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Kinetics of reactions involving bromate in fused alkali nitrates

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KINETICS OF REACTIONS INVOLVING BROMATE IN

FUSED ALKALI NITRATES

by

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I. INTRODUCTION

Investigations of reaction mechanisms have mainly been carried out in aqueous media, but for many years chemists have considered solvent effects on reactions and have used both organic and inorganic fluids other than water in order to determine how solvation affects reactivities. Non-aqueous media have allowed reactions to be studied not only under various conditions of polarity but also outside the hundred-degree limit imposed by the properties of water. Changes in dipole moment, ionic strength and structure of the solvent have long been recognized as factors in establishing the activities of reactants. Hydrogen-bonding and Bronsted-type acid-base reactions complicate the study of reactions when water is used as solvent.

Some of the more recently investigated solvents are the molten inorganic salts. For the most part these studies have been aimed at elucidating the character of the solvent itself and determining properties of materials dissolved in the fused salts. Much work has been done concerning transport phenomena and related electrode processes but very little has been done in regard to the study of reaction kinetics in these solvents.

Reactions of halate with halide in water solution have been studied by many investigators. Most recently, J. Sigalla

(1) has examined kinetically the reaction of bromate with chloride and bromide and discusses his results in relation to previously reported investigations. In all cases a first order dependence on bromate and second order dependence on hydrogen-ion concentrations have been reported. The order in bromide seems to be uncertain with some reports of simple first order dependence and others of two terms, the second containing a second order dependence on bromide concentration.

One proposed mechanism for the reaction involves the fast formation of a complex $(H_2BrO_3^+)$ followed by rate determining reaction with halide (2), accounting for a first order dependence on halide:

$$H^+ + BrO_3^- = HBrO_3 \qquad \text{(fast)}$$

$$H^+ + HBrO_3 = H_2BrO_3^+ \qquad \text{(fast)}$$

$$I^- + H_2BrO_3^+ \xrightarrow{k} IBrO_2 + H_2O \qquad \text{(rate determining)}$$

$$IBrO_2 \longrightarrow \text{products}$$

or

$$I^- + BrO_2^+ \xrightarrow{k} (IBrO_2) \longrightarrow \text{products}$$
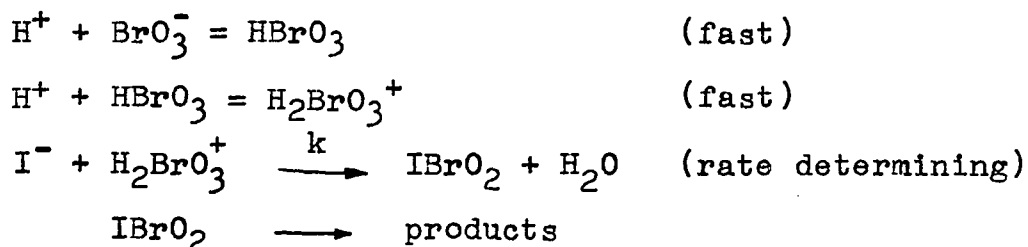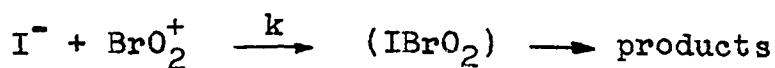
in which case $I - Br \begin{smallmatrix} O \\ O \end{smallmatrix}$ is postulated as a donor-acceptor intermediate. The following equation is suggested to account for higher orders in halide and for mixed halide reactivities: $R = k_3 (AO_m^{-n}) (B^x) (H^+)^{n+1} (N^-)$

Examples studied were: $(BrO_3^-) (Br^-) (H^+)^2 (Br^-)$

$$(BrO_3^-) (Cl^-) (H^+)^2 (Cl^-)$$

The mechanism for this is given as:

$$AO_m^- + H^+ = HAO_m \qquad \text{(fast)}$$

$$HAO_m + H^+ = H_2AO_m^+ \qquad \text{(fast)}$$

$$H_2AO^+ + B^x = BAO_{m-1}^{x+1} + H_2O \qquad \text{(fast)}$$

$$BAO_{m-1}^{x+1} + N^- \longrightarrow NB^{x+1} + AO_{m-1}^- \qquad \text{(rate determining)}$$
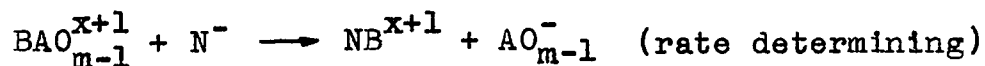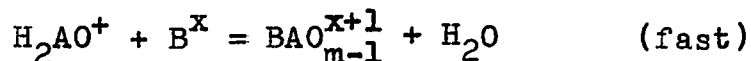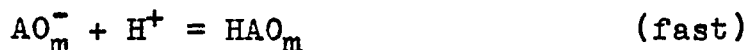
In relation to this reaction Edwards (2) states:

"Isolated salts of NO_2^+, NO^+, I^+ and Br^+ show NO_3^-, NO_2^-, OI^-, and OBr^-, respectively, can be changed to acceptor, anhydride-like intermediates. It is assumed that BrO_2^+, IO_2^+, Cl^+, and others are also intermediates."

It was known that some divalent metals, for example zinc (II), would react vigorously with bromide and bromate in fused sodium-potassium nitrate eutectic at 250°C to produce bromine and the metal oxide (3). In view of this information it was thought that the mechanism of the aqueous reaction might be related to that in the fused melt except for a first order term in metal ion concentration replacing the second order proton concentration. It was further thought that the "acidity" of several metal ions could be compared by observing a series of reactivities under the same conditions without the complication of hydrolysis confusing

the result. In other words, it was thought possible that the reaction might be dependent on the free energy change in going from the metal ion to metal oxide.

II. EXPERIMENTAL INVESTIGATION

A. Apparatus

A sketch of the apparatus is shown in Figure 1. A mixture of lithium, potassium, and sodium nitrates in concentrations approximating that of the ternary eutectic (30Li : 17Na : 53K on a molar basis) was prepared and fused in a 10 quart enameled pot, supported on a layer of fire bricks, recessed into the top of which was a Chromalox 230V, 1250W ring heater. This heater, wired for medium heat and used at full 220 line voltage, along with a nichrome wire wound auxilliary immersion heater was used to control this constant temperature bath. A Pyrex flask with ground glass joint was used as the reaction vessel and a set of Pyrex glass bubblers, having high surface area and containing sulfite-water, were used as scrubbers for collecting bromine samples during a run. The apparatus was purged continually with a dried and metered stream of inert gas. A magnesium perchlorate-filled drying tower was used for drying, an orifice meter was used for metering, and a mercury manometer was used to observe pressure in the gas stream and to act as a relief-valve. This latter was deemed necessary in case of power failure or heater burn-out, which would result in freezing of the mixture and possible explosion of the hot melt. Also the precipitated metal oxide, formed as

