

and phosphates, is retarded or inhibited by phosphates if the latter are present in sufficient concentration. Within the limits of phosphate concentration found in the ash from animal tissue, the retarding action of phosphate can be removed by slightly increasing the acidity of the system before addition of the reducing agent.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE VELOCITY OF IONIC REACTIONS

BY J. N. BRÖNSTED AND ROBERT LIVINGSTON¹

RECEIVED DECEMBER 15, 1926

PUBLISHED FEBRUARY 5, 1927

1. Introduction

In previous communications² it has been shown that neither the classical expression for the velocity of chemical reactions, which for a bimolecular reaction has the form

$$h = k_1 \cdot c_A \cdot c_B \quad (1)$$

nor the expression given by the "activity theory"

$$h = k_2 \cdot a_A \cdot a_B \quad (2)$$

is compatible with existing evidence based upon the study of ionic reactions. In Equations 1 and 2, c and a indicate concentration and activity, respectively. On the basis of theoretical considerations, the following expression was derived

$$h = k \cdot c_A \cdot c_B \cdot f_A \cdot f_B / f_X \quad (3)$$

in which f_A , f_B , and f_X denote the activity coefficients of A, B and X, respectively. X is a complex ion formed by the collision of A and B, the reaction components. For the details of this theory, the reader is referred to the original papers.²

The applicability of Equation 3 to the calculation of reaction velocities depends upon the fact that the activity coefficients of ions in dilute solution are largely governed by their electric charges and only to a smaller extent by their individual properties. Since the charge of X is the algebraic sum of the charges of A and B, the charge of each substance entering is known, and a numerical calculation is possible.

Despite the large amount of evidence which has already accumulated in favor of the new theory, it is highly desirable to test its scope by new experiments, particularly in the region of very dilute salt solutions where the behavior of activity coefficients is least influenced by specific effects. The present investigation has been carried out from this point of view.

¹ Bruce Howard Memorial Fellow from the University of California.

² (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) **115**, 337 (1925). (c) Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925).

2. The Velocity Expression in Very Dilute Salt Solutions

The classical "velocity constant," k_1 of Equation 1, according to the present point of view, is not a true constant, but is a function of the total salt concentration. Combining Equations 1 and 3, we obtain

$$k_1 = k \cdot f_A \cdot f_B / f_X \quad (4)$$

from which we conclude that in dilute solution k_1 varies proportionately to the "kinetic-activity factor," $f_A \cdot f_B / f_X$.

To compute the value of the "kinetic-activity factor" for dilute solutions, we may use the relation³ $-\log f = Az^2\sqrt{\mu}$, where z is the valence of the ion considered, μ is the ionic strength, and the factor A has a value not far from 0.50. Taking A equal to 0.50, we obtain $-\log f_A \cdot f_B / f_X = 0.50 \cdot [z_A^2 + z_B^2 - (z_A + z_B)^2]\sqrt{\mu}$, or

$$\log f_A \cdot f_B / f_X = z_A z_B \sqrt{\mu} \quad (5)$$

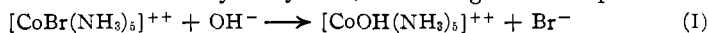
This expression shows that the activity factor is greater than unity if z_A and z_B have the same sign, smaller than unity if they have opposite signs and equal to unity if one of the reactants is electrically neutral. This is in agreement with the results presented in the previous publications,² namely, that reactions between ions of the same sign show a positive exponential salt effect and that reactions between ions of opposite sign show a negative exponential salt effect, but that reactions between an ion and a neutral molecule show a zero (or at least a small and linear) salt effect.

From Equations 4 and 5 we obtain the following equation as a limiting expression of the theory: $\log k_1 = \log k + z_A z_B \sqrt{\mu}$. Accordingly, the theory can be tested by plotting $\log k_1$ as ordinates against $\sqrt{\mu}$ as abscissas. This plot should appear as a straight line, with a slope $z_A z_B$ and with an intercept $\log k$ on the ordinate axis.

