LXI.—*The Decomposition of Carbamide.*

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A PAPER on this subject has already been published by one of us (*Zeitsch. physikal. Chem.*, 1902, **41**, 603), in which the decomposition of carbamide by water alone, and by aqueous solutions of acids and alkalis, was studied.

It was shown then that whilst carbamide is decomposed in these circumstances to ammonia and carbon dioxide, the mechanism of the decomposition is not that of a simple hydrolysis. It was shown, further, that the experimental results could be explained satisfactorily if the decomposition of carbamide is regarded as a transformation into ammonium cyanate, which is then converted into ammonia and carbon dioxide.

In the period that has elapsed since the publication of this paper, other papers have been published, which have made us consider more attentively the mechanism of the decomposition of carbamide. We thought that some experiments on the decomposition of carbamide in water-alcohol solutions might throw further light on the reactions involved, and the results of some experiments on the decomposition of carbamide in the presence of alcohol are recorded

in the present paper. Whilst the results are not exactly what we anticipated, they are, we believe, a further proof of the theory that the decomposition of carbamide by water and acids is not a hydrolysis, but a decomposition through ammonium cyanate.

In the tables given below, the results of experiments are given in which the decomposition of carbamide was carried out in water-alcohol solutions.

Experiments were carried out with and without addition of acid (hydrochloric). The method of following the rate of action was the same as that formerly given (*loc. cit.*), namely, titration of the ammonia produced.

This method is entirely satisfactory for acid solutions. When no acid is added, the method only gives approximately correct results; a small part of the decomposed carbamide in this case is present as ammonium cyanate, and titration of ammonium cyanate with acids results in the escape of varying amounts of undecomposed cyanic acid. The numbers here given for solutions to which no acid has been added are therefore probably correct only to about 5 per cent. The numbers given for acid solutions are probably correct to about 1 per cent.

In preparing solutions which contain both alcohol and water, it may be noticed that there are several ways in which the percentage of alcohol can be expressed.

The following method has here been adopted to make a solution containing x per cent. of alcohol: x volumes of absolute alcohol are mixed with $100 - x$ volumes of water. This mixture is then used to dissolve the carbamide or other substance required.

Aqueous alcohol containing as much as 90 per cent. of alcohol was used in these experiments, but no investigations were made with alcohol containing no water (100 per cent.).

Ordinary absolute alcohol (99.33 per cent.) was used in making up the solutions.

In the details of experiments given here:

t refers to the time in minutes measured from the beginning of the experiment.

A is a measure of the concentration of carbamide at the beginning.

x is a measure of the concentration of the decomposed carbamide at time t .

$$k = \frac{1}{t} \log_{10} \frac{A}{A - x}.$$

Most experiments were made in duplicate, and the mean value $(A - x)_m$ was taken in calculating the constant k .

TABLE I.

N/10-Carbamide in water. Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.
0	12.05	12.05	12.05
2760	11.27	11.27	11.27
5760	10.72	10.82	10.77
9960	10.27	10.27	10.27
17280	9.60	9.60	9.60
22920	9.00	9.00	9.00

TABLE II.

N/10-Carbamide in 40 per cent. alcohol. Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.
0	12.05	12.05	12.05
5700	11.15	11.15	11.15
11460	10.90	10.95	10.92
20160	10.35	10.35	10.35
23040	10.15	10.15	10.15

The addition of alcohol diminishes the velocity of decomposition of the carbamide. Comparing the time occupied in the decomposition of one-seventh of the carbamide in tables I and II: for water the value is 9430 minutes; for 40 per cent. alcohol the number is 20,300 minutes.

The effect of alcohol in decreasing the velocity of the reaction is not exactly the result that we expected. Addition of alcohol sometimes decreases and sometimes increases the velocity of reactions as measured for aqueous solutions, but it more usually increases the velocity. In particular, it increases the velocity of transformation of ammonium cyanate into carbamide (Walker and Kay, T., 1897, 71, 504), and the decomposition of carbamide is closely related to its formation.

