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The effect of the addition of "inert" salts on ionic reaction rates is discussed. For reactions between ions of the same charge sign, the effect is caused almost exclusively by the concentration and character of salt ions of charge sign opposite to that of the reactants. The rate is not dependent upon the ionic strength of the solutions. In reactions between ions of opposite charge sign, both salt ions may affect the rate, but the effect of one type may be dominant. The effects are quantitatively interpretable in terms of an ion association constant and specific rate constants for the associated and non-associated reactants. The further introduction of activity coefficients is not necessary. The reactions upon which the Livingston Diagram is based have been explored from this viewpoint and found to be in quantitative accord.

THE rate of reaction between bromopentammine cobaltic ion, $Co(NH_3)_5Br^{++}$, and mercuric ion in dilute aqueous solution was investigated by Brønsted and Livingston.[1] Their results are shown graphically in Fig. 1. The dashed line shows the theoretical change in specific rate with ionic strength as calculated from the Brønsted theory of salt effects,[2] $k = k_0(f_A f_B / f_X)$, combined with the Debye-Hückel limiting law for the activity coefficients of ions in aqueous solutions. Apparently, the only hydrogen ions in the solution came from an unspecified amount of nitric acid added to the stock solution of mercuric nitrate to prevent hydrolysis. This might account for the rapid drop in the specific rate at low ionic strengths, since the smaller the amount of such stock solution added to the reaction mixture, the smaller would be the concentration of hydrogen ions, and the greater would be the degree of hydrolysis. We have therefore reinvestigated this reaction, taking advantage of the improved precision made possible by the use of a quartz spectrophotometer and the very high extinction coefficient of the bromo-cobaltammine in the ultra-violet. The large absorption of nitrate ion in this region made it desirable to employ the perchlorate compounds.

Bromopentammine cobaltic bromide was prepared by the method of Jörgensen.[3] Mercuric perchlorate solution

was prepared by permitting perchloric acid to react with an excess of freshly precipitated mercuric oxide. The centrifuged and filtered solution was analyzed for mercury by titration with thiocyanate[4] which had been standardized against redistilled mercury. The perchloric acid content of the solution was determined by titration with sodium hydroxide after complexing the mercuric ion with a large excess of sodium bromide. Methyl red indicator was used. The final stock solution was approximately $0.1M$ in mercuric perchlorate and $0.004M$ in perchloric acid. Sodium perchlorate solution was prepared by the neutralization of standardized perchloric acid with analytical reagent grade sodium carbonate, boiling off carbon dioxide, and diluting to a known volume. Lanthanum perchlorate solution was prepared by permitting standardized perchloric acid to react with an excess of pure lanthanum oxide which had been ignited and weighed. After a few hours stirring, the excess oxide was filtered off, washed, and ignited. The weight of oxide used checked with the amount of perchloric acid added within a few tenths of a percent.

The large difference between the extinction coefficients for the two cobaltammine compounds in the ultraviolet region, and the use of a modern spectrophotometer permit precise rate determinations at very low reactant concentrations. Absorption spectra of the cobaltammines involved in this reaction and one to be discussed later are shown in Fig. 2. A Beckman quartz

[1] J. N. Brønsted and R. Livingston, J. Am. Chem. Soc. **49**, 435 (1927).

[2] J. N. Brønsted, Zeits f. physik. Chemie **102**, 169 (1922); **115**, 337 (1925).

[3] S. M. Jörgensen, Zeits. f. anorg. allgem. Chemie **17**, 455 (1898).

[4] I. M. Kolthoff and E. B. Sandell, *Quantitative Inorganic Analysis* (The Macmillan Company, New York, 1943), pp. 480 and 575.
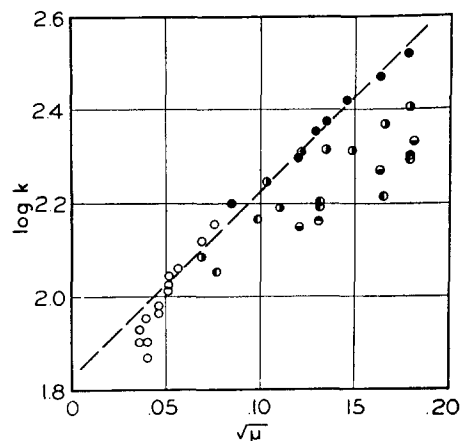
FIG. 1. Data of Brønsted and Livingston (see reference 1) for the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$. ○ no added salt, ● HNO_3 added, ◐ KNO_3 added, ◑ $Ba(NO_3)_2$ added, ◒ $Sr(NO_3)_2$ added, ◔ $La(NO_3)_3$ added. Dashed line: Debye-Hückel limiting slope from Brønsted equation as drawn by Brønsted and Livingston.

