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SPECIFIC EFFECTS OF NEUTRAL SALTS ON

THE RATE OF IONIC REACTIONS

IN SOLUTION
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TABLE OF SYMBOLS USED

- $c_A$ ... concentration of A.
- $a_A$ ... activity of A
- $f_A$ ... activity coefficient of A
- $z_A$ ... charge of A.
- $\mu = \frac{1}{2} n m^2$ ionic strength

Na-Na reaction ... reaction between $\text{BrCH}_2\text{CO}_2\text{Na}$ & $\text{Na}_2\text{S}_2\text{O}_3$
K-K reaction ... reaction between $\text{BrCH}_2\text{CO}_2\text{K}$ & $\text{K}_2\text{S}_2\text{O}_3$
Na-K reaction ... reaction between $\text{BrCH}_2\text{CO}_2\text{Na}$ & $\text{K}_2\text{S}_2\text{O}_3$
K-Na reaction ... reaction between $\text{BrCH}_2\text{CO}_2\text{K}$ & $\text{Na}_2\text{S}_2\text{O}_3$
INTRODUCTION

PRIMARY SALT EFFECTS.

It has long been known that the rate of a chemical reaction involving ions in solution is a function of the total electrolyte concentration, even in systems where there is no displacement of equilibria. This primary salt effect operates whether the ions are present as reactants or purely as catalysts.

Quantitative information about this effect cannot be obtained from every reaction, as the theoretical treatment, as well as the experimental method imposes certain limiting conditions. A suitable reaction must occur at a measurable rate with no complicating side reactions and back reactions, and without change in ionic strength. Moreover there must be a quick and accurate method of analysing the reacting mixture at intervals of time in order to determine the rate constant.
THE ACTION OF THE THIOSULPHATE ION ON ALIPHATIC HALIDES

Slator\(^1\)\(^2\) has shown that reactions of the type

\[ RX + S_2O_3^{2-} \rightarrow R S_2O_3^- + X^- \]

where \( X \) is a halogen and \( R \) an aliphatic radical, are simple substitutions, remarkably free from side reactions. The thiosulphate radical becomes attached to the carbon of the aliphatic chain through a sulphur atom.

Slator used reactions of this type where \( R \) was an alkyl group to measure the relative reactivities of the substituted halogens. He then extended his work to the case where \( RX \) was a halogeno-acetate, and made the first measurements on the bromoacetate-thiosulphate reaction.

This reaction

\[ BrCH_2CO_2^- + S_2O_3^{2-} \rightarrow S_2O_3Br^- + CH_2CO_2^- \]

is typical of the class. It is a simple second order reaction, and satisfies all the conditions for a reaction suitable for kinetic study. The rate constant may be readily and fairly accurately determined by titrating the unreacted thiosulphate in the solution with iodine, using starch solution as an indicator, and calculating \( k \) from the equation

\[ k = \frac{1}{\frac{a}{a-x}} \]

where \( a \) is the initial concentration of the reactants, and \( x \) the amount that has reacted at a time \( t \). This equation is applicable to second-order reactions when the initial concentrations of the reactants are equal.
The bromoacetate-thiosulphate reaction, then, may be used as a tool for testing generalised statements about reaction rates, and is particularly suitable for measuring primary salt effects.
The reaction between the bromoacetate ion and the thiosulphate ion may be formulated in terms of the transition state theory, as taking place with the formation of an intermediate complex.

\[ \text{BrCH}_2\text{CO}_2^- + \text{S}_2\text{O}_3^- \rightarrow \text{X} \rightarrow \text{S}_2\text{O}_3\text{CH}_2\text{CO}_2^- + \text{Br}^- \]  \hspace{1cm} \text{(1)}

The critical complex \( \text{X}^{\text{iii}} \) \( 5, 6, 7 \) corresponds to the maximum potential energy attained by the system as it passes through a series of states, as the reacting ions approach, interact, and finally give the products. All these intermediate states are of lower probability than either the initial or final states, so that it may be assumed that when the system has passed through the transition state, the least probable of them all, the reaction is completed. The activated complex behaves in most respects as an ordinary molecular species. Its formation involves the usual changes in free energy, entropy, etc., and all the rotational and translational energy states are distributed in the same manner as in an ordinary molecule or ion i.e., the potential energy in all these states is a minimum. One of the vibrational states, however, is exceptional in having the potential energy a maximum. This state has become what has been called an intramolecular translational state, and it represents the motion of the parts of the complex relative to one another, corresponding to the reaction about to take place. It is this maximum potential energy which leads to the low probability of the complex.

Eyring and Polanyi dispensed entirely with the pictorial method of describing the reaction mechanism, and treated the transition state purely as a mathematical concept. It is possible, however,
to reach the same conclusions by treating the activated complex as a molecular species, and picturing the reaction as taking place in two steps. The first step is the formation of the complex from the unactivated molecules or ions, and the second the decomposition of X into the products.