The action of acids on carbamide is a somewhat simpler reaction to study practically than the decomposition of carbamide starting with a neutral solution, as the ammonium cyanate formed is immediately decomposed by the acid. The only detectable products of decomposition in this case are ammonia and carbon dioxide.

The results for the action of acids on carbamide are given below.

As one of us has already shown that the free carbamide in a solution of carbamide hydrochloride is the active carbamide in the decomposition, experiments were made to discover whether addition of alcohol to a solution of carbamide and hydrochloric acid had any marked effect on the hydrolysis of the carbamide hydrochloride.

The amount of free acid was determined by the effect of the solution on the hydrolytic decomposition of sucrose at 40°.

TABLE III.

N/10-Hydrochloric acid and 10 per cent. of sucrose in water.

As before,

$$k = \frac{1}{t} \log_{10} \frac{A}{A-x}.$$

<i>t</i> .	<i>A</i> - <i>x</i> .	<i>k</i> .
0	58.0	—
10	54.8	0.00246
20	51.5	0.00258
36	46.5	0.00266
50	42.6	0.00268
64	39.0	0.00269
Mean.....0.00265		

TABLE IIIa.

N/10-Hydrochloric acid + 10 per cent. of sucrose + *M*/20-carbamide in water.

<i>t</i> .	<i>A</i> - <i>x</i> .	<i>k</i> .
0	73.7	—
45	56.6	0.00255
74	47.4	0.00259
86	41.1	0.00259
136	32.6	0.00261
170	26.6	0.00260
210	21.1	0.00259
Mean.....0.00259		

From these figures the concentration of hydrogen ion in the solution containing *M*/20-carbamide is 0.98 of that in the solution containing no carbamide.

TABLE IV.

N/10-Hydrochloric acid and 10 per cent. of sucrose in 25 per cent. alcohol.

<i>t</i> .	<i>A</i> - <i>x</i> .	<i>k</i> .
0	68.7	—
30	57.9	0.00248
60	48.1	0.00258
80	43.0	0.00254
101	37.9	0.00256
120	33.9	0.00256
165	26.1	0.00255
Mean.....0.00255		

TABLE IVa.

N/10-Hydrochloric acid + *M*/20-carbamide with 10 per cent. of sucrose in 25 per cent. alcohol.

<i>t.</i>	<i>A-x.</i>	<i>k.</i>
0	68.8	—
20	61.3	0.00251
45	53.3	0.00246
75	44.7	0.00250
90	41.0	0.00250
150	29.1	0.00249
192	22.8	0.00250
Mean.....0.00250		

The concentration of hydrogen ion in the solution containing *M*/20-carbamide is 0.98 of that in the solution without carbamide.

TABLE V.

N/10-Hydrochloric acid with 10 per cent. of sucrose in 50 per cent. alcohol.

<i>t.</i>	<i>A-x.</i>	<i>k.</i>
0	65.0	—
36	54.4	0.00215
50	50.4	0.00221
63	46.5	0.00231
78	43.0	0.00230
96	39.0	0.00231
109	36.0	0.00236
134	31.1	0.00239
157	27.4	0.00239
182	24.0	0.00238
Mean.....0.00230		

TABLE Va.

N/10-Hydrochloric acid + *M*/20-carbamide with 10 per cent. of sucrose in 50 per cent. alcohol.

<i>t.</i>	<i>A-x</i>	<i>k.</i>
0	64.6	—
62	47.3	0.00218
75	44.9	0.00211
110	37.0	0.00220
134	32.7	0.00221
150	30.0	0.00222
175	26.5	0.00221
191	24.3	0.00222
227	20.3	0.00222
Mean.....0.00220		

The ratio of hydrogen ion in these two experiments is 0.956.

TABLE VI.