ORIFICE
METER

DRYING TOWER

REACTION
VESSEL

INERT GAS

Hg
MANOMETER

GLASS
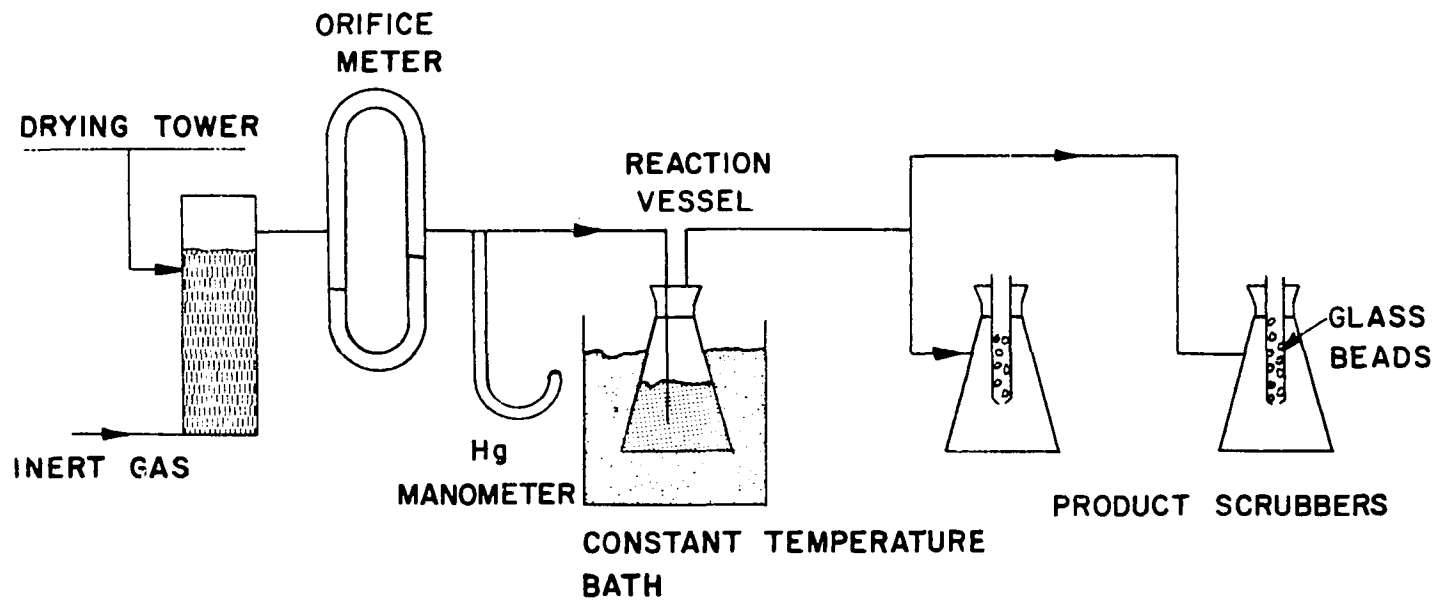BEADS

CONSTANT TEMPERATURE
BATH

PRODUCT SCRUBBERS

Figure 1.   Apparatus used to study kinetics of the decomposition of bromate when
it is reacting with divalent transition metals in fused alkali
nitrate solvents

a result of reaction, had a tendency to collect on the nozzle of the bubbler in the reacting mixture. In order to further reduce the hazard of explosion the gas regulator valve was kept at 5 psig. A tapered ground-glass joint without clamping devices was used at the top of the reaction vessel, which also served as a pressure release valve. The opening of this joint by pressure buildup, of course, would have resulted in loss of product and a worthless determination. Therefore the back-pressure on the system was kept under constant surveillance. A fine powder of salt was carried over by the purging gas and collected in the tubing connected to the collection vessels. This was periodically washed out.

This assembly was most useful for studying low concentration, large volume solutions but when smaller volumes were permissible and fast temperature changes were desired a smaller bath in a tubular furnace was used. The furnace was wired for 220V also but was equipped with a Variac and Brown Electronik temperature control. For the larger bath a thermometer was used in a Pyrex thermowell; in the smaller system a chromel-alumel thermocouple was used to determine the temperature of the system. The Brown controller was also activated by thermocouple and indicated temperatures in the furnace. The regulator couple was positioned next to the furnace wall in order to avoid large temperature fluctuations and therefore was not suited

to indicating the bath temperature. Both assemblies used the same purging and scrubbing train. The gas flow rate was kept at about 0.25 liters per minute for most samples.

For the determination of the amount of oxygen evolved during a reaction, a special assembly was prepared (see Figure 2). A round-bottom flask contained a fused solution of the metal nitrate in the bottom and another fused solution of sodium bromate in a separate depression in the neck. The flask was constructed in such a way as to allow the individual solutions to come to thermal equilibrium and allow evacuation of the system before mixing. Then the reaction vessel was rotated on a ball joint. The material from the neck was allowed to mix into the bottom and react. Gas evolved from the reaction was collected in a gas collection tube and analyzed by scrubbing in conc KOH solution and then in alkaline pyrogallol in an Orsat-type apparatus.

TO VACUUM

SODIUM BROMATE IN
NITRATE EUTECTIC

ZINC NITRATE IN NITRATE
EUTECTIC

CONSTANT TEMPERATURE
BATH
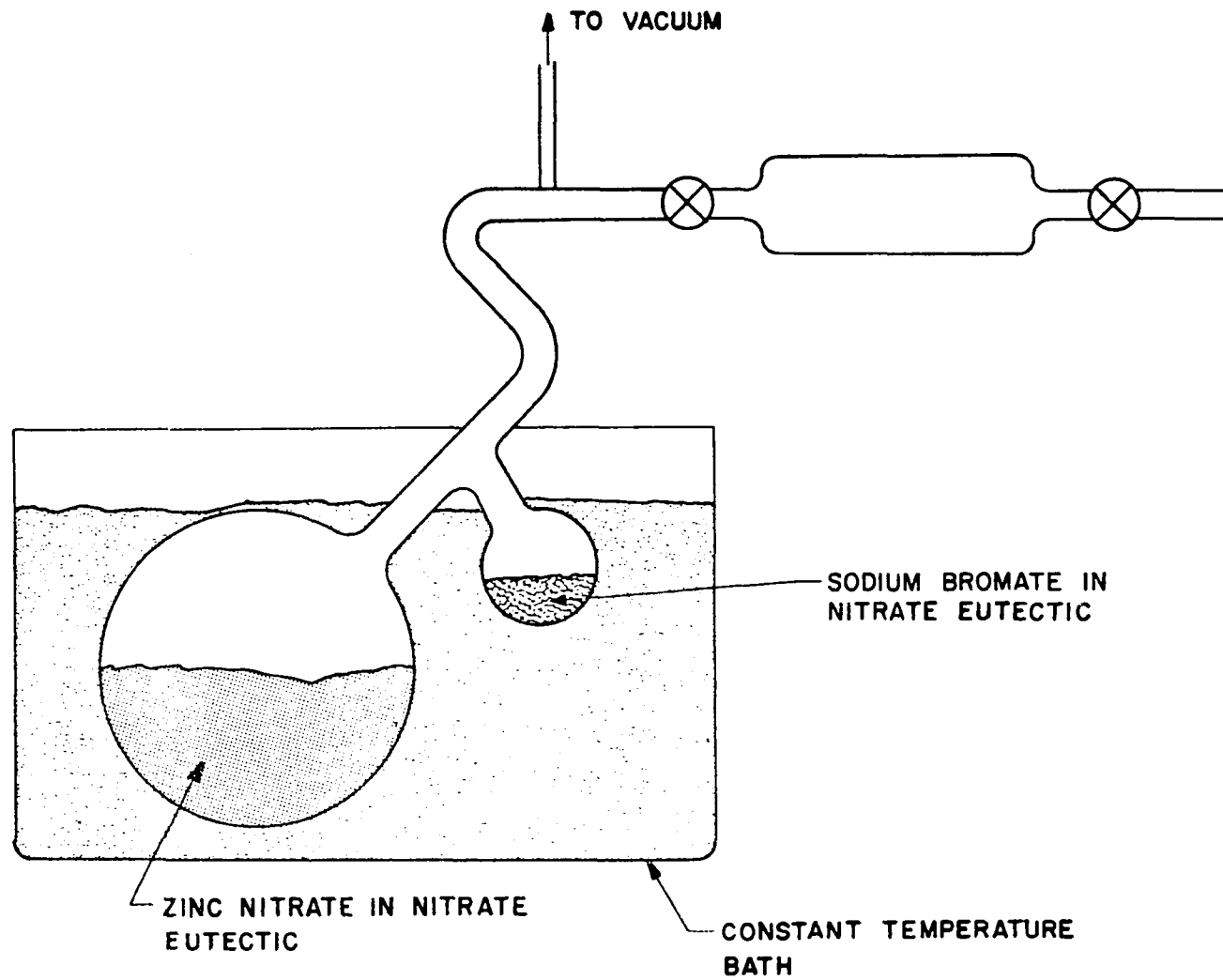
Figure 2. Apparatus used to determine the amount of oxygen evolved in the reaction

