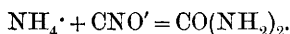


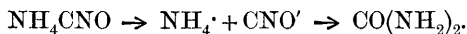
## XLVIII.—*Velocity of Urea Formation in Aqueous Alcohol.*

By JAMES WALKER, Ph.D., D.Sc., and SYDNEY A. KAY, B.Sc.

In a previous paper (Walker and Hambly, *Trans.*, 1895, **67**, 746), it was shown that the transformation of ammonium cyanate into urea in aqueous solution obeys the formula of a bimolecular, and not that of a unimolecular, reaction; and by the influence of various foreign substances in accelerating the reaction, the active molecules were proved to be ammonium ions and cyanic ions, so that the transformation may be formulated thus:



It appeared to be of considerable interest, from the point of view of the electrolytic dissociation hypothesis, to investigate the action more closely than has hitherto been done, in order to determine exactly the parts played by the dissociated and by the undissociated cyanate respectively. In decinormal aqueous solution, which was the concentration usually employed, ammonium cyanate is dissociated to the extent of about 80 per cent. There consequently remains 20 per cent. undissociated, and we must assume that this amount passes first into the form of ions before its transformation into urea can take place. The process of urea formation from ammonium cyanate is therefore to a certain extent not a direct action, but an action taking place in two stages, namely



From our general experience of chemical actions in aqueous solution, and from the rate of change in the electric conductivity of solutions with varying conditions of dilution, &c., we know that the processes of dissociation and reassociation of ions are so rapid as to escape measurement by the ordinary methods at our disposal. The first stage of the complex reaction, then, is practically instantaneous, the second stage alone occupying the whole time required for the complete transformation, even though we suppose the two stages to proceed successively instead of simultaneously, as is actually the case. The rate that we measure is consequently, within the experimental error, the rate of the second stage, and the action appears to be a simple bimolecular reaction. A theoretical discussion of the speed of graded actions of this and of other types will be given in another place. The question to be answered at present is, how the speed of urea formation as actually observed depends on the degree of dissociation of the ammonium cyanate.

Let the concentration of the ammonium cyanate originally present be  $A$  gram-molecules per litre, that of the urea originally present being  $B$ ; and let  $x$  be the quantity of the urea produced after the action has gone on for  $t$  minutes. The concentration of the cyanate is then  $A - x$ . If at this concentration the degree of dissociation of ammonium cyanate is  $p$ , then we shall have  $(1 - p)(A - x)$  for the concentration of the undissociated cyanate and  $p(A - x)$  for the concentration of each of the ions formed on dissociation. The rate of urea formation at the time  $t$  will therefore be

$$\frac{dx}{dt} = kp^2(A - x)^2 - k'(B + x)$$

where  $k$  and  $k'$  are the velocity constants of urea formation and decomposition respectively. At the end-point of the reaction, when the quantities of urea formed and decomposed in a given time are equal, we have

$$k\pi^2(A - \xi)^2 = k'(B + \xi),$$

$\pi$  and  $\xi$  being the values of  $p$  and  $x$  at that point. For the ratio of the velocity constants, we have therefore

$$\frac{k'}{k} = \frac{\pi^2(A - \xi)^2}{B + \xi} = \pi^2 K$$

or  $k' = \pi^2 K k$

if we make  $K = \frac{(A - \xi)^2}{B + \xi}$  (compare Walker and Appleyard, Trans., 1896, 69, 195). Substituting this value for  $k'$  in the first equation, we get

$$\frac{dx}{dt} = k \{ p^2(A - x)^2 - \pi^2 K(B + x) \} \quad \dots \dots \dots \quad \text{I}$$

If we integrate this finally on the supposition that  $p$  remains constant over the range included in the integration, and that  $x = 0$  when  $t = 0$ , we have

$$k = \frac{1.15}{p^2 t \sqrt{a^2 - b}} \log \frac{b - x(a - \sqrt{a^2 - b})}{b - x(a + \sqrt{a^2 - b})} \quad \dots \dots \dots \quad \text{II}$$

where  $a = \frac{1}{2}(2A + r^2K)$ ,  $b = A^2 - r^2KB$ , and  $r = \pi/p$ .

In reality,  $p$  does not remain constant, but varies slowly with  $x$ . If, however, the diminution in the concentration of the ammonium cyanate is not very great, the variation of  $p$  is so small as to permit of it being considered *nil*.

It has been shown (Trans., 1895, 67, 753) that, for decinormal solutions, the reverse transformation of urea into cyanate may be neglected if for  $A$  we substitute  $E$ , the whole range between the beginning and the point where equilibrium is reached, that is,  $\xi$

when the transformation is not disturbed by secondary processes. The simplified expression for the reaction is then

$$\frac{dx}{dt} = k_1 p^2 (E - x)^2 \dots\dots\dots \text{III}$$

On integration, we obtain

$$k_1 = \frac{1}{p^2 t E} \cdot \frac{x}{E - x} \dots\dots\dots \text{IV}$$

The "constant,"  $k_1$ , here introduced is not equal to the real constant  $k$  of the direct transformation, but is a function of  $k$  and  $k'$ . The calculation, however, by which it is obtained is much simpler than the tedious evaluation of  $k$  from equation II, and it is not difficult to find a closely approximate relation between it and the real constant  $k$ . If the reaction proceeds between two given points, its rate may be expressed exactly by equation I, and approximately by equation III. We may therefore equate the right-hand members of I and III, and so obtain

$$k\{p^2(A - x)^2 - \pi^2 K(B + x)\} = k_1 p^2 (E - x)^2$$

$$\text{or } k = \frac{k_1 (E - x)^2}{(A - x)^2 - \pi^2 K(B + x)} \dots\dots\dots \text{V}$$