N/10-Hydrochloric acid with 10 per cent. of sucrose in 75 per cent. alcohol.

<i>t.</i>	<i>A-x.</i>	<i>k.</i>
0	62.9	—
41	48.8	0.00269
62	42.4	0.00276
73	39.5	0.00277
92	37.0	0.00251
102	34.7	0.00253
110	30.5	0.00286
134	26.5	0.00280
150	23.2	0.00289
164	21.5	0.00284
		Mean.....0.00274

TABLE VIa.

N/10-Hydrochloric acid + *M*/20-carbamide with 10 per cent. of sucrose in 75 per cent. alcohol.

<i>t.</i>	<i>A-x.</i>	<i>k.</i>
0	62.2	—
22	55.3	0.00233
37	50.9	0.00235
56	45.1	0.00249
65	43.0	0.00247
84	37.8	0.00257
101	34.4	0.00255
125	29.8	0.00256
148	25.6	0.00260
163	22.6	0.00270
177	21.1	0.00265
190	19.8	0.00262
		Mean.....0.00258

The ratio of free hydrogen ion in these two experiments is 0.941.

These experiments show that alcohol, in the concentrations used, has very little effect on the hydrolysis of the carbamide hydrochloride.

The next experimental work was on the velocity of decomposition of carbamide in acid solution containing alcohol.

These experiments were carried out at three temperatures, namely, 98.2°, 71.25°, and 61.05°.

The results are given in the following tables.

TABLE VII.

N/10-Carbamide + *N*/10-hydrochloric acid in water. Temperature, 98.2°.

<i>t</i> .	(<i>A</i> - <i>x</i>) ₁ .	(<i>A</i> - <i>x</i>) ₂ .	(<i>A</i> - <i>x</i>) _m .	<i>K</i> · 10 ⁵ .
0	19.70	19.80	19.75	—
60	17.58	17.48	17.53	84.3
141	15.10	15.10	15.10	82.7
170	14.28	14.20	14.24	83.6
268	11.80	11.90	11.85	84.6
479	7.80	7.90	7.85	83.7
601	6.30	6.30	6.30	82.6
Mean.....				83.6

TABLE VIII.

N/10-Carbamide + *N*/10-hydrochloric acid in 10 per cent. alcohol. Temperature, 98.2°.

<i>t</i> .	(<i>A</i> - <i>x</i>) ₁ .	(<i>A</i> - <i>x</i>) ₂ .	(<i>A</i> - <i>x</i>) _m .	<i>K</i> · 10 ⁵ .
0	20.00	20.00	20.00	—
71	17.55	17.60	17.58	78.9
171	14.60	14.60	14.60	79.9
261	12.44	12.45	12.45	78.9
374	10.30	10.30	10.30	77.0
576	7.25	7.20	7.23	76.7
Mean.....				78.3

TABLE IX.

N/10-Carbamide + *N*/10-hydrochloric acid in 20 per cent. alcohol. Temperature, 98.2°.

<i>t</i> .	(<i>A</i> - <i>x</i>) ₁ .	(<i>A</i> - <i>x</i>) ₂ .	(<i>A</i> - <i>x</i>) _m .	<i>K</i> · 10 ⁵ .
0	20.28	20.25	20.27	—
75	17.85	17.80	17.83	74.3
141	15.92	15.85	15.89	75.1
230	—	13.60	13.60	75.4
363	10.98	11.00	10.99	73.2
531	8.27	8.33	8.30	73.0
636	6.95	7.05	7.00	72.6
Mean.....				73.9

TABLE X.

N/10-Carbamide + *N*/10-hydrochloric acid in 40 per cent. alcohol. Temperature, 98.2°.

