2. The activity coefficient has been calculated for sodium silicate solutions with various ratios of sodium oxide to silica.

3. Sodium metasilicate solutions behave as typical uni-bivalent electrolytes. The value of ν in the freezing point equation is taken equal to 3 instead of 4 as taken by previous authors. Although sodium metasilicate solutions are largely hydrolyzed, the choice of $\nu = 4$ is not consistent with our conventions regarding the definition of activity coefficients.

4. Sodium acid silicates are not largely hydrolyzed. The formula is taken as $NaHSiO_3$ rather than $Na_2Si_2O_5$, and $\nu = 2$ rather than $\nu = 4$. The acid silicates show extremely low activity coefficients.

5. The low activity coefficients of the acid silicates are explained by the assumption of the existence of ionic micelles which are not entirely dissociated into simple ions except in very dilute solutions.

6. The percentage of substance existing as micelles in the silicates increases with the ratio of silica to sodium oxide.

7. The number of aggregated acid silicate ions forming a micelle increases as the percentage of silica increases.

8. The effect of the ionic micelle upon the individual ion activity of sodium ion is discussed.

BERKELEY, CALIFORNIA

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

PRIMARY SALT EFFECT IN A ZERO TYPE REACTION

BY MARTIN KILPATRICK, JR.[1]

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The present work is a further attempt to distinguish experimentally between the "activity rate theory" and the Brönsted formula for reaction rate in dilute solution.

According to the activity rate theory, the velocity of a reaction between A and B can be expressed by the equation

$$v = ka_Aa_B$$

where a_A and a_B are the activities of A and B, respectively.

Brönsted's[2] general formula may be written

$$v = kc_Ac_B \cdot f_Af_B/f_X$$

where k depends on the temperature and the solvent and f_A, f_B and f_x are the activity coefficients of A, B and the "critical complex," respectively. For a solution so dilute that the activity coefficients of molecules and ions depend only on the charge, the general formula is

$$v = kc_Ac_B \cdot f_{z_A}f_{z_B}/f_{z_A + z_B}$$

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[1] National Research Fellow.

[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

where f_z represents the activity coefficient of an ion of valence z. The effect of salt upon the rate of reaction due to change in the value of the kinetic activity factor, $f_{zA} f_{zB}/f_{zA + zB}$, is called "primary salt effect." For the case of a reaction between a non-electrolyte and an ion

$$A^0 + B^z \longrightarrow (A,B)^z \longrightarrow \text{products}$$

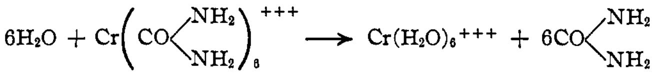
the kinetic activity coefficient becomes $f_0 f_z/f_z$ and in dilute solution should have a limiting value of one. The deviation from unity is linear with the concentration and consequently a linear salt effect is expected. According to the activity rate theory an exponential salt effect is predicted, since the rate is considered proportional to the product of the activities of the reactants.

The results of kinetic studies of reactions of this type (chiefly hydrogen and hydroxyl ion catalysis) have been used in an attempt to establish an experimental basis for the activity rate theory.[3] However, as already pointed out,[4] these experiments were carried out in solutions of high electrolyte concentration and are unsuitable for the purpose. In the first place, an investigation of the specific effect of the catalyst's activity cannot be carried out in concentrated salt solutions where numerous other factors influence the reaction rate and veil the effect sought. In the second place, one is prevented from taking advantage of the pronounced and uniform variations shown by ionic activity coefficients in dilute solution with change of salt concentration. For reactions studied in dilute solution the effect is linear and contradictory to the activity rate theory. A more critical test would be furnished by the study of a reaction involving a polyvalent ion, as in this case an exponential salt effect would be of much greater magnitude.

