described by Ditte,[1] can be formed by bringing hydrogen chloride into contact with selenium dioxide. The 2 substances unite at moderately low temperatures to form an amber-colored liquid of the formula $SeO_2.2HCl$. It is possible to remove the elements of water from this compound by means of phosphorus pentoxide, calcium chloride, or a similar dehydrating agent. The reaction can be carried out in the laboratory in one of 2 ways.

Selenium dioxide can be treated with hydrogen chloride, the resulting liquid mixed with excess of the dehydrating agent and the oxychloride distilled off, or selenium dioxide can be first mixed with the dehydrating agent and this mixture treated with hydrogen chloride. The operation can be conducted by either first passing hydrogen chloride into the mixture of selenium dioxide and dehydrating agent in the cold and subsequently heating to drive off the selenium oxychloride formed, or the mixture can be heated, hydrogen chloride passed in, and selenium oxychloride distilled from the hot mixture as it forms.

The author takes this opportunity of acknowledging the valuable help rendered by his assistant, Mr. A. J. Snyder, for various preparations of material in the above processes.

MADISON, WISCONSIN.

THE IONIZATION OF AQUEOUS SOLUTIONS OF AMMONIA IN THE PRESENCE OF UREA.

BY WINTHROP M. BURKE.

Received August 27, 1920.

Introduction.

According to the Nernst-Thomson hypothesis,[2] the dielectric constant of a solvent largely determines its power to ionize electrolytes dissolved in it. In cases which have been investigated[3] in solvents of lower dielectric constant than water, the ionization of the electrolyte has in general been found to be lower than in water. It has been found that aqueous solutions of urea have a dielectric constant higher than water; that of water is 78.83, while for a 2 *M* solution of urea it is 83.98 at 18.0°.[4] Consequently, according to the Nernst-Thomson hypothesis, we should expect to find a greater ionization constant for an electrolyte, which obeys the mass-action law, in an aqueous urea solution than in water alone. Assuming the mass-action law to be obeyed, the ionization constant for binary dissociation may be derived from the expression

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K.$$

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[1] *Ann. chim. phys.* [5] **10**, 82 (1877).

[2] Thomson, *Phil. Mag.*, **38**, 320 (1893); Nernst, *Z. physik. Chem.*, **38**, 487 (1901).

[3] Kraus and Bray, THIS JOURNAL, **35**, 131 (1913).

[4] Harrington, *Phys. Rev.*, **8**, 581 (1916).

where C is the total salt concentration, γ is the degree of dissociation, and K is the ionization constant. In this case the assumption is made that the degree of ionization is equal to the ratio Λ/Λ_0, of the equivalent conductance Λ, at any dilution, to the limiting value Λ_0. The mass-action law may be expressed in terms of Λ and Λ_0, by means of the equation

$$\frac{C\Lambda^2}{\Lambda_0\ (\Lambda_0 - \Lambda)} = K.$$

At the suggestion of C. A. Kraus, an investigation of the conductance of a weak base in the presence of urea was undertaken. Ammonium hydroxide was used as an electrolyte since this substance obeys the mass-action law in dilute solution.

Apparatus.

The Kohlrausch method was employed in determining the conductance of the solutions. A Kohlrausch slide-wire bridge with extension coils was employed. Two resistance boxes were used, one of 110,000 ohms with Curtis wound coils for higher resistance; for the lower resistances a bifilar wound box. A variable air condenser was placed in the circuit for the purpose of compensating the effects of capacity and inductance. All connecting wires were lead-covered and carefully grounded. The thermostat was also grounded.

A small induction coil was used as a source of e. m. f. for determining the conductance of the urea-ammonia solutions, and a Vreeland oscillator was employed in standardizing the cell and in measuring the conductance of the water and the urea solutions.

The temperature was maintained constant at 25° ± 0.01°. The thermostat was filled with kerosene oil and was regulated by means of a mercury filled regulator and a thermometer graduated in 0.1°.

The cell employed consisted of a glass cylinder 45 cm. long and 6 cm. in diameter and was constructed as shown in Fig. 1. The neck having the stopper was inclined at an angle of about 45° to the tube containing the electrodes, which facilitated the tipping of the cell so that the solution could fill the arm containing the electrodes and thus be kept at the same height above them. This was accomplished by the aid of the small tube, shown in Fig. 1, which was fitted with a piece of rubber tubing and a pinchcock.