<i>t</i> .	(<i>A</i> - <i>x</i>) ₁ .	(<i>A</i> - <i>x</i>) ₂ .	(<i>A</i> - <i>x</i>) _m .	<i>K</i> · 10 ⁵ .
0	20.30	20.40	20.35	—
70	18.35	18.40	18.38	63.1
182	15.60	15.60	15.60	63.5
307	12.90	12.94	12.92	64.3
424	10.95	11.05	11.00	63.1
544	9.45	9.45	9.45	61.2
666	8.22	8.20	8.21	59.1
Mean.....				62.4

TABLE XI.

N/10-Carbamide + *N*/10-hydrochloric acid in water. Temperature, 71·25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	13·35	13·40	13·38	—
2818	11·17	11·20	11·19	2·76
4718	9·80	9·90	9·85	2·82
8596	7·70	7·70	7·70	2·79
9223	7·50	7·50	7·50	2·73

Mean.....2·77

TABLE XII.

N/10-Carbamide + *N*/10-hydrochloric acid in 10 per cent. alcohol. Temperature, 71·25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	13·70	13·65	13·68	—
2818	11·65	11·60	11·63	2·49
5695	9·72	9·78	9·75	2·58
8594	8·30	8·30	8·30	2·53
10582	7·55	7·55	7·55	2·44

Mean.....2·51

TABLE XIII.

N/10-Carbamide + *N*/10-hydrochloric acid in 20 per cent. alcohol. Temperature, 71·25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	16·50	16·54	16·52	—
2818	14·10	14·10	14·10	2·44
5700	11·85	11·88	11·87	2·52
8598	10·10	10·10	10·10	2·49
10584	9·90	8·95	8·98	2·50
12917	8·16	7·95	8·05	2·42

Mean.....2·47

TABLE XIV.

N/10-Carbamide + *N*/10-hydrochloric acid in 30 per cent. alcohol. Temperature, 71·25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20·30	20·35	20·33	—
2799	17·40	17·45	17·43	2·39
5697	14·70	14·75	14·73	2·46
7683	13·28	13·30	13·29	2·40
10016	11·80	11·72	11·76	2·37
12907	10·22	10·26	10·24	2·31
16266	—	8·70	8·70	2·27

Mean.....2·37

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TABLE XV.

N/10-Carbamide + *N*/10-hydrochloric acid in 40 per cent. alcohol
Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.25	20.25	20.25	—
2895	17.40	17.50	17.45	2.24
4881	15.50	15.50	15.50	2.38
7214	13.72	13.78	13.75	2.33
10106	12.12	12.18	12.15	2.20
13452	10.44	10.42	10.43	2.14
17334	8.66	8.66	8.66	2.13
				Mean.....2.24

TABLE XVI.

N/10-Carbamide + *N*/10-hydrochloric acid in 49.67 per cent.
alcohol. Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.40	20.40	20.40	—
1982	18.55	18.55	18.55	2.08
4315	16.60	16.50	16.55	2.10
7208	14.62	14.58	14.60	2.02
10554	12.60	12.64	12.62	1.98
14438	10.60	10.66	10.63	1.96
17264	9.50	9.56	9.53	1.91
				Mean.....2.01

TABLE XVII.

N/10-Carbamide + *N*/10-hydrochloric acid in 60 per cent. alcohol.
Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.65	20.65	20.65	—
2331	18.60	18.60	18.60	1.95
5224	16.40	16.38	16.39	1.92
8571	14.30	14.28	14.29	1.87
12455	12.30	12.21	12.26	1.82
15281	11.00	11.00	11.00	1.79
18166	9.84	9.84	9.84	1.77
				Mean.....1.85

TABLE XVIII.

N/10-Carbamide + *N*/10-hydrochloric acid in 70 per cent. alcohol.
Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.45	20.45	20.45	—
2890	18.33	18.33	18.33	1.64
6237	16.16	16.12	16.14	1.65
10122	14.02	13.98	14.00	1.63
12947	12.60	12.56	12.58	1.63
15832	11.42	11.46	11.44	1.59
20144	10.00	10.06	10.03	1.54
				Mean.....1.61

TABLE XIX.