3. The Reactions Studied

The best evidence for this theory can be obtained by a study of reactions of high valence type which show both positive and negative salt effects. As suitable for this purpose, we have selected two reactions involving a complex cobaltamine ion.

The bromopentamine cobaltic ion, $[\text{CoBr}(\text{NH}_3)_5]^{++}$, reacts in aqueous solutions with the hydroxyl ion, according to the equation



which is both the stoichiometric and the kinetic reaction scheme. This reaction takes place when solutions of bromopentamine cobaltic salt and sodium hydroxide are mixed. It occurs with a measurable speed, and under ordinary conditions goes practically to completion.

When a solution of the same complex cobaltic ion is mixed with one of mercuric ion (for instance, mercuric nitrate), the strong affinity between

³ (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). (b) Brönsted and LaMer, *THIS JOURNAL*, **46**, 555 (1924).

mercuric and bromide ions results in the formation of undissociated mercuric bromide, according to the following stoichiometric scheme:⁴

$$2[\text{CoBr}(\text{NH}_3)_5]^{++} + \text{Hg}^{++} + 2\text{H}_2\text{O} \longrightarrow 2[\text{CoH}_2\text{O}(\text{NH}_3)_5]^{+++} + \text{HgBr}_2.$$

This reaction also occurs with measurable speed and goes practically to completion under ordinary conditions. Kinetically, however, the reaction is a bimolecular one.



Thus in both cases the bromo ion is decomposed, forming in the first case hydroxopentammine ion and in the second case aquopentammine ion. The two reactions are both of high valence type. They are quite different, however, in that in the first case the doubly-charged positive ion reacts with a singly-charged negative ion, while in the second case with a doubly-charged positive ion. Therefore, the valence product, $z_A z_B$, has the values -2 and $+4$, respectively. The theory requires that if the results are plotted as we have suggested (see Part 2), the two resulting curves will approximate, in great dilution, to straight lines with slopes of -2 and $+4$, respectively.

4. Preliminary Measurements

A preliminary study of Reaction I was made by a conductance method. Since in the reaction, hydroxyl ion is displaced from the solution by bromide ion, there is a considerable accompanying decrease in conductivity. The conductivity cell was opaque and was kept in a 15° thermostat. The cell was so constructed that a current of air free from carbon dioxide could be passed through the solution, to remove dissolved carbon dioxide from the neutral solution or to stir the reaction mixture. The sodium hydroxide solution was run from a buret (also kept in the thermostat) directly into the cell, so that it was introduced at the temperature of the thermostat and was protected from the air.

To interpret these conductivity readings it was necessary to obtain both an initial and an end-point. It was difficult to make an accurate estimate of the former, because of the speed of the reaction; and of the latter, because the cobaltamines contained in these solutions were apparently unstable in the presence of the platinum electrodes. Experiments showed that the most stable end-points could be obtained by using an excess of base not greater than $5 \times 10^{-4} M$.

The results of fifteen experiments, in which the base concentration fell within these limits, are briefly summarized in Table I. Experiments which were performed with a large excess of base or with an excess of the cobalt salt were less accurate, and are not included in the table. Values of the second-order rate constant, k_1 , expressed in moles per liter and minutes, are listed in Col. 3.

⁴ A similar reaction has been studied by Brönsted and Teeter [*J. Phys. Chem.*, **28**, 579 (1924)], and shown to be in qualitative agreement with the theory.

TABLE I
PRELIMINARY MEASUREMENTS OF THE RATE OF THE REACTION $[\text{CoBr}(\text{NH}_3)_5]^{++} + \text{OH}^- \longrightarrow$ AT 15°

No. of expts. performed	μ	k_1
2	0.002	90 ± 1
7	.004	79 ± 4
2	.006	72 ± 1
4	.009	67 ± 2

It should be noted that these experiments indicate that the value of the rate constant decreases with an increase in the ionic strength, μ , as predicted by the theory.

