THESIS FOR DOCTOR OF SCIENCE DEGREE,

University of Edinburgh

"ON UREA IN AQUEOUS SOLUTION AND ITS DECOMPOSITION"

by

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I declare that this thesis is

the outcome of work which has been carried out en-

tirely by myself.

November 23rd, 1903.

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I N T R O D U C T I O N.

Of late years much advance has been made in the application of physical methods to the study of chemical problems so that these methods have become most useful in giving information as to the molecular state of substances under various conditions, in giving evidence for the constitution of chemical bodies and in determining the mechanism by which these bodies interact with one another.   This research is the outcome of an application of some physical methods to the study of aqueous solutions of urea in order to give some information regarding the state in which urea exists in solution and the way in which it changes on decomposing either alone or under the influence of other substances.

The greater part of this work was carried out a at the University of Leipzig and has been published in the Zeitschrift für physikal Chemie 41,   601 (1902).   The rest was conducted in the chemical department, University of Edinburgh.

UREA IN SOLUTION.

It has been known for a long time that urea forms compounds with acids. These compounds can be isolated as distinct crystalline bodies, but they are very largely split up into the components again by solution in water.

Urea and hydrochloric acid form the compound $CO(NH_2)_2$, HCl and this exists to a certain extent in solution. For half molecular urea and normal hydrochloric acid there is 53.2% free urea in solution at 25° C.[1] and this amount is not much altered by raising the temperature to the boiling point.[2] On account of this formation of salts with acids urea may be considered as a weak base.

The ions of the above salt are thus $CO(NH_2)_2 \overset{.}{H}$ and Cl' and urea in aqueous solution may be considered as split up to a very small extent into $CO(NH_2)_2\overset{.}{H}$ and OH'.

There are, however, other possibilities of ionic formation here. Many substances, inorganic and organic, appear to be capable of acting sometimes/

1. Walker, Zeit. für Physikal Chemie 4, 334 (1889).

2. Fawsitt, Zeit. für physikal Chemie 41, 601, (1902).

times as a base and at other times as an acid, e.g., As(OH)$_3$, Pε(OH)$_2$.

In order to examine whether urea might show the properties of a weak acid, the electrical conductivity of pure aqueous solutions of sodium hydroxide was determined and of sodium hydroxide solutions to which urea had been added.

In the case of urea possessing even a small acidic character, a considerable decrease of conductivity might be expected on addition of urea owing to the greater mobility of the OH$^{\prime}$ ion than all other negative ions.   Let u represent the molecular conductivity of the sodium hydroxide

NaOH $\frac{1}{2}$ normal u = 194.2

NaOH $\frac{1}{2}$ normal+ $\frac{1}{2}$ molecular urea u = 188.7

Decrease per cent. = 2.8.

For comparison numbers are given, which I have obtained by the addition of urea to hydrochloric acid and to potassium chloride.

$\frac{1}{2}$ normal HCl, u = 358.2

$\frac{1}{2}$ normal HCl+ $\frac{1}{2}$ molecular urea, u = 271.2

Decrease per cent. = 24.3

$\frac{1}{2}$ normal KCl, u = 116.4

$\frac{1}{2}$ normal KCl+ $\frac{1}{2}$ molecular urea, u = 114.6

Decrease per cent. = 1.6

From/

From these results it will be seen that the
depression of the conductivity in the case of the
alkali is very much smaller than in the case of the
acid and approximates more to the case of addition
of urea to the neutral salt; the depression in
this last case may be looked on as a viscosity effect.
We may then conclude that if there by any acidic
character in urea at all, it is very small in com-
parison with the basic character.

Substances in aqueous solution may be divided
into electrolytes and non-electrolytes and urea be-
longs to the latter group.   There is, however, no
very sharp line between these two classes as we
have poor electrolytes and substances which, though
at one time were considered to be non-conductors
in solution, have been since found to be feebly
acid or feebly basic.