For the general reaction

\[ A + B \xrightleftharpoons{\text{K}_1} X \xrightarrow{\text{K}_2} C + D \]  

using Brønsted's original treatment, it is assumed that a statistical equilibrium exists between the reacting molecule and the activated complex X.

\[ \frac{a_x}{a_A a_B} = \text{K} = \frac{c_X}{c_{ABC}} \cdot \frac{f_X}{f_{ABC}} \ldots (3) \]

where K is an equilibrium constant. The second process, then, the decomposition of X into the products, is the rate-determining process, so that

\[ v = k_2 c_X \ldots (4) \]

where v is the observed reaction velocity. Then, assuming that \( k_2 \) is a constant independent of the environment,

\[ V = k_2 c_{ABC} \frac{f_{ABC}}{f_X} \ldots (5) \]

If the reaction is second order,

\[ V = k_1 c_{ABC} \ldots (6) \]

and combining (5) and (6)

\[ k_1 = k_2 k \frac{f_{A-B}}{f_X} = k_0 \frac{f_{A-B}}{f_X} \ldots (7) \]

This equation cannot be tested experimentally as it stands, but if the activity coefficients can be expressed in measurable quantities, an experimental test is possible. An expression such as \( \frac{f_{A-B}}{f_X} \) has
physical meaning only in cases where \( z_A + z_B = z_X \). This is a necessary condition of the transition complex; so that the Debye-Hückel limiting law

\[
- \log f_i = A z_i \sqrt{\mu} 
\]

may be applied, and

\[
\log k_1 = \log K_0 + 2A z_A z_B \sqrt{\mu} \quad \ldots \ldots (9)
\]

At 25°C, \( A = 0.5 \), and

\[
\log k = \log K_0 + z_A z_B \sqrt{\mu} \quad \ldots \ldots (10)
\]

This equation has been tested for numerous reactions by measuring the rate constant at different ionic strengths, and plotting \( \log k \) against \( \sqrt{\mu} \). In general it is found that at low ionic strengths, and in the limit as \( \mu \to 0 \), the resulting curve becomes linear, and the slope is the theoretical value \( z_A z_B \) but that at higher ionic strengths deviations become apparent, and the slope falls off quite quickly.

V. K. La Mer \(^3,^9\) studied the variation of the rate constant of the reaction between the bromoacetate ion and the thiosulphate ion in the presence of different univalent cations. In this case, the curves approximated to the same straight line with slope \( z_A z_B = 2 \), at low concentrations, but as the ionic strength increased the discrepancies became very marked, and specific effects developed i.e. the curves for the sodium and potassium cations no longer coincided. It is apparent, therefore, that the equation

\[
\log k = \log K_0 + 2 \sqrt{\mu}
\]

does not describe completely the catalytic effect of the ions in solution on the thiosulphate-bromoacetate reaction. It is important to emphasize that this type of
experiment is as much a test of the Debye-Hückel limiting law as of the transition state theory, and it is generally assumed that the observed discrepancies are due to the failure of the limiting law at higher ionic strengths, and do not reflect doubt on the essential correctness of equation (7). Similar deviations are observed in other applications of the law.
SPECIFIC INTERACTION OF IONS.

The Debye-Hückel limiting law is based on the assumption that there are only simple Coulombic forces acting on an ion in solution.

If this were true, the primary salt effects of all ions in solution would be determined by their concentration and charge, and for a particular reaction and temperature, the plot of log $k$ against $\sqrt{I}$ would give an identical curve, however the ionic strength were made up. This, however, is not the case, except at very low concentrations, and it is necessary to postulate secondary forces exerted by ions, depending on their individual properties.

There are numerous examples of specific effects of ions in solution, and it is clear that the activity coefficient of an ion is a function of the ionic environment, and is not independent of the ions with which it is associated, as the principle of ionic strength implies.

Brönsted first introduced his principle of specific interaction of ions to account for the weight of experimental evidence which did not fit in with the principle of independent activity coefficients of ions developed by MacInnes and Harned. MacInnes had postulated that the activity coefficient of cations and anions in the same solution may differ from one another, and that the activity coefficient of the chloride ion at any given concentration is independent of the cation associated with it.

Brönsted carried out a detailed examination of activity coefficients by measurements of solubility, and found that the activities of ions depend very markedly on their individual natures,
and are influenced by the nature of the salt solutions acting as solvents. On the basis of these and other observations, Brönsted formulated his principle of specific interaction of ions. The activity coefficient of an ion, then, is a function of the nature of the ion itself, and of the solvent containing it. In a dilute salt solution of constant total concentration (most of this theory was developed before Lewis and Randall introduced the concept of ionic strength) ions will be uniformly influenced by ions of their own sign.

Brönsted ascribed these specific effects to the individual character of ions, appreciable even at low concentrations. He claimed that the deviations observed in freezing point measurements, could only be explained, if complete dissociation of the salts was assumed, as being the result of a secondary power exerted by an ion, a power which can exert a specific action on ions of the same or of another type. These secondary forces, according to Brönsted, depend upon the structure and size of the individual ions.