FIG. 2. Ultraviolet absorption spectra of cobaltammines. 1: $Co(NH_3)_5Br^{++}$, 2: $Co(NH_3)_5OH^{++}$, 3: $Co(NH_3)_5H_2O^{+++}$.

spectrophotometer was used for all rate measurements. A small thermostat chamber was constructed to replace the usual cell compartment assembly for 10-cm cells. It consisted of a brass box with fused silica windows in the optical path. Making the box longer (toward the operator) than the usual compartment provided space for a stirrer and a thermoregulator. A grid of copper tubing on the bottom of the box permitted the circulation of a coolant. Insulation was provided by a layer of sheet cork surrounding the thermostat.

Solutions of the cobaltammine and mercuric perchlorate were separately brought to temperature (15.0°C in all these experiments) in the arms of a Y-shaped mixing vessel in a separate thermostat. After rapid mixing, the final solution was transferred to a 10-cm absorption cell which had also been brought to temperature, the cell holder was placed in the spectrophotometer, and measurements begun.

In our experiments the concentration of the cobaltammine was so small compared to that of mercuric ion that the change in ionic strength as well as the change in mercuric ion concentration was less than five percent during the course of the reaction in the most extreme case. For those runs in which the mercuric ion concentration changed appreciably during reaction, bimolecular specific rates have been calculated from the average mercuric ion concentration.

In the first series of experiments, shown in Fig. 3, the rate of the reaction was determined at various concentrations of mercuric perchlorate, keeping the initial concentration of cobaltammine constant ($5.00 \times 10^{-6} M$). The only perchloric acid present came from the mercury stock solution. Figure 4 shows the strictly first-order character of the rate of disappearance of bromocobaltammine in a typical experiment. The curve resulting from this series parallels rather closely the Brønsted and
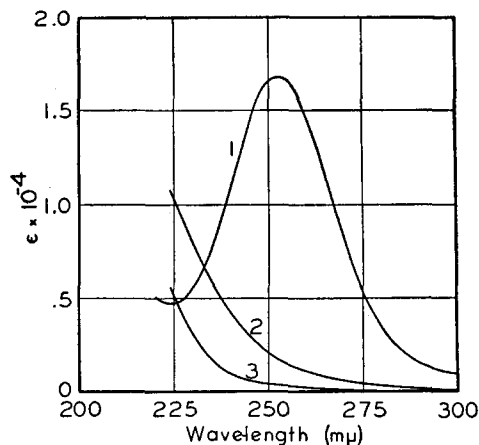
Livingston[1] data, again showing the rapid drop in specific rate at low ionic strengths.

When the series was repeated using enough added acid to make the total perchloric acid concentration $0.001M$, the rapid drop in the specific rate at low mercuric ion concentrations was avoided. This does not mean that hydrolysis of mercuric ion has been eliminated. It means merely that the hydrogen ion concentration is large enough so that the degree of hydrolysis of mercuric ion does not change greatly as the mercuric ion concentration is changed. In fact from the work of Garrett and Hirschler[5] and the free energy data for the mercuric compounds, an appreciable fraction of the mercury may be present as $HgOH^+$. The measured reaction therefore is complex, but this complexity does not vitiate the conclusions to which we are led below. The observations measure the change in the concentration of the bromopentammine cobaltic ion. The relative concen-

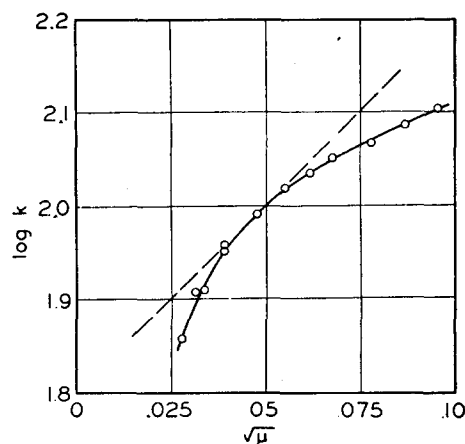FIG. 3. The reaction $Co(NH_3)_5Br^{++}+Hg^{++}$. Cobaltammine concentration $5.0 \times 10^{-6} M$, varying amounts of $Hg(ClO_4)_2$. Dashed line: Debye-Hückel limiting slope from Brønsted equation.