A few similar measurements were made of the rate of an analogous reaction involving the nitratopentammine cobaltic ion, $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{++} + \text{NO}_3^-$. The results of these experiments were as follows: for three experiments at $\mu = 0.0010$, $k_1 = 346 \pm 15$; for three experiments at $\mu = 0.0018$, $k_1 = 299 \pm 6$. Here, as in the case of the bromopentammine reaction, the value of the rate constant decreases with an increase in ionic strength.

In all of the measurements made by the conductivity method, certain systematic variations were observed, which suggested that the observed rate was somewhat influenced by the size and condition of the electrodes. This effect was probably due to catalysis of side reactions by platinum black.

5. The Spontaneous Aquation

The acidopentammine ions undergo "spontaneous" decomposition in neutral or acid solution.⁵ Table II is a summary of the measurements of the rate of this reaction for the bromo ion at 15° in the dark.

TABLE II
RATE DATA FOR THE SPONTANEOUS AQUATION OF BROMOPENTAMMINE COBALTIC ION AT 15°

No.	$[\text{CoBr}(\text{NH}_3)_5]^{++}$, initial M	HClO_4 , M	$k_1 \times 10^4$
1	0.010	0	1.20
2	.0010	0	1.22
3	.0010	5×10^{-6}	0.94
4	.0010	1×10^{-5}	1.15
5	.0006	2×10^{-4}	0.97

k_1 is the first-order constant, computed with natural logarithms (time expressed in minutes). These results indicate that the rate is practically independent of the ionic strength, but is somewhat influenced by the

⁵ (a) Werner and Miolati, *Z. physik. Chem.*, **14**, 515 (1894). (b) Lamb and Marden, *THIS JOURNAL*, **33**, 1873 (1911). (c) Lamb and Fairhall, *ibid.*, **45**, 378 (1923). (d) Freundlich and Pape, *Z. physik. Chem.*, **86**, 458 (1914). (e) Freundlich and Bartels, *ibid.*, **101**, 177 (1922). (f) Brønsted, *ibid.*, **122**, 383 (1926).

hydrogen-ion concentration. The reaction is more rapid⁶ in neutral than in acid solution. Indeed, colorimetric measurements indicated that unless acid were present at a concentration greater than 10^{-4} *M*, the end-product was apparently not a pure solution of aquopentammine ion, but partly colloidal in nature. The rate of Expt. 5 was measured by the colorimetric method, the rates of the other experiments by the conductivity method. The colorimetric measurements were made with the apparatus described in Part 6; the reacting solution was kept in the colorimeter chamber, which was kept in semi-darkness⁷ except for the short intervals while individual measurements were being made. Fresh reference solutions were prepared for each measurement.

Since it may be of interest to compare the rate of this "spontaneous" reaction with the rates observed for similar complex ions, a list of such data is given in Table III. Only average values of the rate constants are

TABLE III
RATE DATA FOR THE SPONTANEOUS AQUATION OF CERTAIN COMPLEX IONS

Complex ion	Temp., °C.	k_1	$A = \frac{TT'}{T' - T} \ln \frac{k_1'}{k_1}$	Reference
[CoCl(NH ₃) ₅] ⁺⁺	25	1.4×10^{-4}		5 b
[CoBr(NH ₃) ₅] ⁺⁺	15	9.6×10^{-5}	1.20×10^4	Table II
[CoBr(NH ₃) ₅] ⁺⁺	25	3.9×10^{-4}		5 b
[CoNO ₂ (NH ₃) ₅] ⁺⁺	15	3.61×10^{-4}	1.30×10^4	5 f
[CoNO ₂ (NH ₃) ₅] ⁺⁺	20	7.57×10^{-4}		5 f
[CoNO ₂ (NH ₃) ₅] ^{++*}	25	1.8×10^{-3}		5 b
[CoNO ₂ (NH ₃) ₄ H ₂ O] ^{++*}	15	$7.6 \times 10^{-4} + 1.07 \times 10^{-5}/C_{H^+}$		5 f
[CoNO ₂ (NH ₃) ₄ H ₂ O] ⁺⁺	20	$1.60 \times 10^{-3} + 3.2 \times 10^{-5}/C_{H^+}$		5 f
[CoCl(NH ₃) ₄ H ₂ O] ⁺⁺	20	$1.3 \times 10^{-4} + 1.6 \times 10^{-6}/C_{H^+}$		5 f
[IrCl(NH ₃) ₅] ^{++b}	25	3.8×10^{-5}		5 c
[IrBr(NH ₃) ₅] ⁺⁺	25	1.35×10^{-4}	9.2×10^3	5 c
[IrNO ₂ (NH ₃) ₅] ⁺⁺	25	2.6×10^{-2}		5 c
[CrCl(NH ₃) ₅] ⁺⁺	25	5.8×10^{-4}	1.09×10^4	5 e
[CrBr(NH ₃) ₅] ⁺⁺	25	3×10^{-3}	1.1×10^4	5 e
[CrI(NH ₃) ₅] ⁺⁺	0	10^{-2}		5 e