B. Procedure

Samples were prepared with high metal ion concentration and low bromate or vice versa. This procedure forces the reaction to follow pseudo-first-order kinetics, allowing the investigator to determine the kinetic order of each of the reactants under these circumstances. Later, different combinations of reactant concentrations were studied in order to test various mechanistic schemes.

Rates of reaction were followed by scrubbing the purge gas, issuing from the reaction mixture, with aqueous sulfur dioxide. This converted the evolved bromine, which was produced by the reaction, to bromide. A titration was then made to evaluate the amount of bromine produced in the elapsed time. This titration was done with standard silver nitrate, using an eosin indicator. At very low bromide concentrations the indicator does not give a good end-point. Therefore when small amounts were to be analyzed an amount of bromide was added to the sample to be titrated from a buret filled with standard potassium bromide solution.

It was found that the eosin solution decomposed in direct light and became worthless as an indicator after a few weeks when left in a clear bottle on the bench. A sample in an opaque bottle or in a dark cupboard kept indefinitely. Also the pH of the solution was critical to

good analysis with this indicator———a small amount of sulfite
works well; silver sulfite precipitates if too much is used.

In order to avoid adding additional unknown variables
to the system the metal ions were introduced into the solvent
melt as the nitrate. Since all of the metal nitrates used
are quite hygroscopic and decompose on heating to give the
metal oxide, water and NO_2, the successful dissolution into
the melt was a major problem. This problem was complicated
further when melts containing lithium were used since
lithium has a great affinity for water. Any water in
solution reacted very rapidly with the divalent metal ions
producing the metal oxide. A sample of the metal nitrate
was placed in a tube and evacuated at relatively low
pressures to drive off most of the excess water. The salt
was then quickly mixed into a hot portion of the solvent. It
was found if this dissolution were made rapidly the
majority of the water would flash off and little metal oxide
would precipitate. This technique worked especially well for
the sodium-potassium nitrate, "binary", eutectic but not at
all well for the lithium, sodium, potassium nitrate, "ternary",
solution (22Li, 19Na, 59K on a molar basis). For the latter
solvent it was found necessary to first dissolve the metal
nitrate in the binary eutectic and then add this anhydrous
melt to the ternary solvent. This procedure never failed to
give the desired solution. It was later found that the most

effective drying procedure was to leave the sample of metal
nitrate under magnesium perchlorate dessication for a week
or more. In preparing the melts special care was not taken
to eliminate formation of metal oxide completely since it is
a product of reaction anyway. All the oxides were found to
be exceedingly insoluble in the melts.

In some cases the nitrate of the metal was not
available but the oxide or metal itself was available. It
was found that these could be converted to the nitrate
directly in the fused nitrate solvent by reaction with
ammonium nitrate. Normally this reaction, when done with the
solid reactants, is violent and explosive. Ammonium nitrate,
itself, decomposes vigorously at about $200^{\circ}C$ but it was
introduced into the melt at $250^{\circ}C$ with only a slow moderate
decomposition taking place. Reaction then occurred with
various metals and their oxides such as the rare earths,
yttrium, cadmium, magnesium, lanthanum, copper, zinc and
palladium. In the latter case the solution was not stable.
As long as there was ammonium nitrate in the melt the
solution was pale green but within a day this color faded and
a dark precipitate appeared. If more ammonium nitrate were
added the precipitate disappeared and the pale green color
deepened. In like manner it was found that the ammonium
stayed in solution for a long time and was not easily
removed. Unfortunately, bromate reacted with the ammonium
nitrate also. Therefore these solutions were not used in

the study of the mechanism of the reaction of bromate with divalent metals.

Stock solutions of the metal ions and bromate in binary eutectic were made so that small solid chunks could be added to the solution being studied to give the ion of low variable concentration in the pseudo-first-order runs. Adding these solid chunks was satisfactory for experiments at $250^\circ C$ or higher since complete solution occurred in about five minutes during which time little reaction occurred. Plots of the results were evaluated in the linear first-order sections after this initial "induction" period. For runs at lower temperatures the low concentration reactant was added molten from a dropper. This made the initial concentration uncertain but analysis was accomplished by collecting all of the bromine evolved. Therefore it was never necessary to know the concentration of the minor constituent. The major constituent could be analyzed before addition of the last reactant. Because of this experimental technique it was always more satisfactory to make the metal ion concentration the major reacting constituent, since the stock containing the metals was invariably wet. Of course some experiments were carried out with high bromate and some with equal metal and bromate concentration but the great majority were run with low bromate.

Analysis of bromate was accomplished with an ordinary

iodometric titration using standard thiosulfate solution. Analysis of the transition metals was done with a standard ethylenediamine tetraacetate technique using naphthyl-azoxime indicator as prescribed by Fritz et al. (4). Analysis of rare earths was done with a procedure recommended by Fritz et al. (5). Other metals were analyzed by common methods recommended to be appropriate in Willard and Diehl (6).

Gruen[1] reported that cobalt (II) salts which he dissolved in fused alkali nitrate solvent remained in the divalent state. Furthermore he found that cobalt (III) was rapidly converted to cobalt (II) upon solution in the fused nitrates.

A sample of the oxide, formed when cobalt (II) was heated in the nitrate solvent at high temperature, was studied by X-ray powder pattern. The lines observed indicated the presence of cobaltous and cobaltic mixed oxide.

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[1]Gruen, Dieter, Argonne National Laboratory, Lemont, Illinois. Discussions on fused salt chemistry. Private communication. 1959.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Preliminary Experiments

A binary eutectic of sodium and potassium nitrate
at 250°C containing fairly high concentrations of zinc
nitrate and potassium bromide was prepared. The solution
was purged with inert gas for sufficient time to remove all
possible moisture present and then a known amount of sodium
bromate was added. The product gases were passed through
Ascarite absorption bulbs which were weighed before and
after. Two experiments of this type were made and in both
cases the increase in weight corresponded to the amount of
bromine which could be obtained by decomposition of the
bromate, leading one to conclude that no NO_2 or other acidic
vapor was being evolved. No bromate could be detected
afterwards in the melt.