If these considerations are applied to the kinetics of the bromoacetate-thiosulphate reaction, the deviations from the Brönsted-Debye equation may be explained in a qualitative manner.

It is impossible to define the exact configuration of the transition complex, but it has certain essential characteristics which are known. It is the state of lowest probability of the system, it is undergoing an intramolecular translational motion, and it is triply negatively charged. Hence it may be pictured as existing in solution at a point of time as an unstable system.
consisting of a core of positive nuclei and a negative charge
distribution. Orientation of the solvent molecules in its immediate
neighbourhood will stabilise it to a certain extent.

If a cation approaches the complex, the extranuclear electrons
which are being attracted towards the positive nuclei of the
constituent atoms, will be attracted in the opposite direction. As
a result the structure will become more rigid and consolidated, and
the potential energy will decrease. Since the only state in which
the potential energy is not already a minimum is the intramolecular
translational state, the movement of the parts of the complex
relative to one another must be inhibited, and the probability that
the system will cross the energy barrier is decreased.

If, on the other hand, an anion approaches the complex in
solution, its negative charge will repel the electrons, so that two
forces will operate upon them simultaneously in the same direction.
The result will be an increase in potential energy.

It is now necessary to consider the probability of either of
these interactions occurring. Since the charge of the transition
complex is equal to the sum of the charges of the reactants, $X$ in
this case will be triply negatively charged. At any instant such
a species must be surrounded in solution by an excess of positive
ions. The probability that an anion will approach closely enough
to interact with the complex is very low, and one would not expect
the second interaction to occur. The stabilising action of the
cations, however, will operate, as the complex will have a number of
positive ions in its immediate neighbourhood.
Since different ions have different electron affinities, the degree of the two effects will vary from cation to cation and from anion to anion. If it is assumed that anions cannot approach the complex closely enough to interact with it, it follows that all anions will influence the complex uniformly, and that specific effects will not be apparent. Cations, however, will have increasing stabilising effect in the order of increasing electron affinities.

\[ K^+ < Na^+ < Li^+ \]

The stability of the complex is reflected in the measured reaction rate, which is determined by the rate of decomposition of the transition complex into the products. Hence anions should show no specific catalytic effect on the reaction rate and cations should have increasing catalytic effect in the order of decreasing electron affinity.

\[ K^+ > Na^+ > Li^+ \]

When these considerations are extended to polyvalent cations there is another factor which must be accounted for. La Mer and Fessenden in studying the effects of different cations upon the bromoacetate-thiosulphate reaction, found that in the presence of divalent cations such as calcium and magnesium, the velocity increased far more rapidly with ionic strength than was calculated by the Brønsted-Debye equation. The curve obtained by plotting \( \log k \) against \( \sqrt{a} \) had initially a slope greater than the theoretical value of 2, which fell off quite rapidly at higher ionic strengths.

Their explanation of this discrepancy was that the effect of a high-valence cation in the environment is to give \( f_x \), the activity coefficient
of the complex, a lower value than that calculated by the Debye-
Hückel limiting law. The corresponding decreases in $f_A$ and $f_B$
are not sufficient to counterbalance the decrease in $f_X$, so that the
net effect is that the term $\frac{f_A f_B}{f_X}$ is greater than the calculated
value, and the velocity constants for the reaction are greater than
the corresponding values for the reaction in the presence of
univalent cations.

It is impossible, therefore, to predict the relative effects
of a divalent and a univalent cation. There are two opposing factors
to be considered, and either might predominate. For instance,
although the magnesium ion has a greater electron affinity than the
potassium ion, it is found that the reaction in the presence of
magnesium ions is faster than in the presence of potassium ions,
i.e. the second effect is greater.

It is possible, however, to compare the effects of a series of
divalent cations. The order of increasing electron affinity a
decreasing ionic radius will be the order of decreasing catalytic
effect,

\[ \text{i.e. } \text{Ba}^{++} > \text{Sr}^{++} > \text{Ca}^{++} > \text{Mg}^{++} \]

Processes involving the formation of a highly negatively
changed complex are not common, so that it is difficult to correlate
the specific effects observed in the bromoacetate-thiosulphate
reaction with sufficient independent data to make a generalisation
possible.

La Mer and Friedman\textsuperscript{20} showed that there were marked specific
effects on the equilibrium
in changing from sodium to potassium salts, but that in general anions influenced it uniformly. Moreover, Just showed that the velocity of the forward reaction was always greater in the presence of potassium ion than in the presence of sodium ion.

Bekker studied the kinetics of the reaction between the chloroacetate ion and the thiosulphate ion. He found that cations increased the rate constants in the order

\[ K^+ > Na^+ > Li^+ \quad \text{and} \quad Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} \]

and attributed this specific catalytic action to the differing mobilities of the cations.