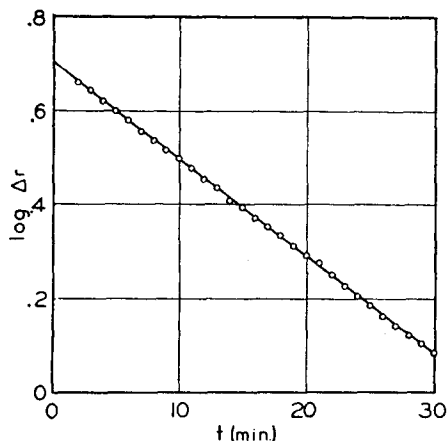[5] A. B. Garrett and A. E. Hirschler, J. Am. Chem. Soc. 60, 305 (1938).

FIG. 4. A typical run showing first-order disappearance of bromo-cobaltammine in the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$. Δr is the difference of two optical densities measured a constant time interval apart (Guggenheim method). Wave-length 253 mμ.

trations of mercuric ion and its hydrolysis products may be and probably are complex functions not only of the hydrogen ion concentration, but also of the "inert" salt concentration. In the presence of a great excess of mercuric ion, as in our experiments, the only important reaction product of mercury is $HgBr^+$.[6] The kinetic data for this series at constant total acidity are shown in Table I and in Fig. 5.

In Table II are shown the results of a series of runs in solutions 0.001M in perchloric acid to which sodium perchlorate or lanthanum perchlorate was added to vary the ionic strength, all other components of the solutions being kept constant. These data are plotted in Fig. 6. In those runs containing the highest salt concentrations the rates are almost twice as great as the rate in the reference solution. The ionic strengths of the lanthanum per-
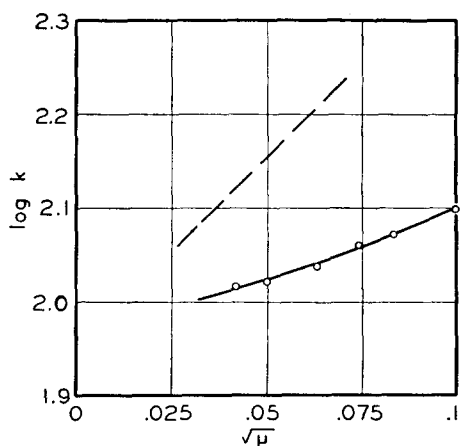
chlorate solutions are almost double those of the corresponding sodium perchlorate solutions. It is obvious that the rate for the addition of sodium perchlorate is identical with that for the addition of lanthanum perchlorate at the same perchlorate ion concentration in spite of ionic strength differences. The functional dependence of the rate of this reaction is on the concentration of negative ions, and not on the ionic strength as such.

We arrive at the same conclusion by examining the data of Brønsted and Livingston[1] for this reaction. Table III includes all the data they presented which permit such a comparison.

The substitution of the bromine in bromoacetate ion by thiosulfate ion was studied by von Kiss and Vass.[7] These investigators added salts of various types to the reactants to change the ionic strength. For convenience we have reproduced in Table IV that portion of their data taken at 25°C which involved the addition of sodium nitrate or sodium sulfate, and we have plotted the results in the usual way in Fig. 7. Data for three runs by the present authors in which potassium nitrate, potassium sulfate, or potassium 'cobalticyanide was added as "inert salt," also shown in Fig. 7, are given in Table V. If we compare sets of runs where in one case sodium nitrate has been added and in the other sodium sulfate has been added as the "inert salt," we see that even up to half-normal the rate is about the same at equal sodium ion concentrations, even though the ionic strength is very different. This is shown in Fig. 8, where we have plotted log$k$ versus the square root of the sodium ion concentration. A similar treatment of their experiments involving the addition of magnesium salts (the only additional group where such a comparison may be made), while more closely conforming to a