A further check was made to determine whether there were
nitrogen compounds in the product gases by collecting these
gases for several hours in a scrubber containing 0.2N KOH
solution. This solution was then placed in a Kjeldahl
apparatus with Devarda's alloy and heated. These vapors were
then collected in boric acid solution containing methyl red
indicator. No color change was observed, indicating that no
nitrogen compounds were present.

Since a sample of zinc (II) in the binary eutectic,

which had been left at full heat on the hot plate, was found to have reacted completely in a day with the nitrate of the solution, producing ZnO and NO_2, it was felt necessary to study the rate of zinc nitrate decomposition at the temperature to be used in this study. Therefore a sample containing 0.2033 molal Zn^{+2} was prepared and allowed to stay at $260°C$. After two days no change in the metal ion concentration could be detected.

The original object of this study was to elucidate the mechanism of the zinc-bromide-bromate reaction in molten solvent; therefore this was the first system investigated. By having two reactants in high concentration at a time the order in divalent metal and bromate were found to be each first-order, as expected, but reaction between metal ion and bromate confused the investigation of the order in bromide.

The reaction was studied at $250°C$ in the binary nitrate eutectic using many combinations of reactant concentration but good reproducible data were not obtained that could easily be interpreted. It was assumed that many zinc bromide or zinc-bromate-bromide complexes were involved which made it a confusing system to study. Therefore the simpler zinc (II)-bromate system was studied.

B. Rate Law Determinations

1. The M^{+2}-bromate reaction

Binary nitrate eutectic solutions containing high

concentration of either bromate or metal ion and low concentration of the other were found to give excellent first-order kinetics, thus indicating that the reaction was first-order in each of the reactants under these conditions. This information eliminated the possibility of a mechanism involving a metal bromate complex reacting with a bromate from the solution to give decomposition as indicated by equation 1:

$$MBrO_3^+ + BrO_3^- \longrightarrow products \tag{1}$$
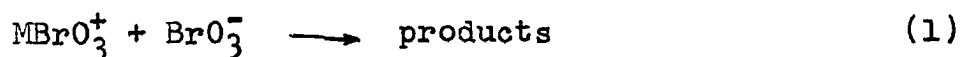
Therefore a simple second-order mechanism for the system was investigated:

$$M^{+2} + BrO_3^- \xrightarrow{k_2} products \tag{2}$$

For this case the rate of formation of bromine should follow an expression such as:

$$\frac{dx}{dt} = k_2(B - 2x)(A - x) \tag{3}$$

where x is the amount of bromine produced, A is the initial concentration of metal, and B is the initial concentration of bromate. This would then integrate into the form:

$$k_2 t = \frac{1}{2A - B} \ln \frac{B(A - x)}{A(B - 2x)} \tag{4}$$

Data were tested against this equation. It was found that values of k_2 varied as the ratio of bromate to zinc varied and

also as the concentrations of both were changed together. This was taken to mean that a complex might be involved in the kinetic mechanism. A situation which might give these results would be a fast equilibrium followed by a slow rate-determining step,

$$M^{+2} + BrO_3^- \underset{fast}{\overset{K}{\rightleftharpoons}} MBrO_3^+ \overset{k_3}{\underset{slow}{\longrightarrow}} products \qquad (5)$$
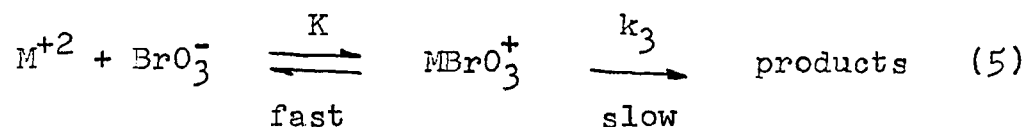
where K would be an equilibrium constant and k_3 a first-order rate constant. This would then lead to a sequence of equations as follows:

Let $\quad A = (M^{+2})$ at any time

$\qquad B = (BrO_3^-)$

$\qquad Ab = (MBrO_3^+)$

$\qquad B_0 = (BrO_3^-)$ at time $= 0$.

Since $\quad A$ is kept high and constant

and $\quad B$ is low and variable,

then the rate of reaction $= k_3 (MBrO_3^+) \qquad\qquad (6)$

$$= k_3 Ab .$$

By definition,

$$K = \frac{Ab}{A(B_0 - Ab)} \qquad\qquad (7)$$

$$AK(B_0 - Ab) = Ab$$

$$Ab(1 + KA) = KAB_0$$

$$Ab = KAB_O/1 + KA.$$

Therefore by substituting into equation 6:

$$\text{rate} = k_3(\frac{KAB_O}{1 + KA}) .$$

(8)

Equation 5 can also be written solely in terms of rate constants instead of using the equilibrium constant:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ab \overset{k_3}{\longrightarrow} \text{products},$$

(9)
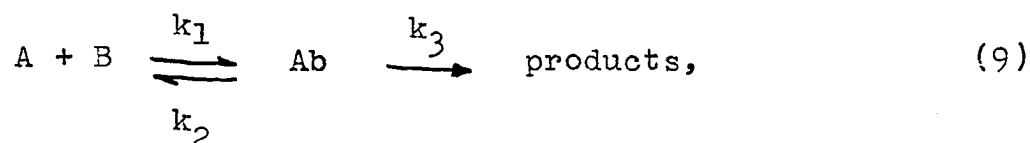
in which case the following equations can be evolved:

$$\frac{d(Ab)}{dt} = k_1AB - k_2Ab - k_3Ab = 0$$

(in the steady-state approximation)

$$k_1AB = (k_2 + k_3)Ab$$

$$Ab = \frac{k_1}{k_2 + k_3} AB; \quad B = \frac{k_2 + k_3}{k_1} \cdot \frac{Ab}{A}$$

$$B_O = B + Ab = (\frac{k_2 + k_3}{k_1A} + 1)Ab$$

$$Ab = AB_O(\frac{k_1}{k_2 + k_3} / 1 + \frac{k_1A}{k_2 + k_3}) .$$

Substituting into equation 6 one obtains:

$$\text{rate} = \frac{k_3(\frac{k_1}{k_2 + k_3})AB_O}{1 + (\frac{k_1}{k_2 + k_3})A} \longrightarrow \frac{k_3KAB_O}{1 + KA} \text{ if } k_3 << k_2 .$$

This treatment may be considered a more rigorous approach to

the kinetics even though the final result is the same.

Since only the concentration of bromate varies during a run this last equation can be written in the form:

$$\text{rate} = k'B$$

in which k' becomes a pseudo-first-order rate constant. At a particular temperature a series of metal ion concentrations can be used to evaluate a series of k' values. From these determinations a separation of constants and test of the mechanism should result as shown by the following equation:

$$k' = \frac{k_3 KA}{1 + KA}$$

$$\frac{1}{k'} = \frac{1}{k_3 KA} + \frac{1}{k_3}$$

A plot of $\frac{1}{k'}$ versus $\frac{1}{A}$ should result in a linear graph with an axial intercept $\frac{1}{k_3}$, slope of $\frac{1}{k_3 K}$, and ordinate intercept of $-K$.

In all cases the concentration rather than activity was used since it was presumed the best first approximation to the activity coefficient is unity.