This series is paralleled in the reaction between the persulphate ion and the iodide ion.

\[ S_{2}O_{8}^{2-} + 2I^- \rightarrow 2SO_{4}^{2-} + I_{2} \]

Howells showed that the salt effects of cations decrease in the order

\[ K^+ > Zn^{++} > Mg^{++} > Be^{++} > Na^+ > Li^+ > H^+ \]

He points out that this is also the order of decreasing ionic radius, and offers the following explanation.

The reaction rate is determined by the rate of formation of the short life complex from the reacting anions. The attractive forces set up between these anions and the small lithium ion are greater than the attractive forces between the anions and the potassium ion. In the presence of lithium ion, therefore, the free motion of the anions in solution is inhibited more than in the presence of the larger ion, and the probability that the ions will collide and interact.
is lower.

This explanation, based on the collision theory requires that the energy of activation should increase on changing the cations in the reacting system from potassium to lithium. The alternate explanation is based on the transition state theory, which according to La Mer requires that the entropy of activation is the main factor influencing the change of reaction velocity with ionic strength.

This may be pictured in the following way. It was seen that the close approach of a cation to the complex in solution causes a decrease in potential energy by inhibiting the intramolecular translational motion. Since the formation of the complex, and its passage across the energy barrier entail a redistribution of the energy of the reacting anions, any factor complicating this rearrangement will cause a decrease of entropy in the formation of the activated complex, and the reaction will be slower. Such a factor is the interaction of cations with the complex. One might expect, therefore, that the entropy of activation would become more negative, on changing the cations in the reacting system from potassium to lithium.

It should be interesting, then, to compare the variations in entropies and energies of activation of the reaction at the same ionic strength in the presence of potassium, sodium and lithium ions.

In the Arrhenius equation

$$k = A e^{-\frac{E_{act}}{RT}}$$

or

$$\log k = \log A - \frac{E_{act}}{2.3 RT}$$

$$= B - 2.3 RT$$
the B factor contains a probability component, and is therefore a measure of the entropy of activation. V. K. La Mer measured the rate constant of the bromoacetate-thiosulphate reaction over a range of temperatures, and calculated the energies of activation and the B factors at different ionic strengths. He pointed out that the Arrhenius equation requires that increasing ionic strength should increase the energy of activation. This leads to a conclusion, which is in accord with none of the accumulated data on primary salt effects, that the addition of neutral salts should decrease the rate of a reaction. La Mer postulated, therefore, that the B factor decreases rapidly with increasing ionic strength, and that it is the entropy, and not the energy of activation which is predominantly affected by ionic strength. His experimental results appear to bear out his theoretical predictions, but must be interpreted cautiously, as the order of accuracy of both E and B is necessarily low.

The problem of the specific cation effects is merely a special case of the more general problem of primary salt effects and it is a corollary of La Mer's hypothesis that specific cation effects result primarily from a varying entropy of activation.
PREVIOUS WORK ON THE BROMACETATE-THIOSULPHATE REACTION.

The reaction has been studied by Slater,\textsuperscript{1,2} Krapavin,\textsuperscript{27} La Mer,\textsuperscript{3,9,26,29-30} Kappanna,\textsuperscript{31,32} Kiss,\textsuperscript{33} and others.

Krapavin measured the rate of the Na-Na reaction in the presence of sodium nitrate, chloride, iodide, and sulphate. The values of the rate constant he obtained suggest very strongly that anions have no specific action on the reaction rate.

Kappanna showed that the temperature coefficient is independent of the ionic strength, and that in general, the effect of a change in temperature is in accord with the Brønsted-Debye equation.

V. K. La Mer and co-workers have studied this reaction very extensively. They showed that in the presence of univalent cations (sodium and potassium) the Brønsted-Debye equation is obeyed at low ionic strengths. The curves obtained by plotting \( \log k + 1 \) against \( \sqrt{\mu} \) tend to a straight line with the theoretical slope \( s_{AB} = 2 \). At higher values of \( \mu \), however, the slope falls off quite rapidly, and specific effects develop i.e., the curves for the reaction in the presence of sodium and potassium ions no longer coincide. In the presence of divalent cations, the Brønsted-Debye equation does not hold even at low concentrations, and again each cation has a specific effect.

La Mer also studied the kinetics of the reaction from the point of view of the Arrhenius equation

\[
k = \alpha e^{-\frac{E}{RT}}
\]

\[
\log k = B - \frac{E}{2.303RT}
\]
He measured the rate constant of the reaction at varying initial concentrations of the reactants, and in the presence of high-valent salts such as barium and lanthanum chloride, and in the presence of non-electrolytes, over a range of temperatures.

These results suggest that a more detailed investigation of specific ion effects could be made.
There are two methods of testing the specific effects of ions on the bromoacetate-thiosulphate reaction.