I have measured the conductivity of urea solu-
tions at various concentrations and have found that
it approaches very closely to the case of the absol-
ute non-electrolyte.   For these measurements I have
purified the urea by repeated crystallisation from
alcohol and the best material which could be prepar-
ed in this way was dissolved in water to form a
solution containing one gram. mol. per litre of
solution/

solution.   The water had a specific conductivity
of 1.5×10^{-6}.   The urea solution had a specific
conductivity of 2.8×10^{-6}.   It will be seen
that the conductivity differs very little from that
of pure water; but, small as the difference is, it
may be considered as being due in great part to im-
purity in the urea and impurity introduced in the
manipulation when making up the solution.

If we assume that urea conducts the current
in virtue of its being a weak base, the dissocia-
tion constant may be calculated[1] from the amount
of salt formation when urea is mixed with hydro-
chloric acid and is found to be 1.5×10^{-14} (25°C.)
The value of the dissociation constant of water is
approximately $.8 \times 10^{-14}$ (this being calculated
from the purest water yet obtained; specific con-
ductivity at $25^{\circ} = .05 \times 10^{-6}$).   From this the
feeble electrolytic conduction of urea solutions
will be understood.   Although we may take the dis-
sociation constant of urea as calculated from its
salts to be the correct value of that quantity, the
measurements of the conductivity of aqueous urea
solutions/

1.   Journ. Chem. Soc. (1903) 83, 484.

solutions are of interest in so far as they show how very pure we may obtain such substances by the ordinary process of crystallization.

UREA AND ACETAMID

Urea in solution is perfectly normal in regard to molecular weight determinations.   It has the molecular weight .60 and measurements of the freezing point depression by Arrhenius[1] gave

| Molecular Concentration	Molecular Weight.
.104	55.5
.259	59.5
.648	61.6
1.080	63.3

Urea belongs to the amide group as does also acetamid.   Now, acetamid gives the normal molecular weight[2] in solution and I have prepared it pure enough to find that it is also a non-conductor in solution/

1.   Zeit. für Physikal. Chem., 2, 491 (1888)
2.   Ibid.

solution and it is a base of almost identical strength with urea. From the physico-chemical point of view, urea and acetamid are therefore very similar substances.

Now it has been shown by Ostwald[1] that when acetamid is heated with acids, it is decomposed in accordance with the law which holds good for a re-action of the second order. This was what was to be expected from the equation which represents the decomposition.

Thus:-

$$CH_3 C O N H_2 + HCl + H_2O = CH_3 COOH + NH_4 Cl.$$
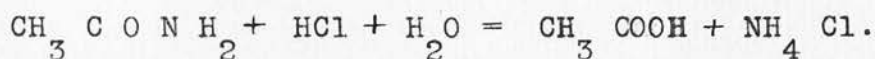
Emmet and Reid[2] have studied the decomposition of aromatic amides with acids and alkalies and find that in both cases the reaction is one of the second order.

Under these circumstances it might appear that any study of the decomposition of urea was super-fluous, but the investigation of this reaction seem-ed to be of interest as we should here have a react-ion/.

1. Journ. f. Prak. Chemie (1) 27, 2.

2. Amer. Chem. Journ., 21, 284 (1899).

ion of the third order:-

$$CO(NH_2)_2 + 2HCl + H_2O = CO_2 + 2NH_4Cl.$$
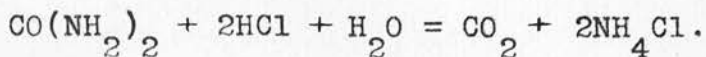
The results of experiment show that urea is quite unique among the amides in its decomposition with acids and alkali: the decomposition of pure aqueous solutions has been studied as it was thought it might be possible in this way to shed light on the experiments with acid and alkali. They were done after the experiments with acid, but are here given first.

THE DECOMPOSITION OF UREA.

General Considerations:

It has been known for a long time that urea decomposes into ammonia and carbonic anhydride either when heated with water, acids, or alkalies; also under the influence of certain micro-organisms in the cold. Exact quantitative measurements of the decomposition have, however, not been carried out. The following quantitative experiments were carried out in a water thermostat at $99.2^{\circ}C$. All the substances used were pure and the solutions were made up with CO_2- free distilled water.

The/

The method of following the reaction was to titrate the ammonia formed by excess of acid and then titrate back with Ba $(OH)_2$ solution, methyl orange being used as indicator.