Instead, then, of the laborious calculation of  $k$  for each observation, we may substitute the simple calculation of  $k_1$ , and convert the mean of the values of  $k_1$  thus obtained into a corresponding mean value of  $k$  by making use of equation V. It is to be observed that this process is only approximate, and cannot be employed when  $E$  differs greatly from  $A$ . In such a case,  $K$  is large and  $k_1$  does not remain constant. The expression for the ratio  $k/k_1$  varies also with  $x$ , and in general it may be said that, if  $k/k_1$  is found to be less than 0.9, it is advisable to calculate  $k$  directly from equation II.

Owing to the variability of  $p$  with the concentration, the values of  $x$  introduced into either of the formulæ must be small. It is therefore necessary to consider separately small portions of the total change, and compare the constants obtained from each of them, rather than to consider the action as a whole, and calculate all values from the initial state. The former method is a much more severe test of a constant than the latter, as will be seen in the sequel.

#### *Mode of Experiment.*

The proportions of ammonium cyanate and urea in the solution at any given time were formerly estimated by precipitating the cyanate as silver salt with a known quantity of silver nitrate, filtering, and estimating the excess of silver nitrate in the filtrate by titration. For our present purpose, it was necessary that we should obtain a more accurate, and also, if possible, a more convenient, method of ascertain-

ing the composition of the solution, since comparatively slight experimental errors are so magnified in the constant as often to preclude any satisfactory comparison. We found in the end that determinations of the electric conductivity of the solution, along with a few chemical estimations performed in the manner indicated above, provided all the requisite data for a fairly accurate calculation of the real constant  $k$  under varying conditions.

Mixtures of alcohol and water were used as solvents as well as pure water, in order to alter the degree of dissociation of the cyanate and to determine the specific influence of the alcohol in accelerating or retarding the urea-formation. Aqueous solutions of ammonium cyanate were made in the manner described by Walker and Hambly (*Trans.*, 1895, 67, 748), the concentration being so chosen that when mixed with the appropriate quantity of alcohol, the solution was of the proper strength both as regards alcohol and as regards the sum of the concentrations of urea and ammonium cyanate. Thus, in making a decinormal solution in 90 per cent. alcohol, we first prepared a normal solution of cyanate by shaking silver cyanate with a normal solution of ammonium chloride for a sufficient time, and filtering. During the agitation, a considerable portion of the cyanate formed was converted into urea on account of the high concentration of the solution; for, as has already been shown, the more concentrated the solution is, the more rapidly does the cyanate undergo transformation. The solution was therefore not normal with respect to the ammonium cyanate, but only with respect to the sum of the concentrations of this salt and the urea formed from it. A measured volume of the solution was then mixed with nine times its own volume of absolute alcohol, heated to the temperature of experiment ( $32^{\circ}$ ), and diluted with 90 per cent. alcohol until it occupied exactly ten times its original volume. In this way, we obtained a solution which contained 90 per cent. of alcohol by volume, and was decinormal with regard to ammonium cyanate plus urea. One portion of it was taken for the chemical experiments, the other portion being reserved for measurements of the electric conductivity.

The electrical measurements were made with the apparatus used by Walker and Hambly (this vol., p. 61). The electrodes in the cell were placed farther apart than usual, on account of the resistances measured being comparatively small; and instead of the ordinary vulcanite cover, a tight-fitting cork, through which the electrodes passed, was used to close the cell so as to prevent evaporation and consequent change in the conductivity. All measurements were made at  $32^{\circ}$ .

When the two portions of solution had assumed the temperature of the thermostat, 5 c.c. of the one were removed for a chemical estima-

tion, and simultaneously the conductivity of the other was determined, the time being accurately noted. The conductivity alone was then determined at short intervals, and after a time, simultaneous chemical and electrical readings were again taken. This process was repeated until five or six pairs of chemical and electrical values were obtained at very different stages of the reaction, many intermediate observations of the conductivity having been recorded. The conductivities were then plotted against the corresponding values of the concentrations of ammonium cyanate as given by the chemical readings, and a curve drawn through the points. This curve enabled us then to get the concentration of ammonium cyanate in the solution for any time at which its conductivity had been observed. As a measurement of the conductivity only occupies a few seconds when the solution is in the cell, and is, in addition, very accurate, we were thus in a position to follow the progress of the reaction much more easily and closely than when chemical experiments alone were made. To get rid of the individual errors of the chemical experiments, it was necessary to smoothe the curve for interpolation. Since the curve always approximated to a straight line, straight line values were calculated from the first and last experiments, and the deviations from the linear formula plotted against the conductivities. From the smoothed deviation curve it was then possible to interpolate with great accuracy (compare Ostwald, *Physico-chemical Measurements*, p. 242). This convenient method of following the course of a reaction may be adopted in almost all cases where the chemical change is accompanied by a change in the electric conductivity.