FIG. 5. The reaction $Co(NH_3)_5Br^{++}+Hg^{++}$. Cobaltammine concentration $5.0\times10^{-6}M$, $HClO_4$ concentration $1.00\times10^{-3}M$, varying amounts of $Hg(ClO_4)_2$. Dashed line: Debye-Hückel limiting slope from Brønsted equation.
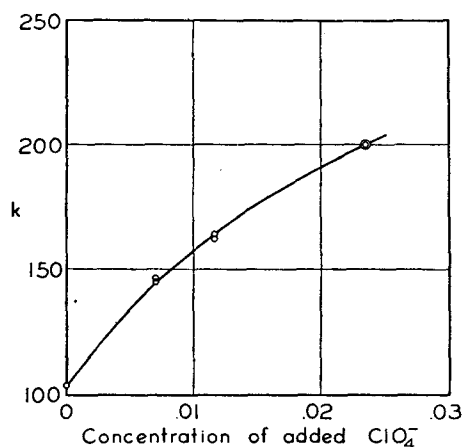
FIG. 6. The effect of the addition of sodium and lanthanum perchlorate to the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$. Concentrations: cobaltammine, $5.0\times10^{-6}M$; $Hg(ClO_4)_2$, $2.50\times10^{-4}M$; $HClO_4$, $1.0\times10^{-3}M$. In each pair of points one is sodium and one lanthanum perchlorate.

[6] L. G. Sillén, Svensk Kem. Tid. 58, 52 (1946). L. G Sillén and G. Infeldt, Svensk Kem. Tid. 58, 61 (1946).

[7] A. von Kiss and P. Vass, Zeits. f. anorg. allgem. Chemie 217, 305 (1934).

TABLE I. Rate data for the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$.

Cobaltammine $5.0 \times 10^{-6}M$ Total HClO$_4$ $1.00 \times 10^{-3}M$ $10^4 \times [Hg(ClO_4)_2]$	$T = 15.0°C$ k	$10^3\mu$
2.50	103.8	1.75
4.98	105.1	2.49
9.97	109.1	3.99
14.93	114.8	5.48
19.90	117.8	6.97
29.89	125.6	9.96

TABLE II. Rate data for the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$.

Concentrations: Cobaltammine $5.0 \times 10^{-6}M$ Hg(ClO$_4$)$_2$ $2.50 \times 10^{-4}M$ HClO$_4$ $1.00 \times 10^{-3}M$ $10^3 \times [NaClO_4]$	$10^3 \times [La(ClO_4)_3]$	$10^3 \times$ [added (ClO$_4^-$)]	k	$T = 15.0°C$ $10^3\mu$
0	0	0	103.8	1.75
7.06		7.06	145.0	8.81
	2.35	7.06	146.7	15.85
11.70		11.70	162.2	13.45
	3.90	11.70	164.2	25.15
23.56		23.56	200.4	25.31
	7.85	23.55	200.4	48.85

concentration than an ionic strength comparison, is somewhat less striking from a quantitative viewpoint than the one discussed above.

The saponification of nitrourethane ion by hydroxide ion, $NO_2=N-COOC_2H_5^-+OH^-=N_2O+CO_3^{--}+C_2H_5OH$, was studied by Brønsted and Delbanco.[8] The first four entries of Table VI, taken from their paper (with the column for ionic strength added by us), show the effect on the rate of adding various potassium salts, all at the same concentration of potassium ion. It is seen that under these conditions the rate is nearly constant, independent of the type of negative ion and of the ionic strength, provided that the change in ionic strength is due to a change in the character and concentration of the added negative ion. The remaining entries of Table VI show further that the rate is influenced very markedly by the character of the added positive ion, even though the ionic strength remains the same. Brønsted and Delbanco noted this effect of positive ion character, and stated that it was in agreement with Brønsted's "principle of specific interaction of ions."[9] The inescapable conclusion from this work is that the rate of this reaction depends on the concentration and character of positive ions, and that it is independent of ionic strength, in complete accord with the preceding examples.