For these reasons a further experimental study of a reaction of the type

$$A^0 + B^z \longrightarrow \text{products}$$

where $z > 1$ in dilute solution seemed desirable. The reaction finally chosen was that between water and the hexa-urea chromium ion



$$6H_2O + Cr\left(CO\begin{matrix}NH_2\\NH_2\end{matrix}\right)_6^{+++} \longrightarrow Cr(H_2O)_6^{+++} + 6CO\begin{matrix}NH_2\\NH_2\end{matrix}$$

It is probable that the reaction takes place in steps and that the equation above does not represent the mechanism of the reaction. This, however, does not affect the kinetic equation

$$A^0 + B^{+++} \longrightarrow (A,B)^{+++} \longrightarrow \text{products}$$

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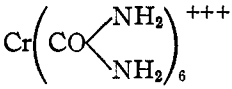
[3] (a) Harned, THIS JOURNAL, **40**, 1461 (1918); (b) Harned and Pfanstiel, *ibid.*, **44**, 2193 (1922); (c) Scatchard, *ibid.*, **43**, 2387 (1921); (d) Fales and Morrell, *ibid.*, **44**, 2071 (1922); (e) Åkerlöf, *ibid.*, **48**, 3046 (1926); (f) Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920); (g) Moran and Lewis, *ibid.*, **121**, 1613 (1922).

[4] Brönsted, "Om Syre-og Basekatalyse" Københavns Universitet, September, **1926.**

The reaction can be followed by determining the rate of disappearance of the 
$\mathrm{Cr}\left(\mathrm{CO}\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right)_6^{+++}$ ion.

Experimental Part

The chromium urea chloride was prepared according to the method of Pfeiffer,[5] and converted to the nitrate by precipitation with nitric acid. Preliminary experiments showed that the reaction was very sensitive to diffused light. The rate of disappearance of the $Cr(NH_2CONH_2)_6^{+++}$ ion was determined by withdrawing samples of the reacting solution and precipitating with $K_3Co(CN)_6$ as $Cr(NH_2CONH_2)_6Co(CN)_6$. To test the quantitative accuracy of the method, known quantities of chromium urea nitrate were weighed out and the chromium urea cobalticyanide precipitated using varying excesses of potassium cobalticyanide and in the presence of different concentrations of potassium nitrate. The solubility of the precipitate increased in the presence of salt. Using a fourfold excess of potassium cobalticyanide (the filtrate being less than 0.01 molar in cobalticyanide) the method yielded results within 1% of the calculated weight in the presence of potassium nitrate up to 0.2 molar. Since the reaction is somewhat faster in pure water than in slightly acid solution, probably due to a slight effect of the OH ion, all experiments were carried out in solutions 0.001 *M* in nitric acid. The reaction is not catalyzed by hydrogen ion. The experiments were performed at 22.50° in a thermostat from which all light was excluded. A typical experiment ran as follows: 1.496 g. of chromium urea nitrate (0.002500 mole) was weighed out, dissolved in water, enough nitric acid was added to make the solution 0.001 *M* in nitric acid, and the whole was diluted to one liter and placed in the thermostat. At suitable intervals 100cc. portions were pipetted out and run into 15 cc. of solutions containing 0.001 mole of potassium cobalticyanide and enough potassium nitrate to make the final concentration of potassium nitrate 0.2 *M*. After cooling the solutions in ice, with frequent shaking, the precipitates were filtered onto weighed porous plate crucibles, washed with 5 cc. of water containing potassium cobalticyanide and finally with alcohol. The precipitates were dried at 90°.

The results are shown in Table I. The velocity constants are calculated by the formula

$$h = \frac{2.30}{t}\log_{10}\frac{c_0}{c_t}$$

where t is expressed in hours, c_0 represents the initial concentration and c^t that at time t.

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[5] Pfeiffer, *Ber.*, **38**, 1926 (1903).