N/10-Carbamide + *N*/10-hydrochloric acid in 80 per cent. alcohol.
Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.33	20.33	20.33	—
3343	18.20	18.20	18.20	1.44
7228	16.20	16.26	16.23	1.35
10053	14.80	14.74	14.77	1.38
12938	13.60	13.50	13.55	1.36
17251	12.00	12.00	12.00	1.33
19139	11.36	11.42	11.39	1.31

Mean.....1.36

TABLE XX.

N/10-Carbamide + *N*/10-hydrochloric acid in 90 per cent. alcohol.
Temperature, 71.25°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	20.27	20.27	20.27	—
6762	17.00	17.00	17.00	1.14
9585	15.78	15.74	15.76	1.14
13898	14.31	14.31	14.31	1.09
15785	—	13.45	13.45	1.13

Mean.....1.12

TABLE XXI.

N/10-Carbamide + *N*/10-hydrochloric acid in water. Temperature, 61.05°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	12.65	12.65	12.65	—
9660	10.80	10.80	10.80	0.711
18340	9.36	9.40	9.38	0.708
28400	7.90	7.90	7.90	0.720

Mean.....0.713

TABLE XXII.

N/10-Carbamide + *N*/10-hydrochloric acid in 30 per cent. alcohol.
Temperature, 61.05°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	13.05	13.05	13.05	—
9660	11.47	11.47	11.47	0.580
18340	10.20	10.18	10.19	0.586
28400	8.80	8.84	8.82	0.599

Mean.....0.588

TABLE XXIII.

N/10-Carbamide + *N*/10-hydrochloric acid in 60 per cent. alcohol.
Temperature, 61.05°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^5$.
0	13.88	13.90	13.89	—
9660	12.38	12.40	12.39	0.514
18330	11.28	11.30	11.29	0.491
28400	10.02	10.06	10.04	0.496

Mean.....0.500

TABLE XXIV.

N/10-Carbamide + *N*/10-hydrochloric acid in 90 per cent. alcohol.
Temperature, 61.05°.

<i>t</i> .	$(A-x)_1$.	$(A-x)_2$.	$(A-x)_m$.	$K \cdot 10^6$.
0	14.15	14.09	14.12	—
9660	13.30	13.28	13.29	0.271
18330	12.40	12.42	12.41	0.306
28400	11.70	11.72	11.71	0.286

Mean.....0.288

Discussion of the Experimental Results and Conclusions Drawn from these.

It is remarkable that throughout tables VII—XXIV the velocity-constants calculated by the "first order" (logarithmic) formula are so satisfactory. Apparently, alteration of temperature or alteration of the solvent by the addition of alcohol does not change the mechanism of the reaction. With regard to the effect of temperature on aqueous solutions, it has already been found by one of us that the temperature-coefficient for 10° for the decomposition of carbamide by water alone, and also by hydrochloric acid solutions, is 3.5 between 90° and 99°. Calculating now from the constants given in tables VII, XI, and XXI, the temperature-coefficient for 10° between 71° and 98° is 3.53, or between 61° and 98° 3.61.

The temperature-coefficient for the aqueous alcohol solutions is also almost identical with that for the aqueous solutions. These results indicate that change of temperature and addition of alcohol do not affect the mechanism of the reaction, although the velocity is altered.

The detailed explanation of the decomposition of carbamide may be here stated as follows:

When carbamide is decomposed by water, the initial decomposition of the carbamide is one into ammonium cyanate, and the rate of this reaction is the same as the velocity of the decomposition of carbamide with acids. We therefore assume that the function of the hydrochloric acid is simply to destroy the ammonium cyanate as soon as it is formed.

The conversion of ammonium cyanate into ammonia and carbon dioxide is rapid, but we do not believe this decomposition to be an infinitely fast reaction. When ammonium cyanate is decomposed by water alone, the reaction is much slower than when acids are present, and the decomposition of carbamide in this case is regulated by the rate of decomposition of the cyanate into ammonia and carbon dioxide.