1. Measure the variation of the rate constant with ionic strength by varying the initial concentrations of the reactants in the presence of different cations. For example compare the rate constant of the reaction

$$\text{BrCH}_2\text{CO}_2^- + \text{Na}^+ + \text{Na}^+ \text{S}_2\text{O}_3^- \rightarrow \text{S}_2\text{O}_3\text{ClH}_2\text{CO}_2^- \text{Na}^+ + \text{Na}^+ \text{Br}^-$$

with the corresponding values for the reaction

$$\text{BrCH}_2\text{CO}_2^- \text{K}^+ + \text{K}_2^+ \text{S}_2\text{O}_3^- \rightarrow \text{S}_2\text{O}_3\text{ClH}_2\text{CO}_2^- \text{K}^+ + \text{K}^+ \text{Br}^-$$

2. Keep the initial concentrations of the reactants constant, and add varying concentrations of neutral salts.

The first method has been used by Le Mer and Fessenden. It is undoubtedly the more satisfactory method experimentally, but it gives no information about the effect produced by a change in anions.

The second method should indicate specific effects in either cations or anions, and results obtained in this way, supplemented by Le Mer's data from the first method will give a complete picture of the catalytic effect of ions in the reacting system.

The work can be divided into three parts.

1. Study of the catalytic action of anions.

The rate constant of the Na-\(\text{Na}\) and K-\(\text{Na}\) reactions in the presence of NaX and KX were measured where

$$X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3^-, \text{and } \frac{1}{2} \text{SO}_4^2-$$
2. Study of the catalytic action of cations.

The effect of added caesium, potassium, sodium lithium, barium, strontium, calcium and magnesium salts on the Na-Na, K-Na, Na-K, and K-K reactions was measured.

5. Calculation of $E$ and $B$.

The rate constant for the Na-Na reactions in the presence of added salts were measured at 25°C and at 35°C, and $E$ and $B$ calculated from the equation

$$\log k = B - \frac{E}{2.3RT}$$
Bromacetic Acid.

Bromacetic acid was prepared by the bromination of acetic acid in the presence of acetic anhydride. The impure product was purified by distillation. The final fraction collected boiled at 103°C at 18 mm. The purity of the compound was tested by titration with 0.3N sodium thiosulphate, as under these conditions the reaction is complete in twenty-four hours, and with 0.2N sodium hydroxide. The ratio of replaceable bromine to replaceable hydrogen from these tests was 1.01, 0.97, 1.01, 1.03, 0.99 in five determinations. The purified product was kept over phosphorus pentoxide in a desiccator.

Solutions.

The standard solutions were made up from A.R. quality reagents, with distilled water. The thiosulphate solutions were stabilised by the addition of a little bicarbonate.

Salts.

The neutral salts added to the reactants were also of A.R. quality, or were recrystallised.

Cesium chloride was prepared from the dichlor-iodide by treating at 80°C to expel iodine.

Starch Solutions.

A fresh starch solution was prepared before each run, from A.R. soluble starch and distilled water.
Experimental.

The initial concentrations of the reactants were kept at 0.01M in all reactions. The two solutions were placed in the thermostat and the equivalent volume of thiosulphate pipetted into the bromoacetate solution when they reached the equilibrium temperature. The time of half-delivery of the pipette was taken as the initial time of reaction. At intervals aliquots of the reaction mixture were removed, the reaction stopped with iodine, and the excess iodine back titrated with thiosulphate solution.

The bromoacetate solution for each run was made up by dissolving the weight of bromoacetic acid in water, neutralising with potassium or sodium hydroxide, using phenol phthalein as indicator, and diluting to the appropriate volume. The thiosulphate and iodine solutions were restandardised after each bracket of five runs, and the purity of the bromoacetic acid tested from time to time. (This did not vary.)

It was found that the most accurate method of carrying out the titrations was as follows. Aliquots of 5ccs. were removed, and the reaction stopped with 2ccs. of iodine solution, approximately 0.02M. These quantities were chosen so that the iodine could be added rapidly, thus minimising the error in time.

It was found, too, that the results varied with the concentration of the added thiosulphate solution. During the titrations atmospheric oxidation became appreciable with time, so that it was essential to run in the thiosulphate solution quickly. This error was least with a small volume of concentrated thiosulphate. If the solution was too strong, however, the concentration error was great, and it was found
that the best compromise was a 0.1M solution.

In order to reduce the error due to atmospheric oxidation further, an approximate value for the rate constant was found for each run (either by analogy with other results, or by carrying out a trial run) and the approximate volume of thiosulphate which would be required to react with the excess iodine calculated for regular time intervals. Under these conditions all but about 0.02cc of the thiosulphate could be run in directly, and there was not time for atmospheric oxidation to cause appreciable error.

When the titrations were carried out in this way, and the starch solution added when only about 0.02cc of thiosulphate was to be run in, the end point was sharp and easily determined. In the presence of barium ions the colour of the starch-iodine solution changed, but this did not affect the end point.