TABLE I

A TYPICAL EXPERIMENT

Time, hours	Wt. ppt.; g. of $Cr(NH_2CONH_2)_6Co(CN)_6$		$k \times 10^5$
0	0.1575		...
46.3	.1154		672
71.9	.0961		687
120.1	.0691		681
144.1	.0602		668
168.2	.0509		669
192.1	.0434		671
		Average	674
		Av. dev.	0.9%

Table I shows that the disappearance of the chromium urea ion follows a unimolecular law. Table II gives a summary of the results of similar experiments carried out in the presence of potassium nitrate.

TABLE II

VELOCITY AT DIFFERENT SALT CONCENTRATIONS

$Cr(NH_2CONH_2)_6^{+++}$ 0.0025 *M* in all experiments; HNO_3 0.001 *M*

KNO_3, moles per liter	$k \times 10^5$	KNO_3, moles per liter	$k \times 10^5$
0	669	0.100	667
0.025	662	.150	667
.050	674	.200	658

From Table II it is evident that if there is any salt effect it is within the experimental error of the measurements (less than 2%). If the reaction rate were correctly expressed by the formula

$$v = k\, a_A a_B$$

the velocity constant would have decreased to approximately one-fourth its original value as the equivalent salt concentration increased from 0.0075 to 0.2075.[5a] My results are in direct contradiction to the activity rate theory and furnish substantial support to the Brönsted formula.

It is interesting to note that while the magnitude of the primary salt effect in this case is within the experimental error of the measurements, there are instances where the salt effect for this type of reaction is of considerable magnitude even in dilute solution. In the decomposition of nitrosotriacetonamine by hydroxyl ion the effect is about 7% in 0.1 *N* salt solution.[6,7] For the diazo-acetic ester reaction catalyzed by hydrogen ion the effect is 14% in 0.1 *N* salt solution.[8] For the mutarotation of glucose the salt effect is again within the experimental error

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[5a] This estimate is based upon the change in the activity coefficient of a trivalent ion calculated from the solubility measurements of luteo hexacyano cobaltiate in potassium chloride solutions [Brönsted and Petersen, THIS JOURNAL, **43**, 2265 (1921)].

[6] Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

[7] Kilpatrick, *ibid.*, **48**, 2091 (1926).

[8] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

of the measurements.[9] Other examples are given by Brönsted.[10] For hydrogen-ion catalysis the salt effect is positive and for hydroxyl-ion catalysis negative. In all cases the effect is linear in dilute solution and consequently cannot depend on the activity of the reacting ion.

The author wishes to thank Professor J. N. Brönsted for many valuable suggestions.

Summary

1. A kinetic study has been made of a zero type reaction in which the reacting ion is trivalent.
2. The reaction serves as a critical test of the activity rate theory and the Brönsted formula. The results are in agreement with the Brönsted formula.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VI THE ELECTRIC MOMENTS OF CERTAIN NITRO DERIVATIVES OF BENZENE AND TOLUENE

BY JOHN WARREN WILLIAMS AND CHRISTIAN H. SCHWINGEL

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Measurements of the dielectric constants of binary mixtures in which the first component, the solvent, is known to have no electric moment permit a calculation of the molar polarization, and therefore of the electric moment, of the second component. This calculation has been detailed in a number of places.[1,2,3] The purpose of this paper is to present dielectric constant and density data for solutions of a number of nitro derivatives of benzene and toluene in the non-polar solvent benzene, with the results of the calculations for the electric moments of the solute molecules.

The method used for the determination of the dielectric constants of the binary mixtures was given in the first paper of the series.[4] Their densities were determined by means of an Ostwald-Sprengel pycnometer. Both dielectric constant and density determinations were made at 25°; in every case the usual precautions for precision work were taken.

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[9] Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[10] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[1] Debye, "Handbuch der Radiologie" (Marx), **6**, 597 (1925).

[2] Lange, *Z. Physik*, **33**, 169 (1925).

[3] Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927).

[4] Williams and Krchma, *ibid.*, **48**, 1888 (1926).