The conductivity of the solution was not due to ammonium cyanate alone, nor did the precipitate with silver nitrate solution consist entirely of silver cyanate. It was found impossible to obtain the solution quite free from ammonium chloride, or from dissolved silver salt; and, as a rule, a small quantity of the former was present. Its amount was in each case determined, and the appropriate correction applied to the concentrations. This correction did not amount to 1 per cent. in the worst cases, and was usually much less. The conductivities were left uncorrected, for, in the first instance, only correct concentrations were required.

It has already been shown (Trans., 1895, 67, 750) that the formation of urea from ammonium cyanate is accompanied by the formation, to a much smaller extent, of ammonium carbonate. The amount of carbonate produced on completion of the transformation was found to be as much as 4 per cent. at 69°, and somewhat less at lower temperatures. As this amount is sufficient to render the application of the exact formula utterly futile, means had to be sought for the elimination of this source of error. Special experiments showed that, after the transformation of the cyanate had proceeded half-way, no carbonate

could be detected in the solution on adding calcium nitrate. Instead, therefore, of following the course of the reaction in one solution, we prepared three different solutions, all of which were decinormal with respect to cyanate *plus* urea, but contained different proportions of these two substances. The first of these solutions was that prepared as above described; the second contained equal portions of the original solution and a decinormal solution of urea; the third was composed of one part of the cyanate solution and three parts of the urea solution. By thus dividing the whole transformation into three parts, we obviated the production of ammonium carbonate and were able to apply the exact formula for the simple action. The replacement of water by alcohol diminishes the amount of carbonate produced; indeed, in solutions containing 70 and 90 per cent. of alcohol, the presence of carbonate could not be proved at all, even when the transformation was at an end.

Experiments were made to find the equilibrium point for each solvent in order that the constant  $K$ , necessary in the calculation, might be determined. The effect of the replacement of water by alcohol is to diminish the amount of cyanate in the solution at the point of equilibrium; whilst in decinormal aqueous solution, 3.2 per cent. of the cyanate remains untransformed at 32°, only 1 per cent. remains when 90 per cent. alcohol is used as solvent. To ascertain the end-points as accurately as possible, solutions were made up containing the cyanate and urea in approximately the proportions expected on equilibrium. In this way, equilibrium was attained in a comparatively short time, and the formation of carbonate avoided.

#### *Data for Degree of Dissociation.*

It was impossible for us to estimate exactly the degree of dissociation of ammonium cyanate at any particular dilution in a given mixture of alcohol and water, for in the first place a pure solution of ammonium cyanate could not be prepared, and in the second place could not be kept for a sufficient length of time without partial transformation into urea. In pure water, the last difficulty is not so serious as the first, as the transformation proceeds slowly at the ordinary temperature in dilute solutions; in mixtures of alcohol and water, however, the rate is much increased, so that considerable uncertainty would be introduced owing to this cause alone. The most probable assumption to make, and the one least likely to lead to serious error, was that the effect of the substitution of alcohol for water in the solvent would be the same for ammonium cyanate as it was found to be for diethylammonium chloride (Walker and Hambly, this vol., pp. 64—66), at least so far as the molecular conductivity at infinite dilution is concerned. By taking the quotient of the molecular conductivity as determined from any pair of chemical and electrical experiments by the molecular conductivity at infinite dilution as given by the method above suggested, we should get

an approximate value of the degree of dissociation at the dilution found from the chemical experiment. No doubt the values thus obtained are liable to considerable error, but it is an error which affects all constants for the same solvent equally; so that it is only in the comparison of the constants for different solvents with each other that uncertainty is encountered.

It is known that the molecular conductivities of corresponding potassium and ammonium salts at infinite dilution in water are practically identical. We therefore made a set of experiments on the conductivity of potassium cyanate which had been purified by recrystallisation from boiling 90 per cent. alcohol, and was proved to be free from sulphate, carbonate, and cyanide. This gave for aqueous solutions 152 as the probable value of  $\mu_{\infty}$  at 32°. The values for the mixtures of alcohol and water, as deduced by the method indicated above, were

Per cent. alcohol by vol....	10	30	49	72	90
Mol. cond. at $\infty$ .....	121	78	62	55.5	55

#### *Aqueous Solutions.*

The quantity of ammonium cyanate remaining in the decinormal solution which had undergone complete transformation at 32° was found to be 0.0032 gram-molecules per litre. From this we obtain  $K = 0.0001058$ . It is necessary in the case of aqueous solutions to calculate the constant  $k$  by means of equation II, as the simpler formula leads to doubtful results. Three solutions were examined, each having approximately half the cyanate concentration of the preceding one.

#### I.

$$A = 0.0942$$

$$B = 0.0058$$

$t$	$A - x$	$x$	$kp^2$
635	0.0747	0.0195	0.00435
1365	0.0604	0.0338	0.00435
1740	0.0549	0.0393	0.00437
2760	0.0445	0.0497	0.00430

$$\text{Mean } 0.00434$$

#### II.

$$A = 0.0471$$

$$B = 0.0529$$

$t$	$A - x$	$x$	$kp^2$
620	0.0414	0.0057	0.00473
1305	0.0367	0.0104	0.00462
1730	0.0342	0.0129	0.00465
2770	0.0294	0.0177	0.00464

$$\text{Mean } 0.00466$$

## III.

A = 0.0236.

B = 0.0764.