* The aquation of the acido-aquotetrammine ions is sensitive to hydrogen ions. For an explanation of the phenomenon see Ref. 5 f.

^b These are extrapolated values. The experimental measurements were made at 95° and 80°. The formation of the acidopentammine iridium ion from the corresponding aquopentammine ion and chloride, bromide or nitrate ion was found by Lamb and Fairhall (Ref. 5 c) to follow the scheme of a unimolecular reaction. This apparent anomaly may be explained on the basis of the present theory of reaction velocity when the negative salt effect to be expected for such reactions is taken into consideration.

⁶ Compare Reference 5 b, Table XIV. Acid concentrations greater than 10^{-5} *M* had the peculiar effect of accelerating the reaction when it took place in a conductivity cell, that is, in the presence of platinized electrodes. This effect was never observed when the reaction did not occur in the cell.

⁷ Some preliminary measurements showed that when the reaction occurred in the conductivity cell, its rate was increased 3-fold by diffuse daylight.

given, since the data of our Table II and of Lamb and Marden's^{5b} Table XIV show that the rate of this type of reaction is practically independent of the initial concentration of the complex ion.

6. Colorimetric Determinations

Since the initial and final substances in both reactions studied differ considerably in color (the bromo ion being purple, the hydroxo ion red and the aquo ion pink), a colorimetric method could be used to follow the course of the reaction. The measurements were made with an apparatus similar to that described by Gillespie.⁸

Fig. 1 is a schematic diagram of the apparatus. The reaction cell F is a glass tube 16 cm. long, with plane glass ends. It is surrounded by a water jacket G, the temperature of which is kept constant within

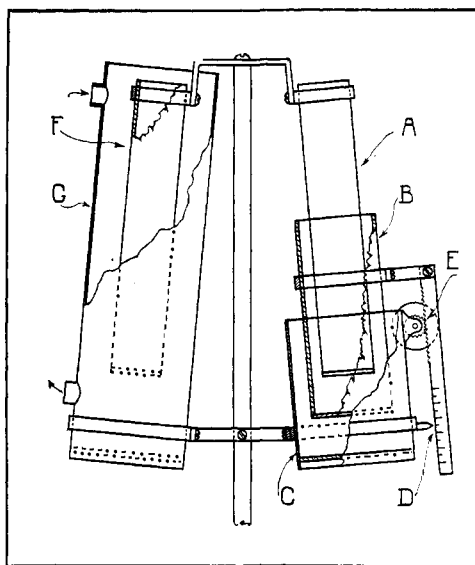


Fig. 1.—Diagram of the colorimeter.

of which is kept constant within 0.01° by a forced circulation of water from a large thermostat. Tube A is identical in construction with Tube F. Tube B is movable and is controlled by the rack and pinion E, its position being indicated by the scale and pointer D. The free space between the bottoms of the tubes A and C is 4.0 cm.