The results of the determinations for zinc (II) at $250^\circ C$ are shown in Table 1 and Figure 3. The data plot has a reasonably straight line with an intercept at about 2.15 and slope of 1.70. This interpretation was made on a basis of "least squares" treatment as outlined in Klotz,

Table 1

Kinetic data for reaction of divalent metals with bromate in
sodium-potassium nitrate eutectic at 250°C

(Zn^{+2}) mol/1000g	Half-life min	k'	$\frac{1}{k'}$	$\frac{1}{(Zn^{+2})}$
0.0312	82	0.0084	119.0	32.0
0.0413	30.5	0.0226	44.2	24.3
0.042	36	0.0192	52.1	23.8
0.022	59	0.0117	85.5	45.4
0.262	8.1	0.085	11.8	3.8
0.190	7.0	0.0985	10.1	5.27
0.0542	25	0.0267	36.2	18.5
0.069	18.5	0.0373	26.8	14.5
0.0233	47	0.0147	68	43.5
0.117	7.3	0.0946	10.6	8.56
0.48	2.5	0.276	3.6	2.1
0.045	27	0.0256	39.1	22.2
0.044	25	0.028	36.7	22.7
0.22	8.7	0.080	12.7	4.6
0.27	4.3	0.16	6.2	3.7
(Ni^{+2})				$\frac{1}{(Ni^{+2})}$
0.044	30	0.023	43.5	22.5
0.0776	15	0.046	21.7	12.9
0.103	7.5	0.092	10.9	9.8
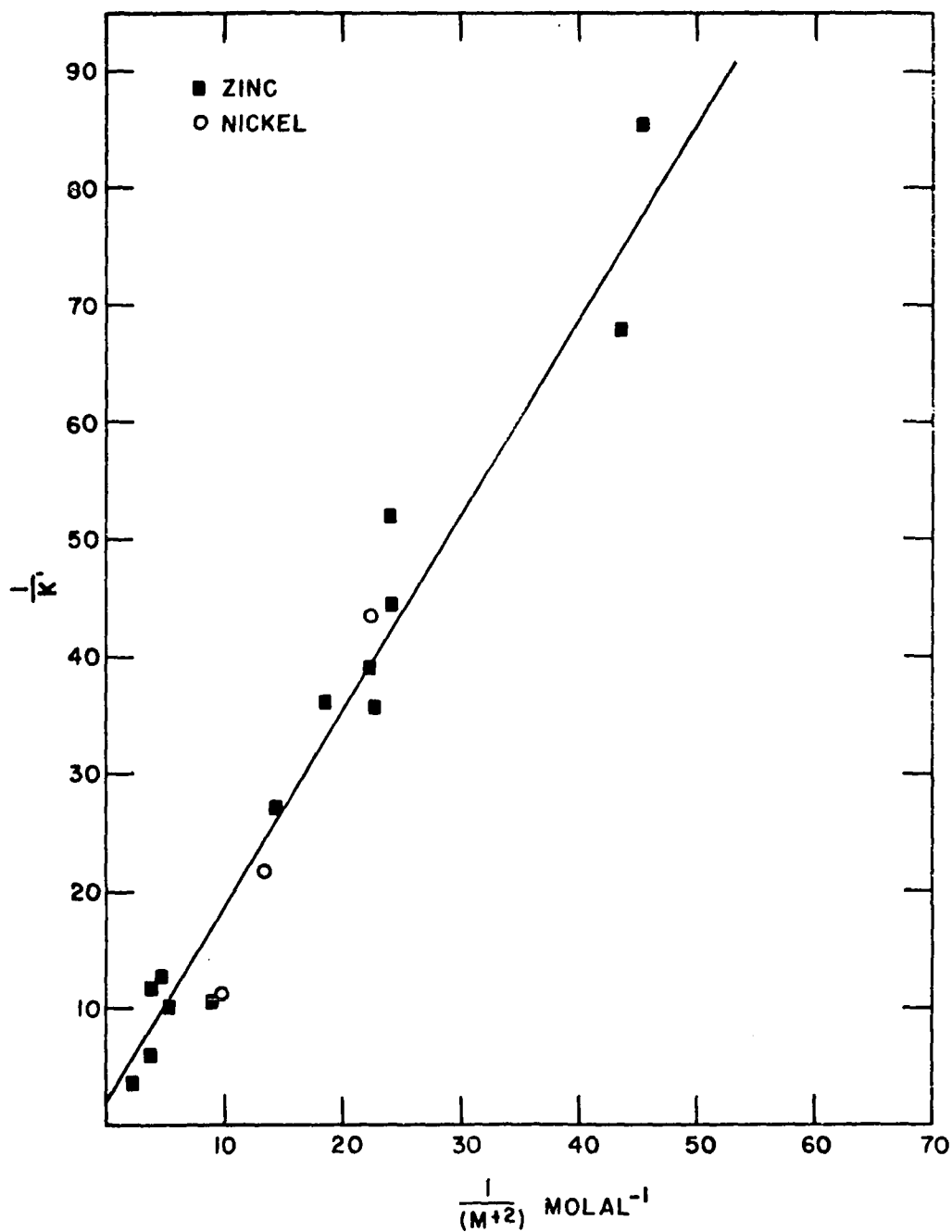
Figure 3. Kinetic data for reaction of divalent metals with
bromate in sodium-potassium nitrate eutectic at
250°C

(7, p. 21).

The scatter in data makes the exact value of the intercept uncertain and, since it is near zero, the value of the rate constant is uncertain. The slope, and thus the product k_3K, involves much less uncertainty.

These data would indicate k_3 equal to 0.46 min^{-1} and $K = 1.28$ m^{-1} for zinc at 250°C.

Since the rate constant might be expected to decrease and the equilibrium constant to increase at lower temperatures, a series of experiments with zinc (II) were made at a temperature of 230°C. This is just above the melting point of the solvent. These data are listed in Table 2 and plotted in Figure 4. A rate constant of 0.0250 min^{-1} and equilibrium constant of 12 m^{-1} are obtained from this treatment. Note that a much better separation of constants is possible at the lower temperature.

A sample of sodium bromate was dissolved in the binary nitrate eutectic along with potassium bromide to give fairly high concentrations of each. This solution was then thermostated at 250°C. A small amount of zinc nitrate in the same solvent was added and the rate of bromine evolution followed. The first-order half-life, $t_{\frac{1}{2}}$, was 7.0 min. Using the same solution a portion of nickel nitrate was added in the same manner, a $t_{\frac{1}{2}}$ of 7.0 min was again observed. The experiment was repeated with the same result,

Table 2

Kinetic data for reaction of divalent metals with bromate in
sodium-potassium nitrate eutectic at 230°C

(Zn^{+2}) molal	Half-life min	k'	$\frac{1}{k'}$	$\frac{1}{(Zn^{+2})}$
0.041	85	.00812	123.2	24.4
0.047	78.5	.0088	113.6	21
0.095	52.5	.0132	76	10.5
0.20	35	.0197	51	4.9
0.260	41.5	.0166	60	3.85
0.270	28	.025	40	3.7
0.28	37.5	.0184	54.5	3.6
(Ni^{+2})				
.074	57	.0121	82.5	13.5