$t$	A - $x$	$x$	$k p^2$
1330	0.0205	0.0031	0.00490
2770	0.0181	0.0055	0.00475
4190	0.0161	0.0075	0.00482
5685	0.0145	0.0091	0.00482

Mean 0.00482

In these tables,  $t$  is given in minutes and all concentrations in gram-molecules per litre.  $A - x$  is the concentration of cyanate at the time  $t$ , as determined by the combined chemical and electrical methods. The values in the last column are the calculated values of the expression  $\frac{1.15}{t \sqrt{a^2 - b}} \log \frac{b - x(a - \sqrt{a^2 - b})}{b - x(a + \sqrt{a^2 - b})}$ , and are practically equal to the constants which would be obtained if electrolytic dissociation were entirely neglected. The following table shows more clearly the increase of this value with the dilution :

A	$k p^2$	$p$	$k$
0.0942	0.00434	0.852	0.00598
0.0471	0.00466	0.880	0.00602
0.0236	0.00482	0.909	0.00584

Mean 0.00595

This increase is accounted for on the theory of electrolytic dissociation by the increase in the relative number of ions, which are here the reacting substances, as the dilution increases. To get the real constant, the values must be divided by  $p^2$ . The numbers for  $p$  in the third column are those which were observed directly in the case of potassium cyanate solutions, and must be very nearly equal to the numbers for ammonium cyanate solutions, on account of the general equality in the conductivity of corresponding potassium and ammonium salts already referred to. Even though the absolute values are not identical, the relative variation of  $p$  will certainly be the same in the two cases within the experimental error of the velocity determinations. Dividing by  $p^2$ , we get the numbers in the fourth column, which represent the real constant for the interaction of the ions. The deviation from the mean is now less than 2 per cent. and irregular, instead of more than 6 per cent. with a steady increase, as it was when the degree of dissociation was neglected. In view of the various sources of error, this constancy is fairly satisfactory, and it will be seen that, in the case of the alcoholic solutions, the agreement is still better.

It is evident, from the constancy of  $k$ , that the presence of urea has



no influence on the speed of the transformation, except in so far as it takes part in the reversed action. As it was of some importance to establish this with certainty, we made a series of comparative observations with N/20 cyanate solution, the solvent in the one case being water, and in the other a 3 per cent. solution of urea. According to equation II, the quantities of cyanate transformed in these solutions in two days should be equal within our experimental error, provided the urea has no other effect than that of reversing the transformation. This we found to be the case, so that we are justified in concluding that the replacement of a small proportion of the solvent water by urea has no appreciable effect on the rate at which the transformation proceeds.

*Solutions in 10 per cent. Alcohol.*

The equilibrium value of cyanate in this case is 0.0030, whence  $K = 0.0000927$ . Three solutions were again prepared, and the constant calculated from equation II.

I.			
A = 0.0936		B = 0.0064	
<i>t</i>	A - <i>x</i>	<i>x</i>	<i>kp</i> <sup>2</sup>
270	0.0821	0.0115	0.00553
535	0.0735	0.0201	0.00546
1655	0.0505	0.0431	0.00551
			Mean 0.00550

II.			
A = 0.0468		B = 0.0532	
<i>t</i>	A - <i>x</i>	<i>x</i>	<i>kp</i> <sup>2</sup>
1290	0.0345	0.0123	0.00594
1705	0.0317	0.0151	0.00605
2790	0.0265	0.0203	0.00593
			Mean 0.00597

III.			
A = 0.02372		B = 0.07628	
<i>t</i>	A - <i>x</i>	<i>x</i>	<i>kp</i> <sup>2</sup>
1290	0.02000	0.00372	0.00620
1700	0.01900	0.00472	0.00630
			Mean 0.00625
A	<i>kp</i> <sup>2</sup>	<i>p</i>	<i>k</i>
0.0936	0.00550	0.841	0.00777
0.0468	0.00597	0.881	0.00770
0.0237	0.00625	0.900	0.00772
			Mean 0.00774

Here once more we see that the value,  $kp^2$ , in which the change of dissociation with dilution is neglected, gives steadily increasing values, whilst  $k$ , in which this change is involved, remains constant. The values of  $p$  were determined from the conductivities at the beginning of each series in the manner indicated on p. 494.

In all the alcoholic solutions, the composition of the solvent is given by volume, and not by weight.

*Solutions in 30 per cent. Alcohol.*

When equilibrium is attained in decinormal solution, the concentration of the ammonium cyanate is only 0.0018 gram-molecule per litre, which corresponds to  $K = 0.000033$ . The comparatively small difference between A and E enables us here to use the simple formula, with the correcting factor, for the two most concentrated solutions; but equation II must be used to calculate the true constant of the most dilute solution.

I.

	A = 0.0920	E = 0.0902	B = 0.0080	
$t$	A - $x$	E - $x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E-x}$
195	0.0789	0.0771	0.0131	0.00966
455	0.0672	0.0654	0.0248	0.00925
1325	0.0437	0.0419	0.0483	0.00964
1665	0.0387	0.0369	0.0533	0.00962
				Mean 0.00954

Dividing this mean by  $k_1/k = 1.040$ , we obtain 0.00918 for  $kp^2$ .

II.

	A = 0.0461	E = 0.0443	B = 0.0539	
$t$	A - $x$	E - $x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E-x}$
190	0.0425	0.0407	0.0036	0.0105
450	0.0386	0.0368	0.0075	0.0102
1370	0.0288	0.0270	0.0173	0.0106
1695	0.0265	0.0247	0.0196	0.0106
				Mean 0.0105

Dividing by  $k_1/k = 1.09$ , we obtain  $kp^2 = 0.00964$ .