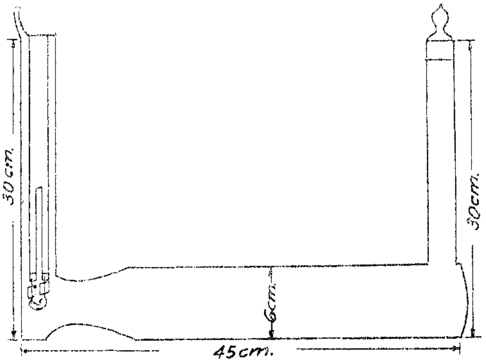

Fig. 1.

The platinum electrodes, coated with platinum black, were about one cm. square and about one cm. apart and were sealed into the bottom of the tubular extensions by stiff platinum wires. These extensions led into a larger tube located within the arm of the cell and connected to it at the top by a Dewar seal.

The cell was standardized by comparing it with a standard pipet cell whose constant had been previously determined. It was found that the constant of the cell was 0.22878.

Materials.

Urea.—The urea used was a commercial sample. As it was impure material it had to be purified. This was effected by crystallizing it 5 times from 95% ethyl alcohol and once from absolute alcohol. The urea obtained in this manner had a high degree of purity, giving a colorless aqueous solution and having a conductance of about 4.0×10^{-6} for a 2 *M* solution.

A small amount of an imported sample of reputed purity was available and the conductance of a molar solution of this was determined. Using water of a conductance of 3.5×10^{-6}, the increase in conductance due to the addition of urea amounted to 3.3×10^{-6}.

Small amounts of the urea in a water solution were tested with phenolphthalein, methyl orange and congo red, and no trace of acid or base could be found. The indicators showed the solutions to be neutral.

Ammonium Hydroxide.—The ammonium hydroxide solutions were made up in approximately *N* and 0.1 *N* concentrations by passing ammonia gas into water.

The solutions were standardized against hydrochloric acid of approximately the same concentrations. The hydrochloric acid was standardized against silver nitrate by weighing the chloride precipitated from a measured amount of the acid. In this manner the normalities of the ammonium hydroxide solutions were found to be 1.0272 *N* and 0.11049 *N*. Density determinations were made; at 25° one g. of the stronger solution was found to contain 0.035581 g. of NH_4OH and occupy 1.0111 cc., and one gram of the weaker solution contained 0.003874 g. of NH_4OH and occupied 1.0037 cc.

The density of a 2 *M* solution of urea at 25° was found to be 1.0291. Also when one gram of urea dissolves in water it displaces 0.8102 cc., the volume of the solution being increased by this amount.

The densities were all referred to water at 4° as 1.0000.

Water.—The water used in this work was distilled directly into the cell from dil. alkaline permanganate solution and the carbon dioxide was further removed by passing air through it. Water of a conductivity of about $1. \times 10^{-6}$ was obtained in this manner.

Procedure.

In making a run about 250 g. of water was weighed in the cell and the amount of urea calculated to make a 2 *M* solution was added. As the urea undergoes gradual decomposition in water, the conductance of the urea solution was measured about 20 minutes after the addition of urea, and then ammonium hydroxide was run in from a previously weighed pipet which was then weighed again. The addition of ammonium hydroxide checked the decomposition and the solution came to equilibrium in about 15 to 20 minutes after the addition of ammonium hydroxide. Immediately following the addition of ammonium hydroxide an amount of urea was added which was calculated to compensate for the change in volume, thus keeping the concentration constant.

Experimental Results.

The results of 6 independent determinations are given in Table I. Expts. 2 to 5 show the data on aqueous solutions of urea and ammonium hydroxide, and Expts. 6 and 7 show the data on aqueous solutions of ammonia.

TABLE I.