We believe it is possible that a small amount of decomposition of carbamide into ammonia and carbon dioxide, either direct or via ammonium carbamate, may go on, but the amount of this is quite insignificant in comparison with the amount decomposed after passing through the intermediate stage of ammonium cyanate.

If there were any appreciable amount of decomposition of carbamide to ammonia and carbon dioxide via ammonium carbamate, it seems to us that addition of salts of calcium to aqueous solutions of carbamide should increase the velocity of the reaction, but we find that this is not the case. We feel compelled also to believe that the amount of any direct decomposition of carbamide to ammonium carbonate is very small, and may be neglected. The same conclusion appears to have been formed by J. Walker and others who have worked with carbamide and cyanates.

Let k be the velocity-constant of the reaction carbamide $\rightarrow$ ammonium cyanate, and let k' be the velocity-constant of the opposing reaction, ammonium cyanate $\rightarrow$ carbamide. Then the true value of " k " is in our opinion approximated to very closely by the velocity-constant which can be calculated from the decomposition experiments with acids.

The values in tables XI and XXI are:

$$2.77 \times 10^{-5} \text{ at } 71.2^\circ \text{ and } 0.713 \times 10^{-5} \text{ at } 61^\circ.$$

If the whole of the carbamide were free in these acid solutions, the numbers would be, probably, 2.83×10^{-5} and 0.73×10^{-5} respectively. Corrected further by turning the logarithms used in their calculation into natural logarithms, the values are 6.5×10^{-5} at 71.25° and 1.7×10^{-5} at 61.05° .

Calculating the velocity-coefficient for the reverse action, ammonium cyanate $\rightarrow$ carbamide, from the results of Walker and Hambly (T., 1895, 67, 746), we have the values 0.445 at 71.25° and 0.157 at 61.05° . The values ($\bar{K}$) for the equilibrium constants are therefore:

$$\bar{K}_{75.21} = \frac{6.5 \times 10^{-5}}{0.445} = 0.000146,$$

$$\bar{K}_{61.05} = \frac{1.7 \times 10^{-5}}{0.157} = 0.000107.$$

From determinations of the quantity of carbamide in equilibrium with ammonium cyanate by Walker and his colleagues, we calculate that the equilibrium constants are:

$$\bar{K}_{100} = \frac{0.0065 \times 0.0065}{0.0935} = 0.000457.$$

$$\bar{K}_{82} = \frac{0.0032 \times 0.0032}{0.0968} = 0.000106.$$

We believe these results show very conclusively that the decomposition of carbamide by acids is none other than the decomposition of carbamide into ammonium cyanate.

With regard to the effect of alcohol on the velocity of decomposition of carbamide, there is a gradual reduction in velocity corresponding with the proportion of alcohol added. This is best seen in examining tables XI—XX.

It is not likely that the decreased velocity due to the addition of alcohol is on account of a retarding effect on the reaction carbamide $\rightarrow$ ammonium cyanate, for other work indicates that a decrease is hardly to be looked for there.

Taking the numbers of Walker and Kay (T., 1897, 71, 489) for the velocity (k') of the reaction ammonium cyanate $\rightarrow$ carbamide, and also the proportions of the compounds at the point of equilibrium, it is possible to calculate the value of k at 32°.

TABLE XXV.

Percentage of alcohol.	k' .	K .	k (calculated).
0	0.00595	0.0001058	0.63×10^{-6}
10	0.00774	0.0000927	0.72×10^{-6}
30	0.01290	0.000033	0.42×10^{-6}
49	0.02950	0.000026	0.767×10^{-6}
72	0.09300	0.00002	1.86×10^{-6}
90	0.57500	0.00001	5.75×10^{-6}

The tendency is rather for the velocity-constant k to increase with addition of alcohol.