The method of studying salt effects by adding neutral salts to the reactants, has several limitations. Since the reaction is one of simple substitution

\[
\text{BrCl}_2C_2O_2 + S_2O_3^{2-} \rightarrow S_2O_3Cl_2C_2O_2 + \text{Br}^{-}
\]

it is possible that other anions in the solution may react with the bromoacetate ion in an analogous manner. This will not cause appreciable error unless the rate of the secondary reaction is comparable with that of the bromoacetate-thiosulphate reaction. That hydrolysis of the bromoacetate ion occurred during the reaction was evident from the fact that the solution became faintly acidic. It was measured the rate of hydrolysis, and found that it was negligible at 25°C.
A. V. Kiss criticises La Mer's results for the reaction in the presence of .05M barium chloride and .05% lanthanum chloride on the grounds that the reaction

\[
\text{BrCH}_2\text{CO}_2^- + \text{Cl}^- \rightarrow \text{ClCH}_2\text{CO}_2^- + \text{Br}^-
\]
takes place.

His results for the reaction in the presence of sodium nitrate are open to a similar criticism. He records values for the rate constant for a reacting solution up to 3M in sodium nitrate, and it has been found that the reaction is not strictly second order for concentrations greater than about .025N in NaNO_3.

It was found that most anions reacted to some extent, but that the rate of the secondary reactions was not appreciable in the range of \(\mu = .02 - .06\). Only the bromide ion could be used over a large concentration range. The choice of anions was further restricted by the use of iodine in measuring the reaction rate. The nitrite ion, for example, could not be used, as it reacted with the iodine.

The choice of cations, too, was somewhat restricted. Many of the heavy metal bromocacetates and thiosulphates are insoluble, i.e., zinc and cadmium, and silver and barium.
CALCULATION OF RATE CONSTANTS.

At each time interval the rate constant was calculated from the formula

\[ k = \frac{1}{\Delta t} \cdot \frac{x}{a-x} \]

where \( a \) is the initial concentration of the reactants and \( x \) is the amount that has reacted at a time \( t \).

It was essential for this work that the rate constant for the reactions in the absence of added salt should be known as accurately as possible. For the Na-Na reaction, the value at initial concentrations \( .01 \) has been variously reported as \( .445, .454 \) and \( .477 \). This measurement, therefore, was repeated, using fresh thiosulphate and iodine solutions each time, until a result reproducible within \( .001 \) was obtained. These values are shown in Table 2.

The most accurate value of \( k \) for each reaction was calculated by a method developed by Roseware. The integrated equation for a second order reaction when the initial concentrations of the reactants are equal is

\[ k = \frac{1}{t} \left( \frac{1}{C} - \frac{1}{C_0} \right) \]

where \( C \) is the concentration at a time \( t \), and \( C_0 \) the concentration at \( t=0 \). The probable error in concentration, \( x \), is small compared to the concentration, and therefore one may use the series expansion

\[ \frac{1}{C-x} = \frac{1}{C} - \frac{x}{C^2} + \frac{x^2}{C^3} - \ldots \]

and neglect all except the first two terms.

The error in \( \frac{1}{C} \) will then be \( \frac{x}{C^2} \), and the probable error in \( k \) due
to errors in concentration will be
\[ r_k = \frac{1}{t} \left[ \left( \frac{r}{C_0} \right)^2 \cdot \left( \text{or} \frac{y}{y^3} \right) \right]^{1/2} \]
Let \( y = \frac{C}{C_0} \), and \( k = \frac{1}{C - C_0} \),
then \[ \frac{r_k}{k} = \left( \frac{r}{C_0} \cdot \frac{y^2}{y - 1} \right)^{1/2} \]
The probable error will be a minimum when
\[ \frac{d}{dy} \left( \frac{r_k}{k} \right) = 0 \]
i.e., when \[ \frac{1}{C_0} \left( \frac{1}{y - 1} \right) \cdot \frac{2x^2}{y^3} \cdot \left( x_0^2 + \frac{x^2}{y^4} \right) \cdot \frac{1}{y^3} \left( x_0^2 + \frac{x^2}{y^4} \right) \left( \frac{1}{y - 1} \right) = 0 \]
or when \[ \left( \frac{r}{C} \right)^2 - 2y = 1 \]
In the thiosulphate-bromoacetate reaction, the time-error is negligible in comparison with the concentration error, and therefore it may be assumed that the error \( r \) is solely due to error in concentration. Since the probable error in concentration, instead of being a constant percentage error, is almost always a constant quantity, independent of concentration,
\[ x_0 = r \]
Hence the condition for minimum error in \( k \) reduces to \[ y^3 + 2y = 1 \]
i.e., \( y = .36 \)
This means that the most accurate value of the rate constant will be that calculated for when about 36% of the thiosulphate has reacted.
In practice, the average of rate constant calculated for six time intervals was compared with the value for which the fraction which had reacted was nearest to .36. If these did not agree within .001, the reaction was repeated. It was found that this was not often
necessary, and that in all cases the value for y = 36 gave more reproducible results.
DISCUSSION OF RESULTS

The results obtained for typical runs are shown in Table I. The most accurate k-values (calculated by Roseveare's method) are given in Tables 2-6, and the graphs show the curves obtained by plotting \( \log k + 1 \) against \( \nu \).