This was found to be a very reliable method. The solutions were heated in tubes of special construction made of Jena Glass: when alkalies were used, platinum tubes had to be employed for heating the solutions in.

We shall express the concentration of the various substances as so much "normal" except with urea when the word "molecular" will be used, as a molecular solution of urea (60 grams per litre) is really twice normal.

In order to have an expression which will represent the velocity so that the different experiments may be compared with one another, I have calculated for all experiments the constant "k" as for a reaction of the first order: that is, according to the equation

$$\frac{dx}{dt} = k \ (a - x) \qquad \underline{or,}$$

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

A = concentration of urea at beginning of reaction.

x = concentration of urea decomposed.

t = time in minutes.

k/

k = a constant.

$K = \frac{1}{t} \log_{10} \frac{A}{A - x}$ has been used instead.of

$\frac{1}{t} \log_e \frac{A}{A - x}$ in order to shorten the calculation.

By allowing experiments to go on for a long time I find that the decomposition of urea is a reaction which goes completely to an end, i.e., into Ammonia and Carbonic Anhydride, whether carried out with pure water, acid or alkali.

Decomposition of urea with water.

t	x_1	x_2	x_A	$K \times 10^5$
½ molec solution:				
70	0·25	—	0·25	—
1034	1·34	1·36	1·35	5·4
1214	1·51	1·56	1·54	5·4
2900	3·31	3·31	3·31	5·8
5400	5·48	5·68	5·58	6·4
¼ molec. solution:				
250	0·70	0·70	0·70	—
860	1·40	1·46	1·43	5·8
1135	1·68	1·70	1·69	5·5
1500	1·99	2·01	2·00	5·2
2900	3·35	3·25	3·30	5·4
5700	5·36	5·51	5·44	5·7
8500	6·79	6·94	6·87	5·7
14200	8·76	8·82	8·79	6·4
⅛ molec. solution:				
1100	1·96	1·98	1·97	—
2500	3·32	3·34	3·33	5·8
2900	3·67	3·71	3·69	5·8
4000	4·58	4·58	4·58	5·9
5600	5·56	5·62	5·59	5·8
10100	7·59	7·60	7·60	5·8
15500	8·90	8·70	8·80	5·7
1/16 molec. solution:				
1100	2·50	2·52	2·51	—
2900	4·37	4·41	4·39	7·0
4000	5·26	5·27	5·27	6·9
5600	6·24	6·27	6·26	6·7
8500	7·51	7·52	7·52	6·5
16000	9·22	9·23	9·23	6·6

x_A is the average of x_1 and x_2, 2 parallel expts.

A = 10·00 in the above experiments.

The constants are not calculated from the start but by using the first time given in the tables as starting point.

It will be seen that we have to do with a very slow reaction and the rate of urea decomposition is proportional to the whole amount present.

The action of many neutral salts on this rate is a slightly accelerating one: this may be considered as being due to a change of solvent. Ammonium salts, however, produce a retardation.

$\frac{1}{16}$ molec urea + normal NH_4Cl:

t	x_1	x_2	x_A	$K \times 10^6$
1150	1·42	1·39	1·40	—
2900	2·02	2·04	2·03	1·89
5400	2·74	2·80	2·77	1·78
8270	3·42	3·52	3·47	1·67

A reason for this will be given further on.

THE ACTION OF ACIDS.

The following experimental results were obtained.

norm. HCl + ½ molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	19·06	19·06	19·06	—
92	16·95	16·99	16·97	55
238	13·88	13·90	13·89	58
358	11·66	11·60	11·63	60
465	10·02	9·95	9·98	60

½ norm. HCl + ¼ molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	14·86	14·86	14·86	—
77	13·10	13·11	13·10	71
206	10·46	10·43	10·44	74
243	9·74	9·76	9·75	75
269	9·25	9·28	9·27	76
319	8·39	8·42	8·41	78
359	7·75	7·84	7·79	79
409	7·02	7·08	7·05	79
429	6·72	6·75	6·74	80

½ norm. HCl + ½ norm. NH₄Cl + ¼ molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	14·86	14·86	14·86	—
77	13·11	13·14	13·13	70
206	10·43	10·42	10·43	74
269	9·31	9·33	9·32	76
319	8·51	8·52	8·52	76
409	7·10	7·10	7·10	79