The reaction of bromopentammine cobaltic ion with hydroxide ion, $Co(NH_3)_5Br^{++}+OH^-=Co(NH_3)_5OH^{++}+Br^-$, was studied by Brønsted and Livingston.[1] Their data, though perhaps as good as could be got by visual colorimetric methods, are not very consistent. We have therefore re-examined the rates for this reaction, again

[8] J. N. Brønsted and A. Delbanco, Zeits. f. anorg. allgem. Chemie 144, 248 (1925).
[9] J. N. Brønsted, J. Am. Chem. Soc. 44, 877 (1922).

using the ultraviolet absorption region which permitted us to work with very low reactant concentrations. The absorption spectra involved are shown in Fig. 2. The first series of experiments was performed by varying the initial hydroxide ion concentration, keeping the initial cobaltammine concentration constant at $5.0 \times 10^{-6}M$. No salts were added. Our data for this series are shown in Table VII and by the filled circles in Fig. 9. For comparison we have included all the Brønsted and Livingston data up to an ionic strength of 0.01. The dashed line shows the limiting slope predicted by the Brønsted theory, employing the Debye-Hückel limiting law for calculating activity coefficients. The line is drawn as it was placed by Brønsted and Livingston. The experiments at the bottom of Table VII, in which the concentration of cobaltammine was increased twenty-fold, indicate that within the experimental limits, the specific rate is independent of the cobaltammine concentration in this concentration region.

These experiments were performed in much the same way as were those in connection with the cobaltammine-mercuric ion reaction described above. The principal difference was the necessity for the exclusion of carbon dioxide. All stock solutions were prepared with carbon
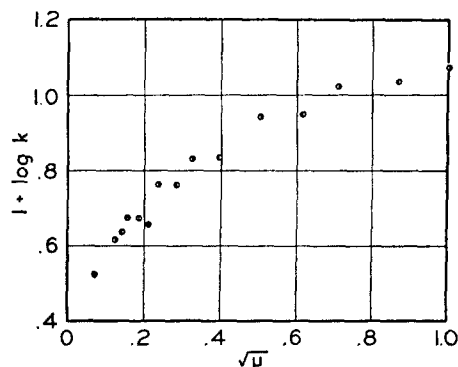

FIG. 7. The effect of the addition of salts to the reaction $BrCH_2COO^-+S_2O_3^{--}$. Data of von Kiss and Vass (reactants 0.00125M): ● no added salt, ◐ NaNO$_3$ added, ◑ Na$_2$SO$_4$ added. Data of present authors (reactants 0.001M): ⊖ KNO$_3$ added, ⊕ K$_2$SO$_4$ added, ⊗ K$_3$Co(CN)$_6$ added.

FIG. 8. The data of Fig. 7 replotted against square root of positive ion concentration.

TABLE III. Rate data for the reaction $Co(NH_3)_5Br^{++}+Hg^{++}$.

		(Brønsted and Livingston) $C_{Hg}=2.78\times10^{-4}M$ (except No. 25 where it is $5.56\times10^{-4}M$)		
$C_{Co}=4.00\times10^{-4}M$ $T=15°C$				
Run	Salt	C_{salt}	k	μ
21	KNO₃	0.0025	122	0.0047
29	Ba(NO₃)₂	0.00125	113	0.0059
23	KNO₃	0.0100	155	0.0122
31	Ba(NO₃)₂	0.0050	160	0.0174
32	Ba(NO₃)₂	0.0050	156	0.0174
25	KNO₃	0.0150	207	0.0182
39	La(NO₃)₃	0.00512	215	0.0329
26	KNO₃	0.0200	205	0.0222
34	Ba(NO₃)₂	0.0100	196	0.0322
36	Sr(NO₃)₂	0.0100	200	0.0322

TABLE IV. Rate data for the reaction $BrCH_2COO^-+S_2O_3^{--}$.

	(von Kiss and Vass) Equimolar reactants, 0.00125M		$T=25°C$	
Normality of added salt	NaNO₃ added		Na₂SO₄ added	
	k	μ	k	μ
0.01	0.412	0.015	0.432	0.020
0.05	0.580	0.055	0.577	0.080
0.10	0.678	0.105	0.682	0.155
0.25	0.875	0.255	0.886	0.380
0.50	1.05	0.505	1.10	0.755
1.00	1.18	1.005	1.40	1.505

dioxide free water and kept in bottles provided with guard tubes. Vessels used in solution preparation were swept out with purified air, and a stream of this air was introduced into each flask during dilution to the low concentrations employed.