Now, although these calculated values of k are for 32°, and the results we have obtained are for temperatures not lower than 61°, we think that, even if the experimental results were for the same temperature as the calculated values, a similar disparity would be noticeable.

The effect of the alcohol in our experiments appears to us to be rather in the way of decreasing the velocity of decomposition of ammonium cyanate into ammonia and carbon dioxide.

It is not possible to prove this by a direct experiment on ammonium cyanate, as this decomposes so rapidly into carbamide.

We have tried, however, to discover whether alcohol has any effect in decreasing the velocity of decomposition of potassium cyanate. Our experiments indicate that potassium cyanate does not decompose so completely into carbonate and ammonia in a given time when alcohol is present as when it is absent.

We believe that the mechanism of the decomposition of carbamide, when starting out with acid or neutral solutions, is illustrated by the following equations:

We have not proved, in the second equation, that the ions are the active molecules, but formulate the reaction as if such were the case.

We have not found any evidence to show that the reaction represented by equation (2) is reversible.

On heating normal solutions of ammonium carbonate for several days, no evidence of the formation of carbamide could be detected.

Lewis and G. H. Burrows have recently shown (*J. Amer. Chem. Soc.*, 1912, **34**, 1515) that on heating solutions of ammonium carbamate, about 1 per cent. of the carbamate is converted into carbamide; it seemed, therefore, a possibility that ammonium carbonate might be formed from carbamide, according to the equations:

To test this, we tried the effect of adding calcium nitrate to a (neutral) solution of carbamide, in order to find out whether any acceleration in its rate of decomposition took place. It was found that this was not so, and we have concluded that no measurable amount of carbamide decomposes into ammonium carbonate by way of ammonium carbamate.

The results of our experiments here and in a previously published research exclude the possibility of a measurable amount of direct hydrolysis of carbamide into ammonium carbonate. For if this were the case, the rate of decomposition would not be so independent of the concentration of acid as it is found to be.

There is therefore a great mass of undoubted evidence that the whole, or very nearly the whole, of the carbamide decomposes in neutral or acid solutions via ammonium cyanate.

Chattaway has recently (*P.*, 1911, **27**, 280) made the suggestion that an *isocarbamide* [$\text{HN}:\text{C}(\text{OH})\cdot\text{NH}_2$] is an intermediate substance formed when ammonium cyanate decomposes into carbamide.

E. E. Walker (*Proc. Roy. Soc.*, 1912, *A*, **87**, 539) has suggested that there is possibly an intermediate product of the formula $\text{C}(\text{OH})_2(\text{NH}_2)_2$.

If either of these is an intermediate substance in the formation of carbamide, we should expect it also to be an intermediate substance in the decomposition of carbamide to ammonium cyanate.

We do not think there is any real evidence for the existence of such a substance.

One of us (Fawsitt, *Zeitsch. physikal. Chem.*, 1904, **48**, 585) has shown that if an *isocarbamide*, containing a hydroxyl group, be present in aqueous solutions of carbamide, it can only be present in very small proportions. We have, however, tried to contemplate

the possibility of a very small amount of such an *isocarbamide* being present in equilibrium with carbamide and with ammonium cyanate, but find that it is not possible to use this supposition for any better interpretation of our results than we have given already.

Summary of Results.

(1) The apparent hydrolysis of carbamide by water alone or by aqueous solutions of acids is confirmed to be merely a transformation of carbamide into ammonium cyanate, which is then changed into ammonia and carbon dioxide.

(2) Addition of alcohol to aqueous solutions decreases the velocity of decomposition of carbamide, whether starting from neutral or acid solutions.

(3) Addition of alcohol up to 75 per cent. does not greatly affect the amount of free carbamide in carbamide hydrochloride solutions.

We have pleasure in expressing our thanks to Mr. E. A. Briggs, B.Sc., for conducting the experiments given in tables I and II.

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