¼ normal HCl + ⅛ molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	14·65	14·65	14·65	—
78	12·49	12·53	12·51	88
118	11·49	11·55	11·52	89
168	10·26	10·39	10·33	90
253	8·64	8·73	8·69	90
298	7·93	7·96	7·95	89
368	6·81	6·85	6·83	90
468	5·46	5·47	5·46	92

⅛ norm. HCl + 1/16 molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	8·46	8·46	8·46	—
118	6·45	6·49	6·47	99
358	3·67	3·68	3·68	101
478	2·71	2·72	2·72	103

1/10 norm. HCl + 1/20 molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$K.10^5$
0	25·71	25·71	25·71	—
98	20·47	—	20·47	101
128	19·12	—	19·12	101
198	16·14	16·14	16·14	102
268	13·78	13·77	13·78	101
328	11·94	11·97	11·96	101
400	10·07	10·11	10·09	102

$$t \qquad (A-x)_1 \qquad (A-x)_2 \qquad 15. \qquad (A-x)_A \qquad k \cdot 10^5$$

Normal HCl + 1/16 molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k \cdot 10^5$
0	14.65	14.65	14.65	=
68	13.57	13.64	13.60	48
98	13.03	13.15	13.09	50
238	11.33	11.47	11.40	46
298	10.71	10.77	10.74	45
368	9.61	9.85	9.73	48
500	8.52	8.66	8.59	46
600	7.78	7.80	7.79	46
1415	2.91	3.07	2.99	50

1/2 norm. HCl + 1/16 molec. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k \cdot 10^5$
0	15.37	15.37	15.37	—
98	13.06	13.10	13.08	72
148	12.17	12.20	12.19	68
248	10.36	10.36	10.36	69
333	8.94	8.96	8.95	71
480	7.00	7.02	7.01	71
1130	2.32	2.37	2.34	72

1/16 norm. HCl + 1/16 mol. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k \cdot 10^5$
0	15.21	15.21	15.21	—
93	12.11	12.16	12.14	105
118	11.45	11.50	11.48	104
253	8.45	8.45	8.45	101
328	7.27	7.26	7.27	(98)
521	6.39	6.45	6.42	(72)
1100	5.45	5.67	5.56	—
1680	4.87	4.80	4.83	—

1/64 norm. HCl + 1/16 mol. urea:

t	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k \cdot 10^5$
0	15.21	15.21	15.21	—
38	13.87	13.94	13.90	103
48	13.67	13.70	13.69	95

We have to do here with a reaction of the first order. The velocity is much greater than that with water, even though we use such dilute acid as 1/64 normal hydrochloric acid; but as soon as all the acid is used up, we have the experiments with pure water reproduced again.

The decrease in velocity with higher concentrations of acid will be explained later. In Fig. 1, we have plotted the velocity constant as ordinate and the concentration of the acid as abscissa.
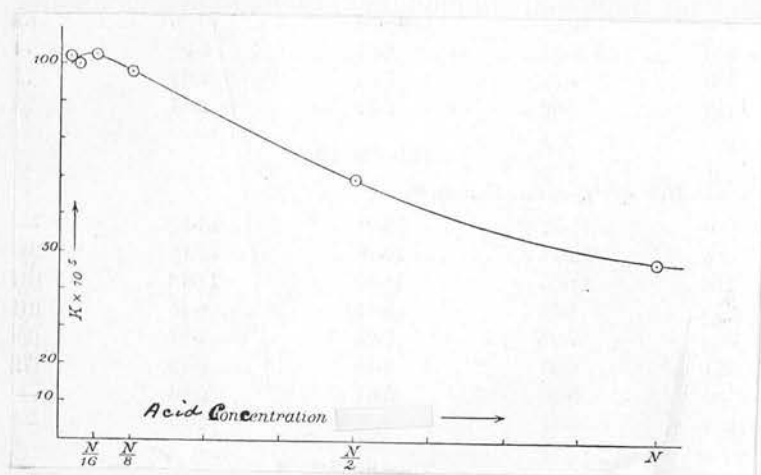
Fig. 1.