The effect on the rate due to the addition of sodium bromide or of sodium sulfate is shown in Fig. 10 and in Table VIII.

In commenting upon the Brønsted and Livingston data for this reaction, Brønsted stated:[10] "The effect seems to be more uniform when in the solution of the various salt types (KCl, BaCl₂, etc.) equivalent concentrations instead of ionic strengths are compared." If the added "inert" salt is restricted to a chloride, or perhaps to one with a univalent negative ion, the above statement is adequate. However, if we include salts of higher negative charge types we see that it is the concentration and character of the negative ion that exerts the dominant effect on the rate. If the two reactants had equal but opposite charges, it appears probable to us that both salt ions might exert noticeable effects.

The reactions discussed above comprise the group upon which the Livingston Diagram[11] is based. This diagram, shown in Fig. 11, has been widely reproduced in support of the Brønsted theory of ionic reaction rates combined with the Debye-Hückel activity coefficient

calculation. We have omitted discussing two of the reactions of the diagram. Reaction 4, the alkaline hydrolysis of ethyl acetate[12] is not a reaction between two ions, and is not relevant to our present work. Reaction 5, the decomposition of hydrogen peroxide by hydrogen bromide was studied by Livingston.[13] The points shown in the diagram for this reaction include no data for any run in which the ionic strength was changed by the addition of "inert" salts. The analogous reaction involving hydrogen iodide was investigated by Liebhafsky and Mohammad.[14] In this case the measured rate is the sum of two reactions. For that part of the total reaction involving hydrogen and iodide ions, these authors found no salt effect over a range of ionic strengths from 0.05 to 0.5 in solutions in which the ionic strength was varied by the addition of sodium or barium perchlorate. Until these results are reconciled, it does not seem advisable to us to consider either of these reactions in testing a theory of salt effects. Livingston used the results of La Mer[15] for Reaction 2, the bromoacetate-thiosulfate reaction. However, since La Mer, in general, did not add "inert" salts to his reactants, we found the data of von Kiss and Vass[7] of more interest to us.

In the other reactions of the diagram, wherever precise experimental data have been available, we have been able to show that the specific reaction rates, to as low concentration ranges as are accessible to experiment, show a functional dependence on the concentration of
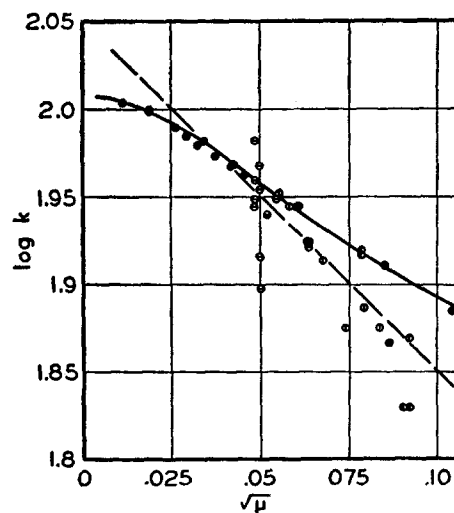
FIG. 9. The reaction $Co(NH_3)_5Br^{++}+OH^-$. Filled circles are data of present authors, cobaltammine concentration $5.0\times10^{-5}M$, sodium hydroxide concentration varied, no added salts. Data of Brønsted and Livingston: ⊖ no added salts, ⊕ BaCl₂ added, ⊕ NaCl added. Dashed line: Debye-Hückel limiting slope from Brønsted equation as drawn by Brønsted and Livingston. Curve is calculated from equation in text.

[10] J. N. Brønsted, Contemporary Developments in Chemistry (Columbia University Press, New York, 1927).
[11] R. Livingston, J. Chem. Education 7, 2887 (1930).
[12] S. Arrhenius, Zeits. f. physik. Chemie 1, 111 (1887).
[13] R. Livingston, J. Am. Chem. Soc. 48, 53 (1926).
[14] H. A. Liebhafsky and A. Mohammad, J. Am. Chem. Soc. 55, 3977 (1933); J. Phys. Chem. 38, 857 (1934).
[15] V. K. La Mer, J. Am. Chem. Soc. 51, 3341 (1929); ibid. 3678.