For each experiment, Tube B was filled with a fresh solution of bromopentammine salt, four times as concentrated as that used in the reaction mixture. Tube C was filled with a solution of hydroxopentammine salt for Reaction I (or aquopentammine salt for Reaction II), of the same concentration as the cobalt in Tube B. Tube A was filled with

water and covered with a plane glass plate. Tube F was then filled with the reaction mixture and covered like Tube A. The position of Tube B was then adjusted at any instant until the apparent color of Tube A was the same as that of Tube F. The scale reading, D, was then equal to the proportion of unchanged bromopentammine salt in the reaction mixture.

The reactants were mixed in a separate vessel (kept in the thermostat), and the reaction mixture was then transferred to the colorimeter cell. From one to two minutes was required to mix and transfer the solution. When the reaction mixture was a basic solution (Reaction I), special precautions were taken to prevent the absorption of carbon dioxide from the air.

⁸ Gillespie, *J. Bact.*, **6**, 399 (1921). See also Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1922, pp. 68-69.

The cobaltamines used were prepared by the methods of Jørgensen,⁹ purified by recrystallization and dried. The dried salts were kept in a desiccator.¹⁰ The standard sodium hydroxide solution was prepared free from carbonate and was standardized against potassium persulfate¹¹ and potassium acid tartrate solutions. The standard mercuric nitrate solution was made up approximately by weight; the concentration of the mercuric ion and of the excess of acid (added to prevent the formation of basic nitrate) was compared to the standard sodium hydroxide solution by a modification of the method of Incze.¹² The standard solutions of inert salts were made up by weight from purified samples of the solid salts

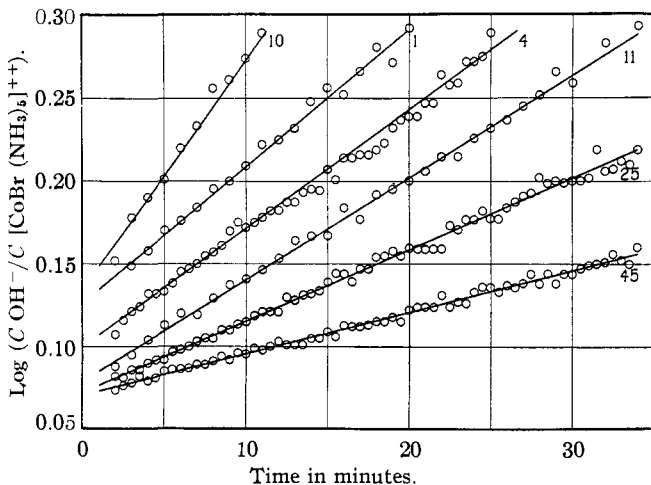


Fig. 2.—Detailed results for six typical determinations of the velocity of Reaction I.

of known water content. The distilled water used in the study of Reaction I was freed from carbon dioxide by having purified air bubbled through it. Conductivity measurements showed that this procedure did remove a large part of the dissolved carbon dioxide.

The individual readings with the colorimeter were reproducible within 4 or 5% for mixtures of bromo- and hydroxypentammine ions (Reaction I) when the total cobalt concentration was $6 \times 10^{-4} M$ or greater. The

⁹ Jørgensen, *Z. anorg. Chem.*, **17**, 455 (1898).

¹⁰ Since the solutions of these salts were made up by weight, this precaution was necessary, particularly for the bromopentammine perchlorate, which takes up from 2 to 3% of water on standing in the air.

¹¹ When an aqueous solution of potassium persulfate is kept at 100° for six hours, it decomposes completely according to the scheme $K_2S_2O_8 + H_2O \longrightarrow K_2SO_4 + H_2SO_4 + \frac{1}{2}O_2$. This reaction (using quartz vessels for the decomposition) has been employed for some time in this Laboratory for standardizing alkali.

¹² Incze, *Z. anal. Chem.*, **56**, 177 (1916).