I give here experiments with sulphuric acid: these
give somewhat similar results to those obtained by
using hydrochloric acid, but owing to an accelerat-
ing effect by the ammonium sulphate, the relation of
one experiment to another is not quite so sharply
defined in the sulphuric acid experiments.

By addition of a neutral sulphate
to sulphuric acid we obtain the
same velocity as with hydro-
-chloric acid alone. This would
seem to be the maximum velo-
-city obtainable with acids: no
acceleration is produced by
the addition of a neutral
chloride to hydrochloric acid.

time. $(A-x)_1$ $(A-x)_2$ $(A-x)_A$ $k.10^5$

$\frac{1}{2}$ norm. $H_2SO_4 + \frac{1}{4}$ mol. urea:

time	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k.10^5$
0	12·93	12·93	12·93	—
100	10·89	10·75	10·82	77
119	10·30	10·34	10·32	81
174	9·10	9·30	9·20	85
298	6·92	6·98	6·95	91
402	5·42	5·46	5·44	94
550	3·84	3·85	3·85	96

$\frac{1}{8}$ norm. $H_2SO_4 + \frac{1}{16}$ mol. urea:

time	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k.10^5$
0	12·93	12·93	12·93	—
88	10·79	10·91	10·85	86
118	10·30	10·33	10·32	82
207	8·39	8·59	8·49	88
338	6·30	6·36	6·33	92
488	4·40	4·41	4·41	96

$\frac{1}{16}$ norm. $H_2SO_4 + \frac{1}{32}$ mol. urea:

time	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k.10^5$
0	12·93	12·93	12·93	—
87	10·73	—	10·73	91
173	9·01	9·17	9·09	88
300	6·82	6·82	6·82	93

$\frac{1}{2}$ norm. $H_2SO_4 + \frac{1}{16}$ mol. urea:

time	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k.10^5$
0	12·93	12·93	12·93	—
80	11·02	11·26	11·14	79
93	10·83	10·86	10·85	81
123	10·12	10·17	10·15	85

$\frac{1}{8}$ norm, $H_2SO_4 + \frac{1}{16}$ mol. urea
         $+$ norm. $(NH_4)_2SO_4$:

time	$(A-x)_1$	$(A-x)_2$	$(A-x)_A$	$k.10^5$
0	12·93	12·93	12·93	—
88	10·47	10·52	10·50	103
118	9·81	9·83	9·82	101
207	7·85	7·91	7·88	104

THE ACTION OF ALKALIES.

Ammonia produces no acceleration of the decomposition of urea in aqueous solution. It produces indeed a slight retardation as has already been mentioned to be true in the case of ammonium salts generally. Sodium hydrate, however, produces an acceleration. $A = 10 \cdot 00$

$\frac{1}{2}$ norm. $NaOH + \frac{1}{2}$ mol. urea:

t	x_1	x_2	x_A	$k \cdot 10^5$
50	0·99	1·03	1·01	92
93	1·94	1·95	1·95	101
112	2·34	2·42	2·38	105
181	3·14	3·27	3·20	92
315	5·07	5·10	5·09	98
440	6·56	6·73	6·64	107

2. $\frac{1}{2}$ norm. $NaOH + \frac{1}{2}$ mol. urea:

35	1·97	—	1·97	272
53	2·68	2·73	2·70	258
139	4·82	5·55	5·18	228
335	8·40	—	8·40	231

4 norm. $NaOH + \frac{1}{2}$ mol. urea:

30	—	—	2·70	456
50	—	—	3·98	432
221	—	—	8·29	347
275	—	—	9·04	370

$\frac{1}{8}$ norm. $NaOH + \frac{1}{16}$ mol. urea:

74	0·84	1·01	0·92	57
115	1·44	—	1·44	59
184	2·30	—	2·30	62
240	2·89	2·83	2·86	61
393	5·04	—	5·04	78

$\frac{1}{2}$ norm. $NaOH + \frac{1}{16}$ mol. urea:

91	1·47	1·48	1·48	77
191	2·57	2·92	2·74	73
470	5·90	6·35	6·17	89

$\frac{1}{2}$ norm. $NaOH + \frac{1}{16}$ mol. urea:

75	1·69	1·71	1·70	108
142	3·04	3·18	3·11	114
230	4·30	4·35	4·32	107
414	6·21	6·34	6·28	104

The action here is approximately one of the first
order.   In the figure,we have $\frac{1}{\delta}$ plotted as ordin-
ate and the concentration of the NaOH as abscissa;
δ = time necessary for the decomposition of one
tenth of the urea.