## III.

A = 0.0238

B = 0.0762

$t$	A - $x$	$x$	$kp^2$
445	0.0215	0.0023	0.0102
1365	0.0180	0.0058	0.0100
2700	0.0146	0.0092	0.0099

Mean 0.01003

A	$kp^2$	$p$	$k$
0.0920	0.00918	0.836	0.0131
0.0425	0.00964	0.870	0.0127
0.0215	0.01003	0.883	0.0129

Mean 0.0129

The general features exhibited by the solutions in 30 per cent. alcohol are the same as before, namely, increase of  $kp^2$  with the dilution, and practical constancy of  $k$ .

*Solutions in 49 per cent. Alcohol.*

On equilibrium being reached, there remained 0.0016 ammonium cyanate untransformed in a decinormal solution. This low value enables us to use the simple formula with correction-factor throughout.

## I.

A = 0.0878

E = 0.0862

B = 0.0122

$t$	A - $x$	E - $x$	$x$	$\frac{1}{Et} \cdot \frac{x}{E-x}$
41	0.0823	0.0817	0.0055	0.0193
121	0.0730	0.0714	0.0148	0.0197
180	0.0683	0.0667	0.0195	0.0188
283	0.0605	0.0589	0.0273	0.0190
337	0.0572	0.0566	0.0306	0.0189
508	0.0488	0.0472	0.0390	0.0189
606	0.0450	0.0434	0.0428	0.0189

Mean 0.0191

Dividing the mean value by 1.04, we get  $kp^2 = 0.0184$ .

## II.

A = 0.0477

E = 0.0461

B = 0.0523

$t$	A - $x$	E - $x$	$x$	$\frac{1}{Et} \cdot \frac{x}{E-x}$
215	0.0397	0.0381	0.0080	0.0212
385	0.0357	0.0341	0.0120	0.0198
605	0.0312	0.0296	0.0165	0.0200

Mean 0.0203

The correction factor is in this case 1.07, so that we obtain  $kp^2 = 0.0190$ .

## III.

	A = 0.0244	E = 0.0228	B = 0.0756	
<i>t</i>	A - <i>x</i>	E - <i>x</i>	<i>x</i>	$\frac{1}{tE} \cdot \frac{x}{E-x}$
210	0.0221	0.0205	0.0023	0.0234
595	0.0190	0.0174	0.0054	0.0229
				Mean 0.0231

The value of  $kp^2$  obtained from this mean is 0.0201, the correcting factor being 1.15.

The last two series are unfortunately very short, owing to the failure of the thermoregulator during the night.

A	$kp^2$	<i>p</i>	<i>k</i>
0.0823	0.0184	0.795	0.0291
0.0397	0.0190	0.802	0.0296
0.0221	0.0201	0.822	0.0297
			Mean 0.0295

*Solutions in 72 per cent. Alcohol.*

The effect of the alcohol in diminishing the degree of dissociation becomes very marked only when the solution contains more than 50 per cent. of alcohol (compare this vol., p. 68). We might therefore expect to see this influence exhibited in 72 per cent. alcohol even with the simple constant calculated in the ordinary way from the beginning of the action. In water this is not so, for the constant calculated in this manner exhibits no tendency to increase, as may be seen in previous papers on urea formation.

As no carbonate was formed in 72 per cent. alcohol, we made all the experiments with a single solution, the results for which are given below. At the end of the transformation, the strength of the cyanate remaining is 0.0014 gram-molecule per litre.

	A = 0.08480	E = 0.08340	B = 0.01660	
<i>t</i>	A - <i>x</i>	E - <i>x</i>	<i>x</i>	$\frac{1}{tE} \cdot \frac{x}{E-x}$
16	0.08014	0.07874	0.00466	0.0444
50	0.07181	0.07041	0.01299	0.0442
80	0.06585	0.06445	0.01895	0.0441
110	0.06070	0.05930	0.02410	0.0443
141	0.05602	0.05462	0.02858	0.0446
181	0.05112	0.04972	0.03368	0.0449
230	0.04600	0.04460	0.03880	0.0453
268	0.04268	0.04078	0.04212	0.0462
348	0.03706	0.03566	0.04774	0.0462
427	0.03245	0.03105	0.05235	0.0473
538	0.02768	0.02628	0.05712	0.0484

The increase of the expression  $\frac{1}{tE} \cdot \frac{x}{E-x}$  as the dilution and dissociation increase is unmistakable, and cannot be attributed to an error in the determination of the end-point; for even though the reversed action is assumed to be altogether absent, there is still a rise, though a smaller one, in the values of the last column.

In order to compare the results with those obtained for the other solutions, four different stages of the transformation were taken as starting points, and the times and changes in concentration reckoned from them. The first set is identical with the first four values of the preceding table, and gives  $\frac{1}{tE} \cdot \frac{x}{E-x} = 0.0442$  as a mean, from which we obtain  $kp^2 = 0.0428$  by division with the correcting factor 1.034.

## II.

A = 0.06070		E = 0.05930		B = 0.03930	
<i>t</i>	A - <i>x</i>	E - <i>x</i>	<i>x</i>	$\frac{1}{tE} \cdot \frac{x}{E-x}$	
31	0.05602	0.05462	0.00468	0.0466	
71	0.05112	0.04972	0.00958	0.0458	
120	0.04600	0.04460	0.01470	0.0463	
				Mean	0.0462

This, on division by  $k_1/k = 1.048$ , gives  $kp^2 = 0.0441$ .