TABLE IV

RATE DATA FOR REACTION I, $[\text{CoBr}(\text{NH}_3)_5]^{2+} + \text{OH}^- \longrightarrow$

No.	$C_{[\text{CoBr}(\text{NH}_3)_5]^{2+}} \times 10^3$	$C_{\text{OH}^-} \times 10^3$	C_{NaCl}	k_1	μ
1	0.5000	0.705	0	91	0.0022
2	.5000	.712	0	89	.0022
3	.530	.604	0	88	.0022
4	.513	.705	0	96	.0022
5	.600	.710	0	90	.0025
6	.600	.706	0	93	.0025
7	.600	.696	0	79	.0025
8	.600	.701	0	82.5	.0025
9	.596	1.004	0	87	.0027
10	.667	1.007	0	89	.0030
11	.750	0.909	0	87	.0032
12	.750	.904	0	84	.0032
13	.909	1.010	0	88	.0037
14	1.000	1.110	0	84	.0041
15	1.000	1.110	0	83	.0041
16	0.600	0.696	0.0050	73.5	.0075
17	.600	.695	.0100	76.5	.0125
18	.600	.691	.0100	76.5	.0125
19	.600	.696	.0150	68	.0175
20	.600	.696	.0200	58	.0225
21	.600	.696	.0250	55.5	.0275
22	.600	.691	.0300	54.5	.0325
23	.600	.696	.0300	59.5	.0325
			C_{BaCl_2}		
24	0.600	0.707	0.00020	89.5	0.0031
25	.600	.709	.00030	88	.0034
26	.600	.707	.00050	84	.0040
27	.600	.705	.00050	84	.0040
28	.600	.704	.00070	82	.0046
29	.600	.707	.00100	75	.0055
30	.600	.707	.00100	75	.0055
31	.600	.703	.00125	82.5	.0062
32	.600	.700	.00125	83	.0062
33	.600	.708	.00125	77	.0063
34	.600	.705	.00150	75	.0070
35	.600	.711	.00188	67.5	.0082
36	.600	.704	.00200	67.5	.0085
37	.600	.696	.00200	74	.0085
38	.600	.702	.0030	72	.0115
39	.600	.698	.0040	67.5	.0145
40	.600	.701	.0050	65	.0175
41	.600	.696	.0070	66	.0235
42	.600	.700	.0080	52.5	.0265
43	.600	.701	.0080	60.5	.0265
44	.600	.706	.0100	56.5	.0325
45	.600	.696	.0100	59	.0325

TABLE V
RATE DATA FOR REACTION II, $[\text{CoBr}(\text{NH}_3)_5]^{++} + \text{Hg}^{++} \longrightarrow$

No.	$C_{[\text{CoBr}(\text{NH}_3)_5]^{++}} \times 10^3$	$C_{\text{Hg}^{++}} \times 10^3$		k_1	μ
1	0.200	0.208		80	0.00135
2	.200	.208		85	.00135
3	.200	.278		90	.0016
4	.300	.208		76	.00165
5	.300	.208		80	.00165
6	.400	.278		96	.0022
7	.400	.278		92	.0022
8	.400	.416		111	.0027
9	.400	.416		106	.0027
10	.556	.278		103	.0027
11	.400	.556		115	.0032
12	.605	.834		132	.0048
13	.605	1.110		144	.0058
No.	$C_{[\text{CoBr}(\text{NH}_3)_5]^{++}} \times 10^3$	$C_{\text{Hg}^{++}} \times 10^3$	C_{HNO_3}	k_1	μ
14	0.400	0.278	0.0050	159	0.0072
15	.600	.834	.0099	198	.0147
16	.400	.278	.0148	227	.0170
17	.400	.556	.0148	238	.0185
18	.400	.278	.0198	264	.0220
19	.400	.278	.0247	296	.0269
20	.400	.278	.0297	330	.0319
			C_{KNO_3}		
21	0.400	0.278	0.0025	122	0.0047
22	.400	.556	.0075	185	.0107
23	.400	.278	.0100	155	.0122
24	.600	.834	.0100	204	.0148
25	.400	.556	.0150	207	.0182
26	.400	.278	.0200	205	.0222
27	.400	.417	.0250	234	.0277
28	.400	.278	.0300	254	.0322
No.	$C_{[\text{CoBr}(\text{NH}_3)_5]^{++}} \times 10^3$	$C_{\text{Hg}^{++}} \times 10^3$	$C_{\text{Ba}(\text{NO}_3)_2}$	k_1	μ
29	0.400	0.278	0.00125	113	0.0059
30	.400	.278	.0025	147	.0097
31	.400	.278	.0050	160	.0174
32	.400	.278	.0050	156	.0174
33	.400	.278	.0075	164	.0274
34	.400	.278	.0100	196	.0322
			$C_{\text{Sr}(\text{NO}_3)_2}$		
35	0.400	0.278	0.0050	145	0.0172
36	.400	.278	.0100	200	.0322
			$C_{\text{La}(\text{NO}_3)_3}$		
37	0.400	0.278	0.00205	141	0.0145
38	.400	.278	.00410	186	.0268
39	.400	.278	.00512	215	.0329