Figure 2.
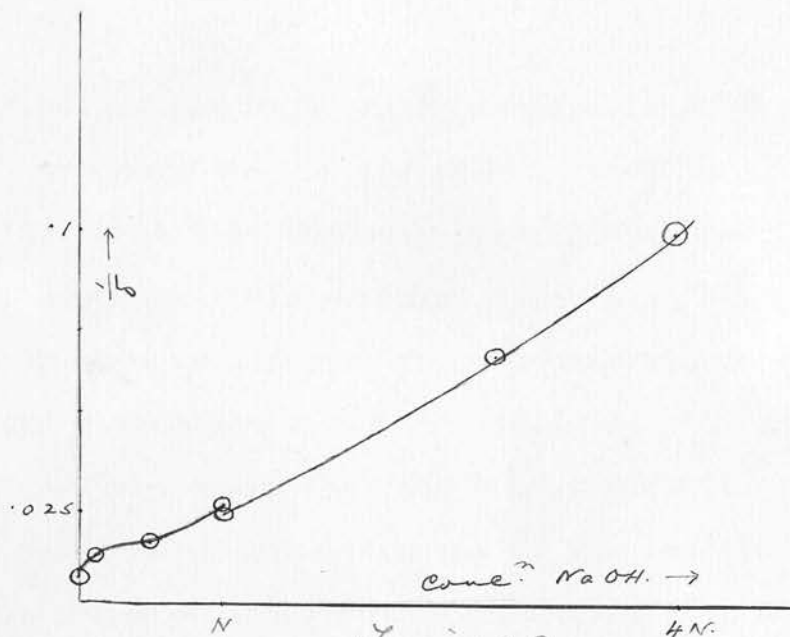
THEORETICAL CONSIDERATIONS.

It will be noticed that the reaction with water
is comparatively slow, and the reaction with acids
10 -- 20 times as fast.   Further, diluting the acid
produces almost no decrease in the velocity.   These
results are at first sight very difficult of explan-
ation.   The explanation was, however, arrived at
as follows.   If we calculate the velocity constants
of/

of the experiments with water from the start, it
will be seen that they begin much larger than be-
fore, and decrease rapidly. $A = 10.0$

$\frac{1}{32}$ mol. urea:

Time	x_1	x_2	x_A	$K \cdot 10^5$
100	0.90	0.96	0.93	42.4
200	1.19	1.23	1.21	28.0
1130	3.15	3.21	3.18	14.7
2900	5.41	5.24	5.32	11.4

I then examined the products of decomposition with
water at the beginning of the action, and found that
during the first hour the only product obtained in
measurable quantity was ammonium cyanate.   We thus
have to do with two reactions;   a decomposition into
NH_4OCN and a decomposition into $(NH_4)_2CO_3$.   I then
endeavoured to measure the rate of decomposition in
aqueous solution at the beginning of the reaction,
by measurements of the electrical conductivity of
the solution. $\frac{1}{16}$ mol. urea:

Time	spec. conductivity	% NH_4OCN	$K \cdot 10^5$
1.6	24×10^{-6}	0.27	73
3.6	53×10^{-6}	0.60	72
6.6	98×10^{-6}	1.15	76
8.9	124×10^{-6}	1.49	74
10.6	142×10^{-6}	1.70	70
19.6	240×10^{-6}	2.90	68

$\frac{1}{32}$ mol. urea:

6.6	55×10^{-6}	1.26	85
10.6	87×10^{-6}	2.04	84

It will be seen that the velocity constant approaches
still more closely to the constant obtained in the
experiments/

experiments with acids. The equation representing the velocity of change from urea into ammonium cyanate was then given the following form:-

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

k' is here the constant for the opposing action $NH_4 OCN \rightarrow CO(NH_2)_2$. This last has been investigated by Walker and Hambly[1] and found to be a reaction of the second order. As k' is very large compared with k, we can hardly expect to get a very close approximation to the formula $\frac{dx}{dt} = k (A - x)$, even when x is small, i.e., at the beginning of the reaction.