Since it had at first been postulated that the reaction
would be dependent upon the "acidity" of the metal ion this
result was surprising. Therefore several experiments in the
absence of bromide were conducted at varying conditions to
compare the zinc and nickel ion reactivities. The results
for nickel are listed in Tables 1 and 2 also, so they may be
compared with the tables and figures of zinc data. It will
be seen that within experimental error the kinetics are
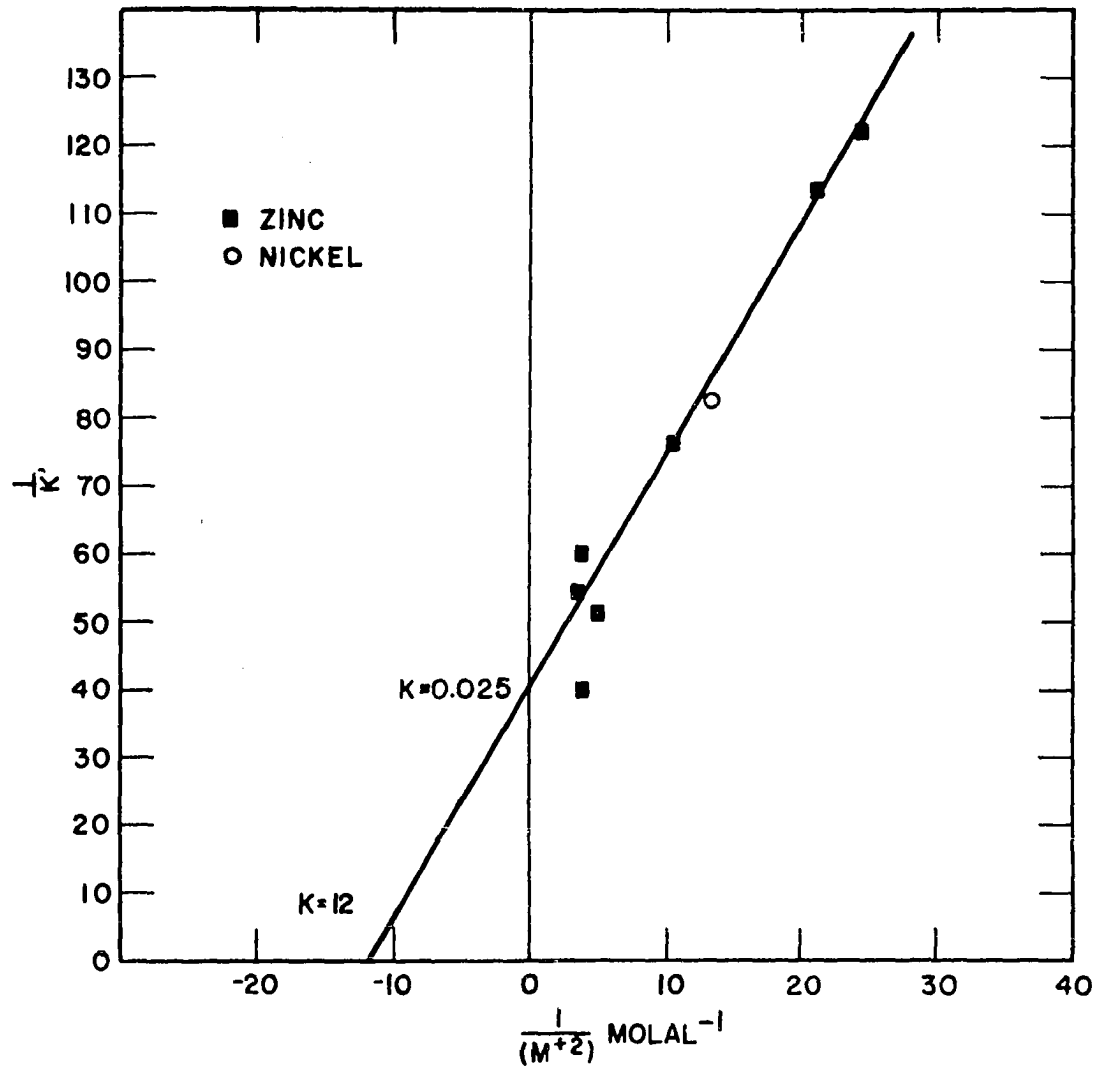
Figure 4. Kinetic data for reaction of divalent metals with bromate in sodium-potassium nitrate eutectic at 230°C

identical.

Various other metal ions were then obtained and experiments attempted with them. The techniques involved in getting them into the molten solvent were discussed in the section on Procedure in Experimental Investigation. All of these experiments were performed at 250°-260°C. A summary of the systems and the results obtained follows:

Ions Added to Binary Nitrate Eutectic	Results
Cadmium (II)-Bromate-Bromide	no Br_2 in 45 min
Cobalt (II)-Bromate	fast Br_2 evolution
Copper (II)-Bromate	fast Br_2 evolution
Bismuthyl-Bromate	fast Br_2 evolution
Manganese (II)-Bromate	fast Br_2 evolution
Mercury (II)-Bromate	no Br_2 observed
Strontium (II)-Bromate	no Br_2 observed
Silver (I)-Bromate	no Br_2 observed
Lanthanum (III)-Bromate	no Br_2
Praesodymium (III)-Bromate	no Br_2
Ammonium-Bromate	fast evolution of Br_2
Yttrium (III)-Bromate	no Br_2
Neodymium (III)-Bromate	no Br_2

More experiments were carried out with copper (II) and cobalt (II) in solution with bromate but even at lowest concentrations and lowest temperatures possible with the

binary eutectic (about 230°C), the rates of reaction were too
fast to study. Eventually satisfactory solutions of these
ions were prepared in a ternary lithium-potassium-sodium
nitrate solution as was discussed in the section on Procedure
in Experimental Investigation.

It was found that reasonable rates could be obtained
for copper (II) and cobalt (II) at about 200°C. Therefore
series of experiments were performed with these ions as was
previously done for zinc. These data were plotted in the
same manner and slope-intercept values obtained:

Ion	Temp	k	K	kK
Cu^{+2}	210°C	0.33	3	1.0
	190	0.022	9.3	0.20
Co^{+2}	180	0.15	45	7.0

The experimental data from which these values were obtained
are listed in Tables 3 and 4 and plotted in Figures 5, 6,
and 7.

Results of this sort in which intercepts considerably
different from zero are shown to further substantiate the
belief that the reaction is not simple second-order.

    a. **Activation energies**   A series of experiments
were carried out at various temperatures using one chosen
zinc concentration to obtain a set of k' values. These
results were treated with the mathematics of the Arrhenius
equation in order to determine an energy of activation, E :

Table 3

Kinetic data for reaction of divalent copper with bromate in
sodium-potassium-lithium nitrate at 210°C

(Cu^{+2}) molal	Half-life min	k'	$\frac{1}{k'}$	$\frac{1}{(Cu^{+2})}$
0.138	8.0	0.086	11.6	7.25
0.069	9.0	.077	13	14.5
.078	10.5	.065	15	12.8
.038	23	.030	33	26
.039	21	.033	30	25.6
.032	19	.036	27.5	30
.041	30	.023	43.5	24
.040	30.5	.023	44.3	25
.073	13	.050	19.7	13.5
.208	4.5	.15	6.5	4.8
.210	5.7	.12	8.2	4.8
.035	24	.029	35	28.6
.017	58	.012	85	58
.074	11.5	.06	16.7	13.5

Figure 5. Kinetic data for reaction of divalent copper with bromate in sodium-potassium-lithium nitrate at 210°C

Table 4

Kinetic data for reaction of divalent metal ions with bromate
in sodium-potassium-lithium nitrate
at various temperatures