same reproducibility was obtained for mixtures of bromo- and aquopentamine ions when the total cobalt concentration was $4 \times 10^{-4} M$ or greater.

In the rate experiments, readings were taken every minute, or half minute, for the first 20 or 40 minutes, for which interval the spontaneous change could be neglected. The detailed results of six typical experiments on the rate of Reaction I are represented in Fig. 2. The ordinates represent time in minutes, the abscissas the common logarithm of the ratio of the concentrations of the reactants. The values of the velocity constants were obtained by multiplying the slopes by 2.30 times the difference between the initial concentrations (expressed in moles per liter) of hydroxyl and cobaltamine ions. The numbers on the figure refer to the experiment numbers of Table IV. Constant factors have been added to the values of the logarithms for Expts. 1, 4 and 10, in order that their plots might be represented in the figure. The values of the rate constants for Reaction II were obtained from similar plots by the use of the following expression: $k_1 = [2/(A - 2B)] \ln [B(A - X)/A(B - X/2)]$, where A, B, A - X, and B - X/2 are the initial and instantaneous concentrations of the mercuric and bromopentamine ions, respectively.

7. The Data Obtained

The measurements of the rates of Reactions I and II are summarized in Tables IV and V. The initial concentrations of the reactants are given in Cols. 2 and 3. These, as well as the concentrations of the inert salts, are recorded as moles per liter. The second-order rate constant, k_1 , and the ionic strength, μ , are listed in the last two columns.

It should be noted that the results of the preliminary measurements (see Table I) are in fair agreement with the data of Table IV; the rate constants have approximately the same average value and show a similar decrease with increasing ionic strength.¹³

TABLE VI
RATE MEASUREMENTS AT 25°

Reaction I					
$C_{[CoBr(NH_3)_5]^{2+}}$	C_{OH^-}	μ	k_1	$k_{25^\circ}/k_{15^\circ}$	$A = \frac{TT'}{T' - T} \ln k'/k$
0.000600	0.000695	0.0025	364	4.09	1.19×10^4
.000600	.000691	.0025	347	3.90	
Reaction II					
$C_{[CoBr(NH_3)_5]^{2+}}$	$C_{Hg^{2+}}$	μ	k_1	$k_{25^\circ}/k_{15^\circ}$	
0.000400	0.000278	0.0020	196	2.04	6.4×10^3
.000400	.000278	.0020	200	2.08	

¹³ Another series of measurements of the rate of this reaction, which were made by the colorimetric method, yielded values consistently 25% lower than those given in Table IV, but which showed the same variation with the ionic strength. Since we were unable to reproduce these results, we have omitted them from the table. In the time at our disposal, we were unable to discover the cause of this discrepancy.

A few measurements were made at 25° to determine the temperature coefficients for the reactions. The results of these experiments are given in Table VI.

It is interesting to note that while the temperature coefficient for the reaction involving hydroxyl ion has the same value (4.0) as that observed for the "spontaneous" change (see Table III), the value of the temperature coefficient for the reaction involving mercuric ion is only half as great.

8. Discussion

The theory presented in Part 2 requires, as has been mentioned, the plot of $\log k_1$ against $\sqrt{\mu}$ to approach with decreasing concentration to a straight line with slope $z_A z_B$, that is, with a slope of -2 and $+4$ for Reactions I and II, respectively. Fig. 3 shows that this is true for Reaction I, at least as a limiting law. The departure, amounting to about 16% in the most concentrated solutions ($\mu = 0.033$) studied is, as one would expect, in the direction of a smaller salt effect.