	Expt. 2.			Expt. 3.			Expt. 4.		
No.	NH_4OH Conc. $\times 10^4$ Equiv./Liter.	Spec. cond. $\times 10^6$ corr.	Λ.	NH_4OH Conc. $\times 10^4$ Equiv./Liter.	Spec. cond. $\times 10^5$ corr.	Λ.	NH_4OH Conc. $\times 10^4$ Equiv./Liter.	Spec. cond. $\times 10^5$ corr.	Λ.
H_2O	.....	0.1537	....	......	0.1288	....	......	0.0972	....
Urea	.....	0.3979	....	......	0.2992	....	......	0.3879	....
1	2.8365	1.508	53.16	2.7662	1.500	54.23	2.6879	1.393	51.82
2	8.6133	1.778	20.64	9.4245	2.756	29.24	8.5048	2.634	30.97
3	19.627	4.214	21.47	23.263	4.588	19.72	18.834	4.027	21.38
4	42.780	6.197	16.38	50.202	6.707	13.36	41.269	6.089	14.75
5	82.873	8.673	10.47	93.449	9.133	9.773	83.340	8.721	10.46
6	112.06	10.139	9.048	115.87	10.330	8.916	109.46	9.943	9.083
7	167.69	12.432	7.414	191.68	13.237	6.906	161.70	12.169	7.526
8	342.75	17.620	5.141	569.51	22.569	3.963	273.51	15.752	5.759
9	678.05	24.616	3.630	......	.....	....	516.53	21.513	4.165
10	1073.7	30.809	2.869	......	.....	....	935.41	29.293	3.080
	Expt. 5.			Expt. 6.			Expt.7.		
H_2O	.....	0.08807	....	......	0.112	....	......	0.1358	....
Urea	.....	0.4538	....	......	.....	....	......	.....	....
1	2.4898	1.275	51.21	2.4406	1.257	51.50	4.7535	2.258	47.50
2	9.4494	2.784	29.46	8.5501	2.961	34.63	14.060	3.993	28.40
3	22.333	4.453	19.94	16.793	4.368	26.01	30.413	6.064	19.95
4	47.840	6.510	13.61	33.807	6.400	18.93	54.747	8.238	15.05
5	100.88	9.608	9.524	59.379	8.643	14.56	91.783	10.758	11.72
6	118.55	10.373	8.750	92.582	10.798	11.66	136.52	13.322	9.759
7	173.89	12.659	7.280	121.72	12.479	10.25	225.66	17.104	7.580
8	277.79	15.846	5.704	191.50	15.820	8.261	337.61	22.141	5.863
9	468.06	20.466	4.373	331.70	20.705	6.242	692.91	30.066	4.339
10	874.27	27.448	3.192	528.37	26.215	4.982	......	.....	....
11	.....	.....	....	774.20	31.818	4.110	......	.....	....

The results of the first experiment are omitted because the solution had stood for a day before any data were taken. The urea and water solution did not come to equilibrium; the resistance in the cell dropping about 100 ohms every 15 minutes. This was undoubtedly due to the partial conversion into ammonium cyanate.

All measurements were made at 25° ± 0.01°.

In the first column is given the number of the observation, in the second the concentration of the ammonium hydroxide present, in the third the specific conductance corrected for the conductance of the solvent. This corrected value was obtained by subtracting the value of the specific conductance of the urea solution from that of the urea-ammonium hydroxide solution. In the fourth column is given the value of the equivalent conductance.

Discussion.

The results are shown graphically in Fig. 2. The points of each experiment are marked with the number of the experiment so that they can be identified. The values of $1/\Lambda$ are plotted against those of the specific conductance. This gives a linear curve if the mass-action law holds. At

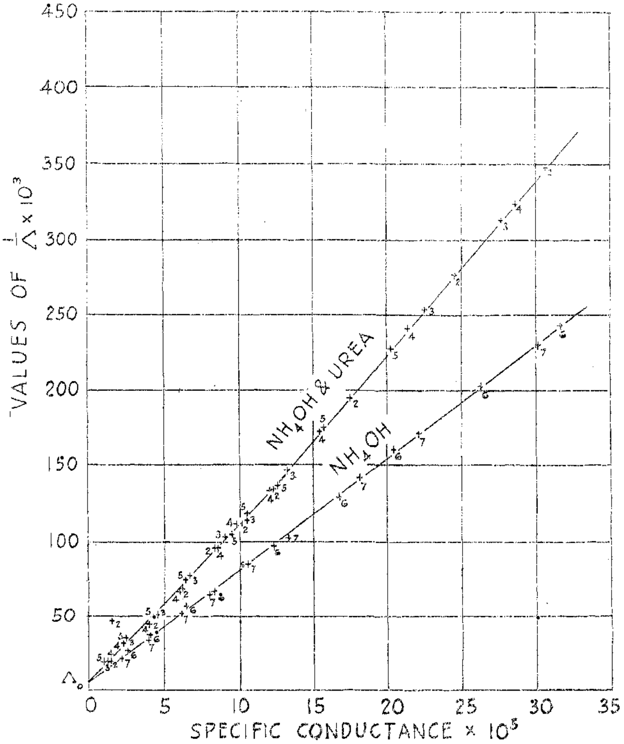

Fig. 2.

the concentration of about 0.01 *N* the slope of the curve increases slightly and then continues in a straight line.