## III.

A = 0.05112		E = 0.04972		B = 0.04888	
<i>t</i>	A - <i>x</i>	E - <i>x</i>	<i>x</i>	$\frac{1}{tE} \cdot \frac{x}{E-x}$	
49	0.04600	0.04460	0.00512	0.0469	
87	0.04268	0.04078	0.00844	0.0478	
167	0.03706	0.03566	0.01406	0.0475	
				Mean	0.0474

The correcting factor 1.057 gives  $kp^2 = 0.0449$ .

## IV.

A = 0.03706		E = 0.03566		B = 0.06294	
<i>t</i>	A - <i>x</i>	E - <i>x</i>	<i>x</i>	$\frac{1}{tE} \cdot \frac{x}{E-x}$	
79	0.03245	0.03105	0.00461	0.0528	
190	0.02768	0.02628	0.00938	0.0527	
				Mean	0.0528

The correcting factor is here 1.080 and gives  $kp^2 = 0.0489$ .

$\Lambda$	$kp^2$	$p$	$k$
0.08014	0.0428	0.660	0.098
0.06070	0.0441	0.689	0.093
0.05112	0.0449	0.705	0.091
0.03706	0.0489	0.733	0.091
			Mean 0.093

*Solutions in 90 per cent. Alcohol.*

The change in the dissociation during the progress of the reaction is here at its greatest, and this series, therefore, offers the best test of the applicability of the dissociation theory to the question in hand. The conditions for the action also are unusually favourable. No carbonate is formed, and only 1 per cent. of the total quantity of material remains as untransformed cyanate when equilibrium is established. The series has been split up into five portions, for the purpose of comparing the constants at different dilutions.

## I.

$A = 0.08080$

$E = 0.07980$

$B = 0.01920$

$t$	$A - x$	$E - x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E - x}$
15.5	0.06948	0.06848	0.01132	0.134
30	0.06135	0.06035	0.01945	0.134
				Mean 0.134

$k_1/k = 1.025$ , whence  $kp^2 = 0.131$ .

## II.

$A = 0.05398$

$E = 0.05298$

$B = 0.04602$

$t$	$A - x$	$E - x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E - x}$
15	0.04841	0.04741	0.00557	0.148
30	0.04367	0.04267	0.01031	0.152
				Mean 0.150

$k_1/k = 1.038$ , whence  $kp^2 = 0.145$ .

## III.

$A = 0.03659$

$E = 0.03559$

$B = 0.06341$

$t$	$A - x$	$E - x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E - x}$
15	0.03340	0.03240	0.00319	0.184
31	0.03057	0.02957	0.00602	0.184
				Mean 0.184

$k_1/k = 1.057$ , whence  $kp^2 = 0.174$ .

## IV.

$A = 0.03057$

$E = 0.02947$

$B = 0.06943$

$t$	$A - x$	$E - x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E - x}$
20.5	0.02761	0.02661	0.00296	0.184
42	0.02491	0.02391	0.00566	0.190
				Mean 0.187

$k_1/k = 1.070$ , whence  $kp^2 = 0.175$ .

## V.

$A = 0.02491$

$E = 0.02391$

$B = 0.07509$

$t$	$A - x$	$E - x$	$x$	$\frac{1}{tE} \cdot \frac{x}{E - x}$
28	0.02205	0.02105	0.00286	0.203
66	0.01905	0.01805	0.00586	0.206
				Mean 0.204

$k_1/k = 1085$ , whence  $kp^2 = 0.188$ .

The following table gives a comparison of the values at the different dilutions :

A.	$kp^2$ .	$p$ .	$k$ .
0.08080	0.131	0.472	0.588
0.05398	0.145	0.512	0.554
0.03659	0.174	0.545	0.586
0.03057	0.175	0.551	0.576
0.02491	0.188	0.572	0.576
			Mean 0.575

In the second column, where the values of the constants are uncorrected for the change in the degree of dissociation, there is a steady rise, the difference between the strongest and weakest solutions being 43 per cent. of the value of the former. In the last column, where the change in the dissociation is allowed for, the values oscillate about the mean, and the difference between the highest and lowest concentrations is now only 2 per cent.

In view of the considerable experimental difficulties encountered, and the fact that the mode of calculation emphasises the errors of individual experiments, the agreement between the actual values and those required by the theory must be accounted satisfactory.

*Influence of Ethylic Alcohol on the Rate of Urea Formation.*

Alcohol might be expected to exert two entirely different kinds of influence on the rate of urea formation. As it replaces the water in

the solvent, it diminishes, on the one hand, the number of active molecules, namely, ammonium ions and cyanic ions, whilst, on the other, it should have an effect on the actual rate at which these molecules interact, by changing the nature of the medium in which the action takes place.

The first mode of action has been discussed at length in the paper by Walker and Hambly already referred to (this vol., p. 61).

The second mode of action may be seen in the comparison of the constants  $k$  for the various solvents.