1. Specific Anion Effects.

The effect of added sodium salts on the reaction between 0.1M sodium bromoacetate and 0.1M sodium thiosulphate is shown in graphs 1 and 2. Within the limits of experimental error these curves coincide with one another, and with La Mer's curve for the Na-Na reaction with varying initial concentrations of the reactants, (graph 2). Three points from Krapaviv's data on this reaction are included. When potassium salts were added to the same initial concentrations of the reactants, the curves shown in graphs 3 and 4 were obtained. Again these curves are identical with one another, but they are distinct from the former set of curves. From a comparison of these sets of data it is evident that the reaction is uniformly catalysed by anions but that the two cations show specific effects. The same conclusion is reached by a similar treatment of the K-K reaction (graphs 5-8).

Lithium salts were found to be an exception to this rule. Graph 9 shows the effect of added lithium chloride and lithium sulphate on the reaction etc. The development of specific anion effects here must be due in some way to the extremely small radius of the lithium ion. It could, of course, be explained by incomplete dissociation of lithium sulphate, but this would seem to
imply that the other alkali metal sulphates are completely dissociated, as they have the same catalytic effects as the corresponding chlorides.

There is no doubt, however, that this method is not sensitive enough to detect incomplete dissociation in salts whose degree of dissociation is very close to one. It is possible, therefore, that the effect of incomplete dissociation can be detected only in the case of lithium, which has a very much stronger tendency to form covalent bonds than the larger alkali metal atoms.
In graph II the effects of added potassium and sodium salts on the Na-Na and K-K reactions are compared. For curve I, the only cations in the solution were potassium ions, and for curve IV sodium ions. Curve II, showing the effect of added potassium salts on the Na-Na reaction is seen to rise steeply initially, and approach curve I as the ionic strength increases, i.e. when the potassium ions are largely in excess of the sodium ions. The addition of sodium salts to the K-K reaction has the opposite effect. The gradient of curve III is lower, and the curve approaches the Na-Na curve at higher ionic strengths.

For the Na-K reaction the ratio of potassium to sodium ions of the reactants is 2:1. The curves, therefore, lie closer to the K-K curve than to the Na-Na curve (graph 12), and curve II fuses with the K-K curve. Curve III does not fuse with the Na-Na curve, but approaches it at higher ionic strengths.

These effects are reversed in the K-Na reaction (graph 13) where the ratio of potassium to sodium ions initially is 1:2.

From these results it appears that the catalytic effects of the two cations are approximately additive.

A more detailed analysis of these results reveals a simple additive relationship between the logarithms of the rate constants.
In each case the replacement of .01 Na\(^+\) by .01 K\(^+\) has increased the logarithm of the rate constant by about .005. The agreement obtained here is probably fortuitous, as the differences involved are very small, and the rate constants are not known sufficiently accurately for much weight to be put on the third place of the log \(k_1\) values.

It seems apparent, however, that the specific catalytic effects of the sodium and potassium ions are approximately additive.
THE RELATIVE EFFECTS OF CATIONS.

Graph 9 shows the effect of different cations on the rate of the Na-Na reaction, and graph 10 shows the corresponding curves for the K-Na reaction. In both cases the catalytic effect increases in the order

\[
\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+
\]

and

\[
\text{Ba}^{++} < \text{Sr}^{++} < \text{Ca}^{++} < \text{Mg}^{++}
\]

The conclusions reached, then, from these measurements are

1. That anions catalyse the reaction uniformly, except when they are associated with lithium ion.

2. That cations of the same valence have an increasing catalytic effect in the order of increasing ionic radius.

3. That divalent cations are in general more powerful catalysts than univalent cations, irrespective of their ionic radii.

The observed catalytic effects decrease in the order,

\[
\text{Ba}^{++} > \text{Sr}^{++} > \text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+ > \text{Na}^+ > \text{Li}^+.
\]
ENTROPY AND ENERGY OF ACTIVATION

Table 6 shows the values of \( \frac{E}{k} \) and \( B \) of the equation

\[
\log k = B - \frac{E}{2.3RT}
\]

calculated from the rate constants of the reaction at 25°C and 35°C. It is clear from an inspection of these results that no definite conclusion can be reached. An error of one percent in the value of \( k \) leads to an error of about 200 calories in the energy of activation \( E \), and of about .15 units in \( B \). Since this is the order of accuracy of the measured rate constants, it is evident that useful values of \( E \) and \( B \) can only be obtained by taking the average of a very large number of measurements.

An interesting point emerging from the measurements at the higher temperature is that the corresponding values of \( k \) for the reaction in the presence of lithium chloride and lithium sulphate are rather closer together than they are at 25°C; the specific effects of the anions associated with the lithium ion seem to be disappearing at higher temperatures. This is to be expected if the effects are attributed to the incomplete dissociation of lithium sulphate, since the degree of dissociation would probably increase with increasing temperature.
SUMMARY

1. Specific anion effects on the rate of the reaction between the bromoacetate ion and the thiosulphate ion have been measured by the method of adding neutral salts to the reactants at constant initial concentration of 0.01M. It has been shown that anions catalyse the reaction uniformly, except when they are associated with lithium ion.