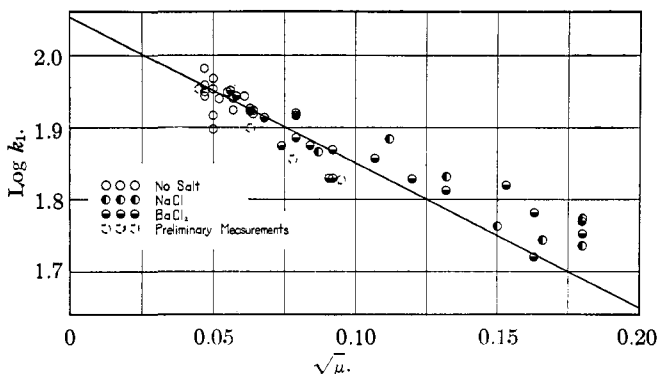


Fig. 3.—A summary of rate data for Reaction I.

For Reaction II, a plot of $\log k_1$ against $\sqrt{\mu}$ (Fig. 4) shows that the points approach a straight line with the theoretical slope of $+4$. The departure for the more concentrated solutions is, as for Reaction I, in the direction of a smaller salt effect; but in this case marked specific effects for the various "inert" ions are evident. There is practically no departure when nitric acid is the added substance; the departure is about 27% for the highest concentrations ($\mu = 0.033$) of potassium nitrate, and is still higher and about equal for barium, strontium and lanthanum nitrates. Such individual deviations are by no means in conflict with the theory, since the equation used is only a limiting one, exact at great dilution. However, the character of these deviations is of great interest in the study of chemical kinetics, and ought to be the object of a more careful investigation.

The measurements recorded in this paper show that while the velocity constant of Reaction II increases over 300% for an increase in ionic strength from 0.0015 to 0.033, the velocity constant of Reaction I decreases about 150% as the ionic strength varies over the same range. These extremely high and opposite salt effects are of particular interest in the theory of the kinetics of ionic reactions. The calculations presented here show that it is possible to account quantitatively for the observed salt effects on the basis of the present theory, while these data are incompatible alike with the classical and with the "activity" theories of reaction velocities.

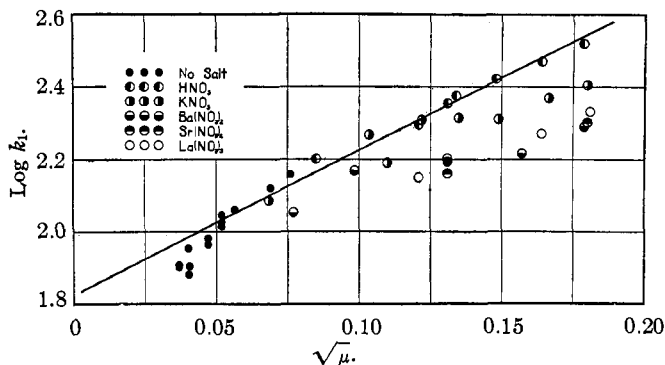


Fig. 4.—A summary of the rate data for Reaction II.

Summary

1. The reactions (I) $[\text{CoBr}(\text{NH}_3)_5]^{++} + \text{OH}^- \rightarrow [\text{CoOH}(\text{NH}_3)_5]^{++} + \text{Br}^-$ and (II) $2[\text{CoBr}(\text{NH}_3)_5]^{++} + \text{Hg}^{++} + 2\text{H}_2\text{O} \rightarrow 2[\text{CoH}_2\text{O}(\text{NH}_3)_5]^{+++} + \text{HgBr}_2$ have been studied kinetically.

2. The very marked salt effects, negative for Reaction I and positive for Reaction II, have been accounted for quantitatively by the recent theory of the velocity of ionic reactions.

COPENHAGEN, DENMARK