Percentage of Alcohol by volume	$k$	$k\rho^2$
0	0.00595	0.00434
10	0.00774	0.00550
30	0.0129	0.00918
49	0.0295	0.0184
72	0.093	0.0428
90	0.575	0.131

The value of  $k$  for 90 per cent. alcohol is nearly 100 times as great as the value for pure water. The alcohol then exerts an enormous accelerating influence on the action between the ions, and this influence entirely outweighs the retardation which the alcohol effects by diminishing the number of active molecules. The values of  $k\rho^2$  in the last column give approximately the total effect of the alcohol on the rate of urea formation in the strongest solutions examined. Here the value for 90 per cent. alcohol is only 30 times the value for pure water, a number corresponding with the increase actually observed. The real constant,  $k$ , for the action between the ions gives the number of gram-molecules per litre which would be transformed in one minute, if the ammonium cyanate solution contained 1 gram-molecule per litre, and were maintained at this concentration, the cyanate being supposed to be fully dissociated.

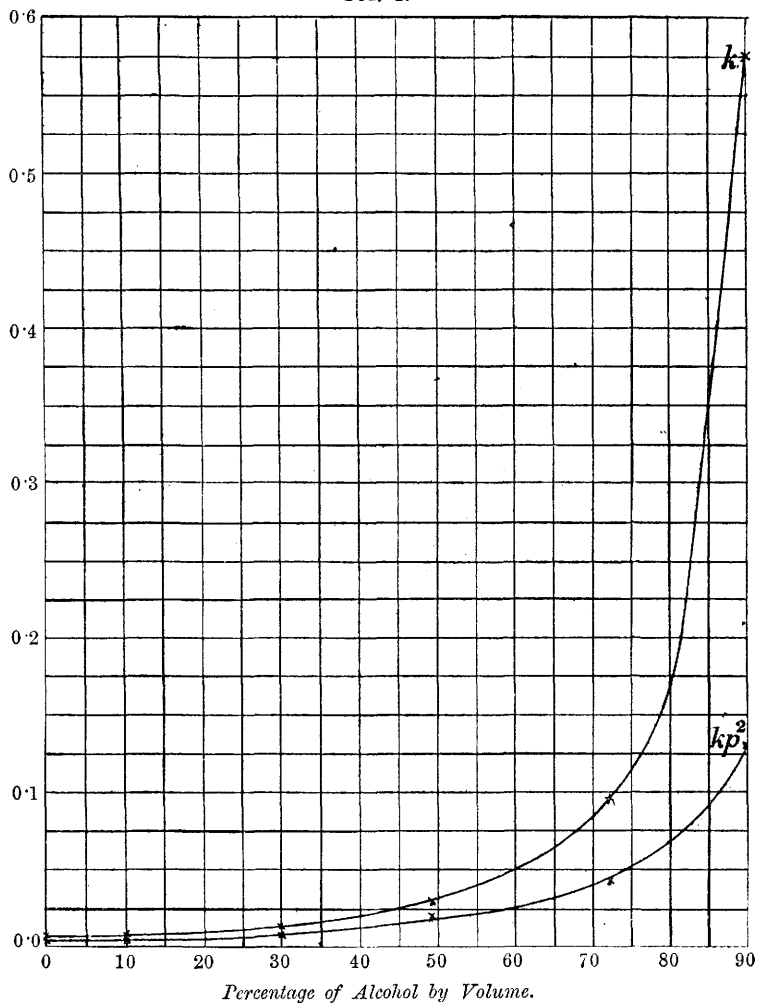
The effect of successive replacement of water by alcohol is best seen in the curves of the accompanying diagram, Fig. 1.

It is evident that the effect on the constant  $k$  is at first comparatively slight, increasing very rapidly only when most of the water is already replaced by alcohol. The effect of the substitution of alcohol for water on the degree of dissociation of a salt in decinormal solution is similar (this vol., 68). The first additions of alcohol reduce the dissociation but slightly; in strongly alcoholic solutions, the reduction produced by a further addition is very marked. We have, then, both the acceleration and the retardation of urea production effected by the alcohol, increasing more and more swiftly as the water is successively replaced. These effects, however, counterbalance each other, so that the total effect pro-



duced by the alcohol does not vary so rapidly as the solution becomes more and more alcoholic as does either of the effects separately. This may be seen from the curve for the values of  $kp^2$ .

FIG. 1.



#### *Influence of other Substances on Urea Formation.*

The experimental results prove beyond doubt that the influence of alcohol as changing the medium in which the ammonium and cyanic ions act is highly favourable to the progress of the reaction. From previously existing data, no conclusion either in this sense or the reverse

could be drawn. Menshutkin (*Zeit. physik. Chem.*, 1890, 6, 41) has shown that the nature of the medium in which a chemical action takes place has a great effect on the speed of the action. The process which he investigated was the combination of triethylamine with ethylic iodide to produce tetrethylammonium iodide. This process is bimolecular, like that which we have studied, and its course is regulated by the simple bimolecular formula. Menshutkin found that solvents of different chemical nature had widely different effects on the rate at which the combination took place, and even that solvents so closely related as the hydrocarbons benzene and hexane gave constants bearing to each other the ratio of 30 to 1. Of the solvents investigated, acetone was one of those most favourable to the reaction. Carrara, on the other hand (*Gazz.*, 1894, 24, 1), found that in the precisely analogous formation of triethylsulphonium iodide from diethylsulphine and ethylic iodide, acetone was the solvent in which the action proceeded most slowly. It is obvious that, from such results, no certain indication can be obtained as to the influence of any particular solvent in promoting or retarding a given action.