If, however, it be possible to destroy the ammonium cyanate as soon as it is formed, we should then have the simple formula $\frac{dx}{dt} = k (A - x)$. Now, I find that ammonium cyanate in contact with acids at 99.2° C. is almost instantaneously changed into ammonium chloride and carbonic anhydride. The following conclusion was then drawn: the velocity constand obtained by the action of acids on urea represents very nearly the velocity constant for the action in which urea changes into ammonium cyanate.

When urea is heated with water alone, I take it that the ammonium carbonate comes from the ammonium cyanate. We cannot show this directly as ammonium/

1. Journ. Chem. Soc. 67, 746.

ium cyanate if heated, decomposes with great rapidity into urea; but potassium cyanate is decomposable by water into potassium carbonate and ammonia, so that a similar decomposition is extremely likely in the case of ammonium cyanate. Again, it will be remembered that ammonium salts retard the rate of decomposition of urea with water, a result which will be seen to follow from a consideration of the equation $\frac{dx}{dt} = k (A - x) - k' x^2$, the effect of the NH_4 ion of the ammonium salt being to increase the second term *on the right hand side* of the equation. Let us next consider the experiments with alkali. I find that NH_4OCN is not nearly so easily decomposed by alkalies as by acids; 1/10 normal NH_4OCN + 1/5 normal NaoH was heated for five minutes at 99°C. and only 10% of the Cyanate had decomposed into sodium carbonate and ammonia.

With alkalies, the second term on the right hand side of the above equation is not zero. We would expect with alkalies a velocity intermediate between that got with water and that obtained with acids.

It will be seen from Fig. 2. that with increasing concentration of alkali the velocity rises from the value with pure water to that obtained by the action of acids, when we have got the length of normal/

normal NaOH.   By using still more concentrated
alkali we get, however, a still greater velocity
than that obtained with acids.   I explain this by
assuming that the alkali causes a direct saponific-
ation of urea in addition to the decomposition via
NH_4OCN.

$$CO\,(NH_2)_2 + Na\,O\,H + H_2O = Na\,H\,CO_3 + 2\,N\,H_3$$
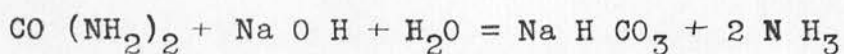
It will be seen in the tables that the "constant" for
these more concentrated alkaline solutions decreases
considerably during the reaction: this would indic-
ate that, in addition to the former decomposition
into NH_4OCN, a reaction of higher order (say, of the
second order) was taking place, as would indeed be
required if a saponification were being effected.

There is no sign of direct hydrolysis with acids,
but as has been shown in the case of other amides[1]
alkalies hydrolyse much faster than the same concen-
tration of acid.

The reason for the decrease of velocity in the
decomposition of urea when greater concentrations of
acid are used, will now be apparent.   The velocity
decreases for concentrations above 1/16 normal acid
when used with 1/16 molecular urea.   These are the
proportions corresponding to the formula $CO(NH_2)_2HCl$.
which/

1)   Amer. Chem. Jour., 21, 284 (1899).

which is the compound existing in solution.   In
the solution we have an equilibrium such that

$$\frac{C_{CO(NH_2)_2} \times C_{HCl}}{C_{CO(NH_2)_2, HCl}} = K$$

where Cx represents the concentration of the respec-
tive substances in solution.   If C_{HCl} increases,
$C_{CO(NH_2)_2}$ will diminish.   If we suppose that the
urea which decomposes is the free urea, then the
reason for the decrease of velocity when greater con-
centration of acid is used is simply a consequence
of the diminution of concentration of free urea.
The above relations exist quantitatively.   I have
taken the amount of free urea in a solution of 1/16
molecular urea and 1/8 normal HCl to be 87% of the
whole urea[1] and from this have calculated the amount
of free urea in the other solutions.   In the table
given below these (X_1) are arranged alongside of the
amounts (X_2) as got by experiment on the supposition
that it is only the free urea which is decomposing
at any time.