TABLE V. Rate data for the reaction $BrCH_2COO^- + S_2O_3^{--}$.

Equimolar reactants, 0.00100M $C_{salt} = 0.02N$	$T = 25.0°C$	
Salt	k	μ
KNO_3	0.472	0.0240
K_2SO_4	0.472	0.0340
$K_3Co(CN)_6$	0.462	0.0440

TABLE VI. Saponification of nitrourethane ion by hydroxide ion.

$C_N^- = 0.00581$	(Brønsted and Delbanco) $C_{OH}^- = 0.0250$ $C_{salt} = 0.07N$		$T = 20°C$
Salt	Total equivalent concentration	k	μ
None	0.0308	0.196	0.0308
KCl	0.1008	0.242	0.101
K_2SO_4	0.1008	0.243	0.136
$K_3Co(CN)_6$	0.1008	0.247	0.171
$Pt(NH_3)_4Cl_2$	0.1008	0.306	0.136
$Co(NH_3)_6Cl_3$	0.1008	0.586	0.171

some particular ion and not upon the ionic strength. This seems to imply that if we retain the Brønsted theory of reaction rates, we must abandon the Debye-Hückel theory either in its limiting or in its more extended forms for calculating activity coefficients of ions; for in these theories, activity coefficients, and therefore Brønsted's "kinetic activity factor," $f_A f_B / f_X$, are functionally dependent on ionic strength. The experimental rates, however, show a quite different functional dependence, as has been shown above. We must emphasize that the Brønsted-Debye combined theory is not being criticized here on the basis of small deviations from quantitative predictions. We are trying to point out that a different kind of comparison gives a much more successful method of correlating the results of kinetic experiments.

With complete freedom of choice of both mathematical form and complexity, a large number of empirical equations could be used to fit the foregoing rate data. Influenced by some other work now in progress in this laboratory, we decided to try the form
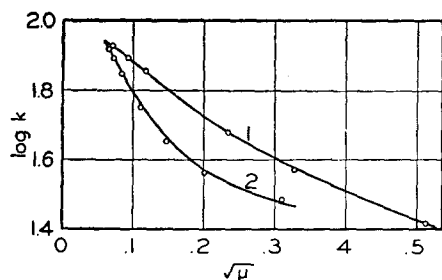
$$k = k_a \left[\frac{1}{1+K(X)} + k' \frac{K(X)}{1+K(X)} \right].$$

That we were successful in fitting the data can be seen from the solid lines in the various diagrams which were calculated from equations of this form. At high salt concentrations or for some reactions involving higher ionic charges, $K(X)$ was replaced by $K(X) + K'(X)^2$, in order to get an agreement to about one percent. In this equation k is the specific rate at some concentration of salts and reactants, k_a the specific rate at some low concentration of these substances, and k' and K are adjustable constants. (X) represents the concentration of a particular ion contributed either by added salts or by the reactants or by both.

Thus for the reaction of bromopentammine cobaltic ion with hydroxide ion, without added salts, the experimental specific rates are expressed by

$$k = 101.7 \left[\frac{1}{1+158.8(X)} + 0.6198 \frac{158.8(X)}{1+158.8(X)} \right]$$

with an average deviation of 0.4 percent. Here (X) is the concentration of hydroxide ion in moles per liter. The value 101.7 is the calculated bimolecular specific rate at this cobaltammine concentration $(5.0 \times 10^{-6}M)$ and zero hydroxide concentration. As mentioned above, another series of experiments at a cobaltammine concentration twenty-fold greater than this indicated no significant change in the specific rate at any hydroxide concentration in this range. We therefore may be justified in assuming that k_a will not change appreciably from its value, 101.7, as we decrease the cobaltammine concen-
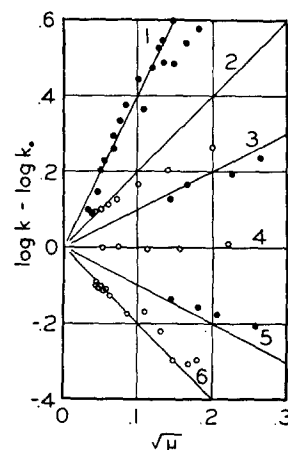
FIG. 10. The addition of salts to the reaction $Co(NH_3)_5Br^{++}$ $+OH^-$. Cobaltammine concentration, $5.0 \times 10^{-6}M$; hydroxide ion concentration $3.46 \times 10^{-3}M$. Curve 1, NaBr added; curve 2, Na_2SO_4 added.

