this number influences the solubility of the silver cyanate. The problem is, therefore, to find the concentration of cyanic ions which will be in equilibrium on the one hand with the undissociated (and solid) silver cyanate, and on the other with the urea. Let the concentration of the ammonium nitrate in solution at the equilibrium be x -normal, then the concentration of the silver nitrate will be $0.5 - x$, and of the urea $2.5 - x$. The concentration of the cyanic ions is determined by the last equation to be 0.000064 divided by the concentration of the silver ions. This concentration may be taken as equal to $0.5 - x$, as the silver nitrate is nearly all dissociated, and the quantity coming from the silver cyanate in solution is very small. We are justified in making these assumptions, which simplify the treatment greatly, by the results of Noyes (*Zeit. physikal. Chem.*, 1890, **6**, 246), who investigated the parallel case of the solubility of silver bromate in presence of silver nitrate. The detailed treatment of the question is given by him at the place cited. The concentration of the cyanic ions is therefore $0.000064/(0.5 - x)$. For the equilibrium between ammonium cyanate and urea we have, then,

$$\begin{aligned} \text{Ammonium} \times \text{cyanic ion} &= K \times \text{urea} \\ x\{0.000064/(0.5 - x)\} &= 0.000263(2.5 - x). \end{aligned}$$

Solving this equation, we find $x = 0.45$ to be the concentration of the ammonium nitrate in solution at the equilibrium point. This is equivalent to the quantity of silver cyanate formed, so that we have $0.45/0.5 = 90$ per cent. of the silver nitrate transformed, the yield actually obtained being 88 per cent.

As it might be thought that the agreement between the calculated and the observed numbers is here due to a chance coincidence from balancing of errors, another experiment was made in which the urea was taken in quantity equivalent to the silver nitrate. It had therefore the concentration 0.5. For this we have the equation of equilibrium

$$x\{0.000064/(0.5 - x)\} = 0.000263(0.5 - x),$$

the only difference being the substitution of 0.5 for 2.5 in the second member of the last equation. Here we find $x = 0.25$. That is, when the silver nitrate and urea are both semi-normal in the solution, 50 per cent. of the silver nitrate should be transformed into silver cyanate. The actual experiment was conducted as follows. Silver nitrate (17 grams) and urea (6 grams) were dissolved separately in hot water, filtered, mixed, heated, and stirred to collect a slight brown precipitate, which was filtered off. The clear solution was made up to 200 c.c. and heated at 100° for four hours with a reflux condenser. After cooling, the silver cyanate was collected, drained, washed, dried, and weighed. The weight obtained was 7.27 grams or 48.33 per cent. of the possible quantity, the predicted yield being 7.5 grams or 50 per cent. The agreement is excellent when the loss in weight by washing is considered. The amount transformed, as estimated by titration of an aliquot portion of the filtrate, was 50.3 per cent. No further precipitate was obtained by continued heating of the solution.

We thus see that the theory of electrolytic dissociation not only enables us to understand the simple equilibrium between urea and ammonium cyanate, but also to account for and predict the phenomena when this equilibrium is complicated by the presence of a salt which reacts with one of these substances.

Heat of Transformation.

We have seen that the influence of temperature on the equilibrium point between urea and ammonium cyanate is very slight, and this corresponds to a small heat of transformation. The formula for calculating the thermal effect cannot be applied in strictness, as the data for the end-points at different temperatures are not sufficiently definite, so that we cannot even say with certainty whether the transformation in dilute solution is accompanied by evolution or absorption of heat; most probably there is a slight heat evolution on the conversion of the cyanate into urea.