On extrapolating to get Λ_0, a value was obtained approximately equal to that for ammonium hydroxide in water solution,[1] $\Lambda_0 = 270.6$.

On applying the mass-action law and taking values from the lower part of the curve, before the slope changes, the results shown in the following table were obtained.

TABLE II.

$\Lambda_0 = 270.6$.

Specific conductance × 10^5.	$\frac{1}{\Lambda} \times 10^3$.	Λ.	$K \times 10^6$.
2.3	28.0	35.71	12.92
5.7	64.0	15.63	12.91
7.5	83.0	12.05	12.92
11.0	120.0	8.33	12.92

This shows that ammonium hydroxide in urea solution obeys the mass-action law.

On determining the ionization constant of ammonium hydroxide in aqueous solution the following results were obtained.

TABLE III.

Specific conductance × 10^5.	$\frac{1}{\Lambda} \times 10^3$.	Λ.	$K \times 10^6$.
1.9	18.0	55.56	18.14
7.6	61.0	16.39	18.11
15.3	119.0	8.40	18.12
23.8	183.0	5.46	18.13

The concentrations are expressed in equivalents per liter. The value given by A. A. Noyes[2] for *K* at 25° is 18.1×10^{-6}, where the concentration is expressed in equivalents per liter.

The value of $\Lambda_0 = 270.6$ is the one given by Noyes and was used in calculating the results.

From the value of the equilibrium constants we see that in the case of urea and ammonium hydroxide we have an apparent exception to the Nernst-Thomson hypothesis. Instead of the ionization constant being increased, it is decreased about 30%. This difference cannot be wholly accounted for by viscosity effects as the viscosity of the urea solutions does not differ appreciably from that of water.

Landolt and Börnstein give the following data:

M.	*Z.*
1.875	1.026
3.75	1.072

where *M* is the number of moles of urea per liter of water and *Z* is the viscosity at 25° referred to water as 1.0000.

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[1] A. A. Noyes, *Carnegie Inst. Pub.*, **83** (1907).

[2] *Loc. cit.*, **1907**, p. 228.

From the great tendency of urea to form complexes with acids, bases and salts,[1] it is possible that an ammonium-urea complex, having an ionization constants less than that of ammonium hydroxide was formed.

WORCESTER, MASS.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]

STATISTICAL MECHANICS APPLIED TO CHEMICAL KINETICS.

BY RICHARD C. TOLMAN.

Received September 13, 1920.

I. Introduction.

The rate at which chemical reactions take place has long been one of the most important and most baffling of the problems of theoretical chemistry. The principles of thermodynamics provide a theoretical basis for predicting just which chemical reactions can take place, namely, those accompanied by an increase in entropy, and for predicting just how far they will proceed until equilibrium is attained. Thermodynamics, however, has been powerless to provide information as to the rate at which the thermodynamically possible reactions will actually proceed. Indeed chemical reactions which are accompanied by very large increases in entropy, such, for example, as the union of hydrogen and oxygen to form water, are often the ones which proceed with the slowest rates. The final solution of the problems of chemical velocity will be of extraordinary importance both for theoretical and for applied chemistry, since the chemist will then be able to predict not only the *possible* reactions in a given mixture of chemicals, but also the *actual* reactions which really do take place. The present article aims to make some contribution towards this final solution.

1. **Previous Work.**—Important contributions to the general theory of chemical velocity have been made by Guldberg and Waage,[2] Arrhenius,[3] Marcelin,[4] Trautz,[5] Perrin[6] and W. C. M. Lewis.[7]

Guldberg and Waage were the first to understand the effect of concentration on rate of reaction.

Considering the reaction

$$aA + bB + \ldots \longrightarrow cC + dD + \ldots \qquad (1)$$

where a mols of the Substance A react with b mols of the Substance B, etc., to form the products C, D, etc., the equation of Guldberg and Waage,

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[1] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1, Pt. 2 (1913).

[2] Guldberg and Waage, Ostwald's "Klassiker" No. 104; *J. prakt. Chem.*, **19**, 69 (1879).

[3] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[4] Marcelin, *Ann. phys.*, **3**, 120 (1915).

[5] Trautz, see summary, *Z. anorg. Chem.*, **102**, 81 (1918).

[6] Perrin, *Ann. phys.*, **11**, 5 (1919).

[7] W. C. M. Lewis, *J. Chem. Soc.*, **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920).