Ion	(M^{+2}) molal	Temp °C	$t_{\frac{1}{2}}$ min	$\frac{1}{k'}$	$\frac{1}{(M^{+2})}$
Cu^{+2}	0.192	190	48	70	5.2
	0.465	190	38	55	2.15
	0.455	188	40	58	2.2
Co^{+2}	0.05	177	8.2	11.9	20
	0.05	177	9.1	12.3	20
	0.06	195	2.8	4	16.7
	0.095	181	5.7	8.25	10.1
	0.036	180	6.8	9.9	27.5
	0.0125	180	12	17.5	80
Zn^{+2}	0.222	250	10	14.5	4.5
	0.213	250	8.7	12.75	4.7

$$\ln k' = \ln A - \frac{E^{\pm}}{RT}, \tag{10}$$

Values are listed in Table 5 at two different zinc ion
concentrations and the curves are shown in Figure 8. Both
series of experiments lead to a reasonable straight line and
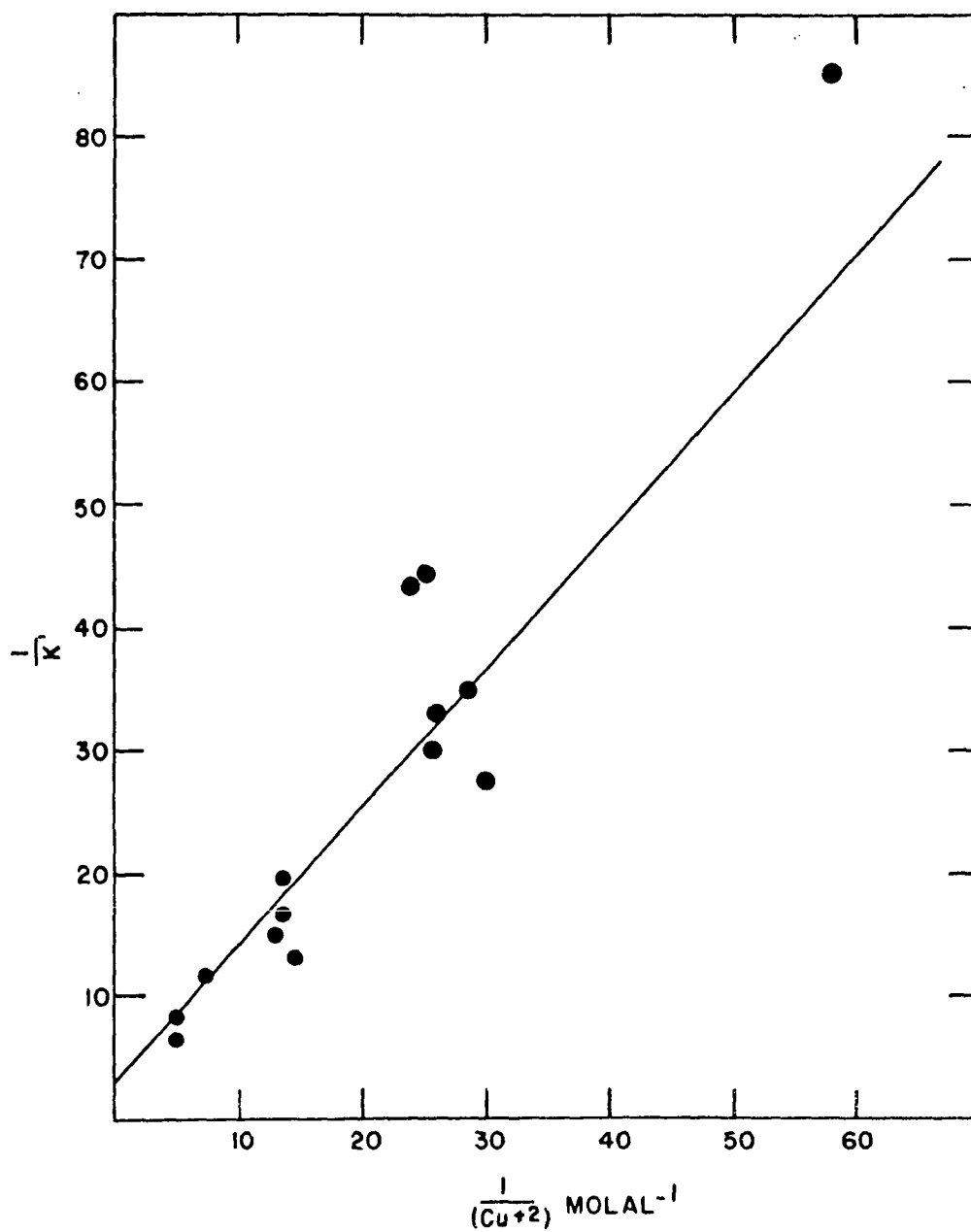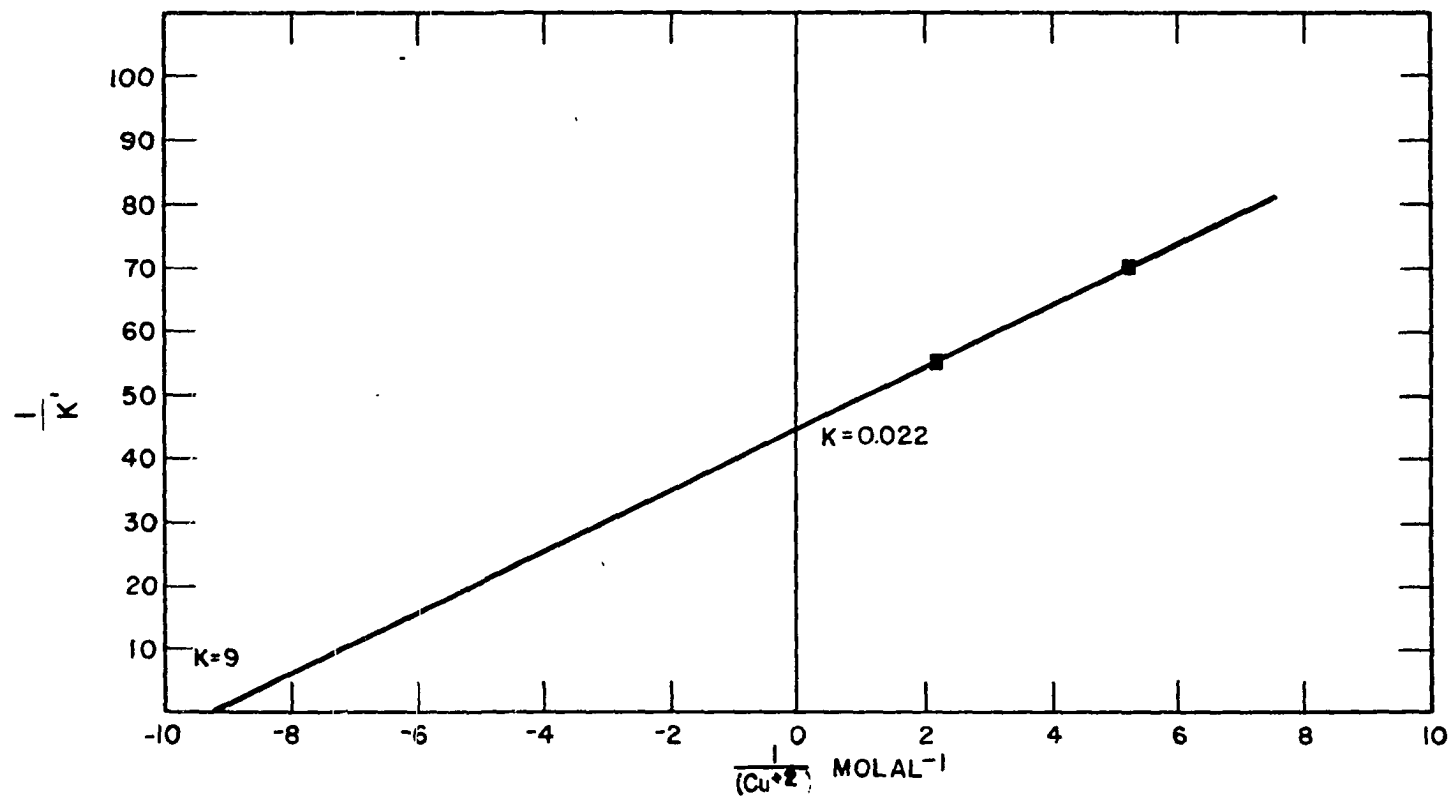a value of about 42 Kcal for $E^{\pm}$. At these temperatures the