FIG. 11. The Livingston Diagram (see reference 11).

1. $Co(NH_3)_5Br^{++} + Hg^{++} + H_2O \rightarrow Co(NH_3)_5H_2O^{+++}$.	Reference 1
2. $BrCH_2COO^- + S_2O_3^{--} \rightarrow S_2O_3CH_2COO^{--} + Br^-$.	Reference 15
3. $NO_2 = N - COOC_2H_5^- + OH^- \rightarrow N_2O + CO_3^{--} + C_2H_5OH$.	Reference 8
4. $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$.	Reference 12
5. $H_2O_2 + H^+ + Br^- \rightarrow H_2O + Br_2$.	Reference 13
6. $Co(NH_3)_5Br^{++} + OH^- \rightarrow Co(NH_3)_5OH^{++} + Br^-$.	Reference 1

TABLE VII. Rate data for the reaction $Co(NH_3)_5Br^{++}+OH^-$.

(No added salts) $10^6 \times$(cobaltammine)	$10^4 \times$(NaOH)	k	$T=15.0°C$ $(\mu)^{\frac{1}{2}}$
5.0	1.202	101.0	0.0116
	3.460	99.8	0.0190
	3.460	99.7	0.0190
	6.91	97.5	0.0266
	8.55	96.4	0.0295
	10.37	95.4	0.0325
	10.88	95.9	0.0332
	13.92	94.0	0.0375
	17.41	92.7	0.0419
	18.05	92.9	0.0427
	20.89	91.6	0.0459
	36.35	88.0	0.0604
	72.6	81.4	0.0853
	109.0	76.7	0.1045
98.6	18.05	92.4	0.0458
	36.35	87.3	0.0627
	72.6	81.3	0.0870

TABLE VIII. Rate data for the reaction $Co(NH_3)_5Br^{++}+OH^-$.

(Cobaltammine) $=5.0 \times 10^{-4}M$ (NaOH) $=3.46 \times 10^{-3}M$ (NaBr)	(Na₂SO₄)	k	$T=15.0°C$ $(\mu)^{\frac{1}{2}}$
0.001557M		85.0	0.0709
0.00520		78.2	0.0932
0.01033		71.5	0.1175
0.0520		47.9	0.236
0.1038		37.4	0.328
0.2600		26.0	0.513
	0.000308M	82.9	0.0664
	0.000621	78.2	0.0731
	0.001233	70.1	0.0847
	0.003080	56.2	0.1128
	0.00621	45.0	0.1487
	0.01240	36.5	0.2018
	0.03102	30.6	0.3110

tration to zero. At infinite dilution then,

$$k=k_0\left[\frac{1}{1+158.8(X)}+0.6198\frac{158.8(X)}{1+158.8(X)}\right].$$

Comparing this expression with Brønsted's equation, we find that if the Brønsted equation is valid,

$$\frac{f_A f_B}{f_X}=\frac{1}{1+158.8(X)}+0.6198\frac{158.8(X)}{1+158.8(X)}$$

for this particular reaction.

The form of this expression is suggestive of an alternative interpretation. Thus, instead of considering an average effect on all of the reactant particles of a given charge type, we might consider a more intimate picture in which we divide each of the reactants into two groups. In the one group would be those particles which have the same specific reaction rate, k_0, as they would have at infinite dilution. This fraction is designated by $1/[1+K(X)]$. In the other group would be those reactant particles that are so closely associated with other particles, usually salt ions of opposite charge sign, that the electric force between the reactants is distinctly altered; i.e., they would have the specific rate constant $k'k_0$. This fraction is designated by $K(X)/[1+K(X)]$. Since such association would always result in a decrease of the absolute value of the electric force between reactant ions, k' must be less than one for a reaction between ions of opposite sign, and greater than unity for reactions between ions of the same sign. This consideration alone gives the qualitative effect of salts on the rates of ionic reactions. Quantitative agreement with experiments may be got by assigning numerical values to k' and K.