Ostwald (*J. pr. Chem.*, 1883, [2], 28, 463) ascertained that the rate of catalysis of ethylic acetate by nitric acid is very slightly increased as the water of the solvent is replaced by acetone. Methylic alcohol, on the other hand, accelerates the action considerably, the effect being of the same order as that which we have found for the influence of ethylic alcohol on the formation of urea.

A few experiments on the rate of formation of unsymmetrical diethyl-urea from diethylammonium cyanate showed that this action also is accelerated by the substitution of ethylic alcohol for water. In decinormal aqueous solution, the amount of cyanate remaining untransformed is about one-third of the total quantity; in 90 per cent. alcohol, almost the whole is converted into urea.

Other neutral substances containing hydroxyl exert the same accelerating influence on urea formation as ethylic alcohol. To compare their effects, decinormal solutions of ammonium cyanate were prepared, the solvent in each case containing 10 per cent. by volume of the foreign substance. The degree of dissociation of the cyanate was assumed to be the same in all the solutions (compare Arrhenius, *Zeit. physikal. Chem.*, 1892, 9, 487). In the following table are exhibited the constants thus obtained, the value for pure water being  $k = 0.00595$  :

Additional substance.	$k$	Percentage increase.
Glycerol .....	0.00763	28.2
Ethylic alcohol .....	0.00777	30.6
Cane-sugar .....	0.00810	36.1
Glycol.....	0.00819	37.7
Methylic alcohol .....	0.00871	46.4
Acetone .....	0.00882	48.2

In every case, there is an acceleration of the action, as may be seen in the last column, which gives the percentage increase on the value obtained for the aqueous solution. Acetone, which contains no hydroxyl group in the ordinary formulation, exercises the greatest accelerating influence of any of the substances investigated. If the accelerations effected by equal weights are compared, the order of influence is the same as above, though the numbers are wider apart.

As has already been stated, urea neither accelerates nor retards the transformation in so far as it acts by changing the nature of the medium. Potassium sulphate and ammonia apparently exercise a slight retarding influence (Trans., 1895, 67, 759 and 764), although it may be rather by affecting the degree of dissociation and the end-point than by the change in the solvent. In any case, their influence is slight, and scarcely comparable with the marked acceleration exerted by substances of alcoholic and ketonic nature. To what this acceleration may be due, we have at present no means of ascertaining.

#### *Heat of Transformation.*

By employing the electrical method of measurement, we found it possible to obtain an approximate value for the heat of transformation of aqueous ammonium cyanate into urea. A decinormal solution was prepared containing 95.23 per cent. of the total substance as urea and 4.77 per cent. as ammonium cyanate. After remaining 30 days in the thermostat at 32°, the solution contained only 3.20 per cent. as cyanate. A similar solution heated for 2 hours at 100° contained 6.50 per cent. as cyanate. To determine if this difference in behaviour at the different temperatures were real, we transferred the solution which had been heated at 100° to the thermostat at 32°; its conductivity fell off from day to day until, after a month, it was below its original value. On heating at 100° once more, the solution showed a conductivity even higher than formerly, but this was probably due to the formation of a trace of carbonate.

Taking the values of 3.20 per cent. cyanate at 32°, and 6.50 per cent. at 100°, we can calculate the heat of transformation by means of van't Hoff's formula

$$2.3 (\log_{10} K_2 - \log_{10} K_1) = \frac{q}{2} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

$T_1$  and  $T_2$  are the absolute temperatures corresponding to those given above;  $q$  is the heat of transformation of 1 gram-molecule;  $K_1$  and  $K_2$  have the same significance as in the equations of the first section, the values being those for  $T_1$  and  $T_2$  respectively. On performing the calculation, we find that the transformation of 1 gram-molecule of cyanate (in the forms of ions) into urea is accompanied by a heat evolution of

4850 cal. This result can only be taken as a rough approximation, but it at least serves to give the order of magnitude of the thermal effect. In the calculation, the dissociation has been supposed to be complete, which is not far from the truth, as the cyanate solution at equilibrium is 0.0032 and 0.0065 normal at the two temperatures.

*Summary.*

A convenient and accurate electrical method is described for following the course of the transformation of ammonium cyanate into urea. This method may be adopted in most cases where a chemical change is accompanied by a change in the electric conductivity.

Ethylic alcohol exerts a marked accelerating action on the rate of urea formation from ammonium cyanate. With 90 per cent. alcohol as solvent, the rate is about 30 times the rate in pure water under similar conditions. The alcohol acts in two ways, which are opposed to each other: (1), it diminishes the degree of dissociation of the cyanate, and therefore the rate of urea formation; (2), it increases the rate at which the ions produced by the dissociation interact. The second mode of action much more than counterbalances the first, so that there is, on the whole, an accelerative effect.

The requirements of the law of mass action are strictly fulfilled for the transformation in water, or mixtures of water and alcohol, if the reverse transformation of urea into cyanate, and the degree of dissociation of the cyanate at the various stages of the process, are taken into consideration.

Methylic alcohol, acetone, glycol, glycerol, and cane-sugar were all found to excite a similar accelerating effect, when part of the water used as solvent was replaced by them.

From the displacement of the point of equilibrium by change of temperature, it appears that the transformation of ammonium cyanate (in the form of ions) into urea is accompanied by a heat-evolution of about 5000 cal. per gram-molecule.

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