Conc^n urea	Conc^n HCl	X_1	X_2
½ molec.	Norm.	53·2%	47%
¼ mol.	½-norm.	65·6%	62%
⅛ mol.	¼-norm.	78·4%	77%
1/16 mol.	⅛-norm.	87 %	87%
1/16 mol.	½-norm.	62 %	62%
1/16 mol.	Norm.	44 %	42%

1.   Zeit. für Physikal. Chemie, **4**, 334 (1889).

EQUILIBRIUM BETWEEN UREA AND AMMONIUM CYANATE.

In the equation $\frac{dx}{dt} = k(A - x) - k'x^2$, k can be got from the above experiments and k' may be calculated from Walker and Hambly's work; hence, we may calculate $K = \frac{k}{k'}$, which is the equilibrium constant for the reaction
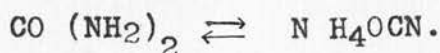
$$CO(NH_2)_2 \rightleftarrows N H_4 OCN.$$

K = .00050 is the value obtained. From this, the point of equilibrium in 1/10 molecular urea solution would be 6.8% of NH_4OCN and 93.2% of $CO(NH_2)_2$. It is difficult to get at the point of equilibrium directly, owing to the decomposition into ammonium carbonate. An approximate determination by Walker and Hambly[1] gave 5% of NH_4OCN and 95% of urea.

Experimenting at $90.1^{\circ}C.$, I have calculated K to be .00031. This is less than the number got at the higher temperature. By raising the temperature the equilibrium point moves toward the ammonium cyanate side.

1.   Jour. Chem. Soc., 67, 746.

CONCLUSIONS.

It is at present supposed that the amides have the formula $R - \overset{O}{\underset{\parallel}{C}} - NH_2$, and not the other suggested formula $R - C{\overset{NH}{\underset{OH}{\diagdown}}}$, but certain facts point to urea not having the formula $CO(NH_2)_2$ but $C{\overset{NH}{\underset{NH_2}{\overset{}{\diagdown}}}}$ OH

1. Urea forms compounds with acids of the type $CO(NH_2)_2$, HCl and not $CO(NH_2)_2$, 2HCl.

2. Urea and acetamid are bases of almost identical strength. It would, however, be expected that urea, the amid of a very weak acid, would be a very much stronger base than acetamid, the amid of a somewhat stronger acid.

3. Direct hydrolysis of urea takes place with much greater difficulty than in the case of other amides.

On the other hand, there is very little sign of any acid character about urea, which one might be led to expect if it had the formula $NH = COH - NH_2$.

We are able, however, to make the following conclusions from the preceding investigation.

1. An aqueous solution of urea is an electrolyte of about the same order as water itself. The small conductivity is due to urea being a very weak base, of which the ions are $CO(NH_2)_2H^{\cdot}$ and $-OH$.

2. Urea is not measurably hydrolysed by water and acids at 99°C: it is, however, decomposed into ammonium cyanate in the first instance and the final products are the same as though hydrolysis had taken place.

3./

3. Urea decomposes into ammonium cyanate also
    when treated with alkalies and the ammonium
    cyanate is slowly decomposed into alkaline
    carbonate and ammonia by the alkali.
    The strong bases, however, e.g., NaOH, are
    able to effect, in addition to the forego-
    ing decomposition, a direct saponification
    of urea.

4. The rate of decomposition of urea into ammon-
    ium cyanate is directly proportional to the
    concentration of the urea in solution and
    can be represented by the formula

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

    where x, A and t have the meanings already
    given above.

5. The equilibrium point between urea and ammon-
    ium cyanate was calculated from the experi-
    mental results and shown to move towards the
    ammonium cyanate end by rise of tempera-
    ture: urea thus absorbs heat when being
    transformed into ammonium cyanate.

6. In solutions of urea and hydrochloric acid
    some of the urea is bound to the acid to
    form a salt: it is only the free urea in
    solution which decomposes at any instant
    of time, the equilibrium $CO(NH_2)_2$, $HCl \rightleftharpoons$
    $CO(NH_2)_2 + HCl$, then adjusting itself
    till finally all the urea is decomposed.