2. Specific cation effects have been shown to increase in the order of increasing ionic radius in a series of cations of the same valence type i.e. the order Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} and Cs^{+} > K^{+} > Na^{+} > Li^{+}

3. An explanation of the specific effects observed has been offered and compared with the alternate explanation offered by Gowells.

4. The energy of activation and B factor have been calculated from the rate constant for the reaction at 25°C and 35°C.
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<thead>
<tr>
<th>Time (Mins.)</th>
<th>cc.0106 Na₂S₂O₃</th>
<th>x × 10²</th>
<th>k = \frac{1}{a-x} × \frac{x}{a}</th>
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</tr>
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<td>.474</td>
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</table>

(b) In the presence of .0625N KBr.  \textbf{Na-Na Reaction.}

<table>
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<th>cc.0106Na₂S₂O₃</th>
<th>x × 10²</th>
<th>k = \frac{1}{a-x} × \frac{x}{a}</th>
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<td>.696</td>
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<td>97\frac{1}{2}</td>
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<td>.694</td>
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2. THE LEAST CONSTANT VALUES.

(a) With no added salt. \textit{Na-\textsubscript{2}Na REACTION.}

<table>
<thead>
<tr>
<th>Time (Mins.)</th>
<th>cc.0106N</th>
<th>x x 10\textsuperscript{3}</th>
<th>( \frac{1}{a} \cdot \frac{X}{a-x} )</th>
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</thead>
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<tr>
<td>55</td>
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</table>

(b) In the presence of .012N. NaCl. \textit{Na-\textsubscript{2}Na REACTION.}

<table>
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<th>Time (Mins.)</th>
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Rate constant for the reaction between sodium bromoacetate and sodium thiosulphate in the presence of neutral salts at 25°C.

\[ a = b = 0.04 \]
\[ k = \text{sat} \cdot \frac{1}{a-x} \]

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<th>Added Salt</th>
<th>( \frac{1}{a} )</th>
<th>Log k1</th>
<th>( \frac{1}{a} )</th>
<th>Log k1</th>
<th>( \frac{1}{a} )</th>
<th>Log k1</th>
<th>( \frac{1}{a} )</th>
<th>Log k1</th>
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<td>1.25</td>
<td>673</td>
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<td>735</td>
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TABLE II (Contd.)

<table>
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<th>Added Salt</th>
<th>( \mu )</th>
<th>log kJ</th>
<th>( \mu )</th>
<th>log kJ</th>
<th>( \mu )</th>
<th>log kJ</th>
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<tr>
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<td>MgCl₂</td>
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<td>.741</td>
<td>.231</td>
<td>.724</td>
<td>.225</td>
<td>.715</td>
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<td>.705</td>
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</tbody>
</table>

L.M. from La Mer's data   K from Krapavin's data
TABLE III

Rate constants for the reaction between potassium bromoacetate and potassium thiosulphate in the presence of neutral salts at 25°C.

\( a = b = 0.01 \)
\( k = \frac{1}{a} \cdot \frac{1}{b} \)

<table>
<thead>
<tr>
<th>Added Salt</th>
<th>( f_1 )</th>
<th>( \log k_{1} )</th>
<th>( f_2 )</th>
<th>( \log k_{2} )</th>
<th>( f_3 )</th>
<th>( \log k_{3} )</th>
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<tr>
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<tr>
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TABLE V

Rate constant for the reaction between potassium bromacetate and sodium thiosulphate in the presence of neutral salts.

\[ k = \frac{1}{a^2} \cdot \frac{x}{a-x} \]

<table>
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<tr>
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<th>( \sqrt{\mu} )</th>
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<th>( \sqrt{\mu} )</th>
<th>( \log k+1 )</th>
<th>( \sqrt{\mu} )</th>
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TABLE VI (Contd.)

The values of $k$, $E$, and $B$, in the equation

$$\log k = B - \frac{E}{2.303}$$

calculated from the rate constants of the Na-Na reaction in the presence of neutral salts at 25°C and 35°C.

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GRAPH I

Na-Cl Reaction.

NaF
NaCl
Na2SO4

0.2 0.25 0.3 0.35 0.4

K from Krafft's Data

GRAPH II

NaBr
NaNO3
From Remer's Data.
I K-K Reaction with added Potassium Salts
II Na-Na Reaction with added Potassium Salts
III K-K Reaction with added Sodium Salts
IV Na-Na Reaction with added Sodium Salts
Graph XII.

1. Na-K reaction with added Potassium Salts
2. Na-K reaction with added Potassium Salts
3. Na-K reaction with added Sodium Salts
4. Na-Na reaction with added Sodium Salts
Graph XIII

1. K-K Reaction with added Potassium Salts
2. K-Na Reaction with added Potassium Salts
3. K-Na Reaction with added Sodium Salts
4. Na-Na Reaction with added Sodium Salts