Figure 6. Kinetic data for reaction of divalent copper with bromate in sodium-potassium-lithium nitrate at 190°C
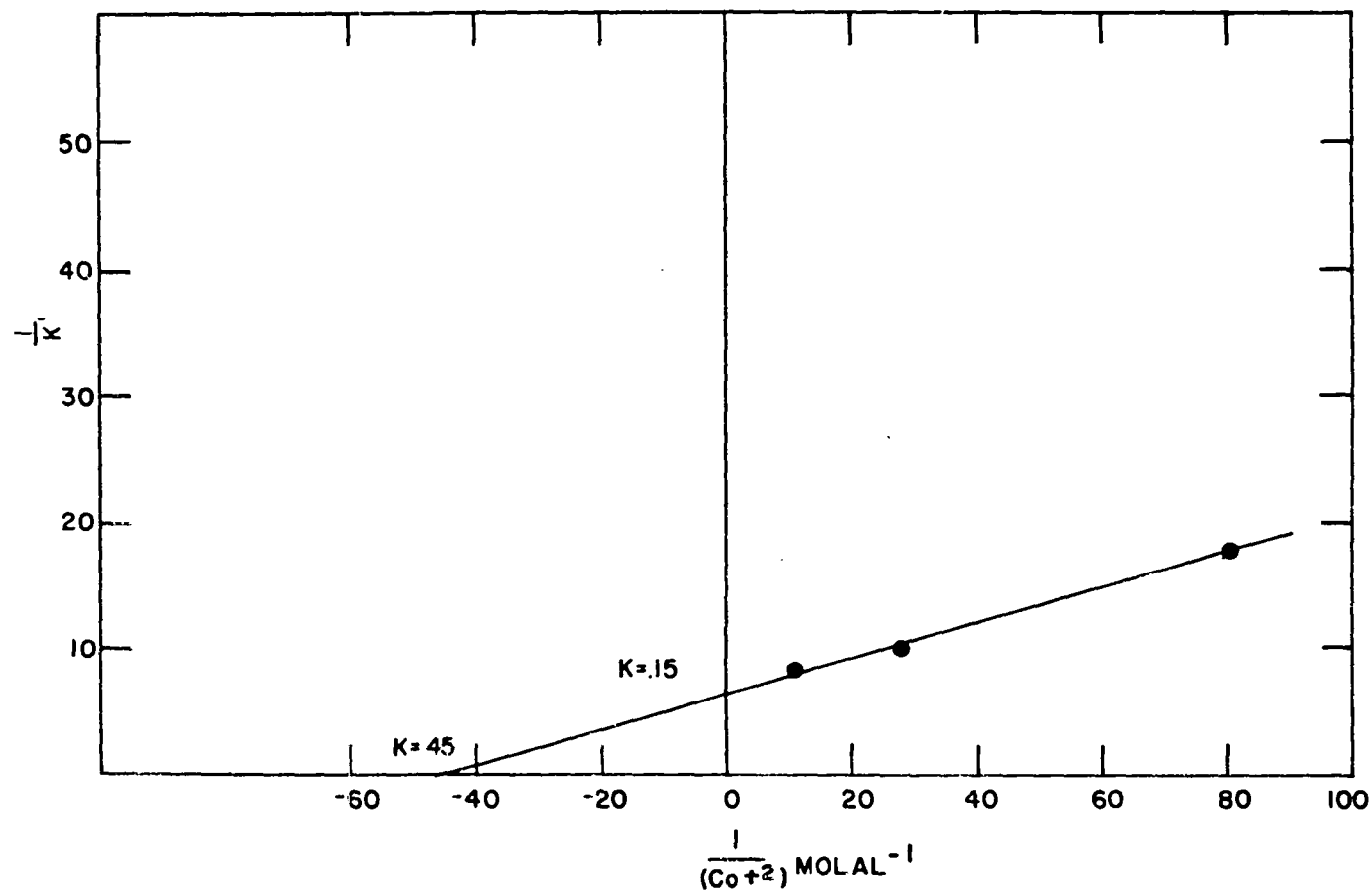
Figure 7. Kinetic data for reaction of divalent cobalt with bromate in sodium-potassium-lithium nitrate at 180°C

difference between energy and enthalpy of activation would
be about 1 Kcal. The data are not good enough to show
whether there might be some curvature to the line in this
temperature range. The form of the rate law and the results
from the two series of data for zinc (II) at 250° and $230^\circ C$
would lead one to believe there might be a slight change or
curvature in a plot of the Arrhenius equation. The size
of the equilibrium constant and concentration of metal in
the denominator of equation 8 may be such as to make any
curvature indistinguishable in view of the uncertainty
involved in the experimental data.

Data for copper (II) and cobalt (II) are included in
Table 5 and Figure 8 in order to show the similarity of
energies of activation for all three ions in their reaction
with bromate. The lines of Figure 8 were purposely drawn
parallel to accent this similarity, but a non-prejudiced
approach would probably only change the slope for the copper
data. Also in this way it is possible to interpolate to a
common concentration and extrapolate to a common
temperature in order to evaluate more quantitatively the
relative reactivities of the various metal ions in this
reaction. This treatment gave the following results:

$$Zn^{+2} \; : \; Ni^{+2} \; : \; Cu^{+2} \; : \; Co^{+2}$$

$$1 \quad : \quad 1 \quad : \quad 50 \quad : \quad 800$$
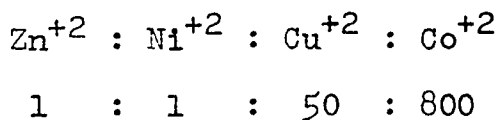
When the values of k, K, and kK for the copper system

Table 5

Determination and comparison of activation energies of
metal ion-bromate reactions

	Temperature $^{\circ}C$	(M^{+2}) molal	k'
Zinc (II)[a]	230	0.047	0.0088
	235	0.041	0.00812
	247	0.039	0.0192
	250	0.04	0.0225
	255	0.04	0.0227
	264	0.043	0.0411
	280	0.043	0.086
	280	0.043	0.052
	294	0.047	0.345
	300	0.039	0.345
	230	0.28	0.0184
	230	0.26	0.0166
	255	0.27	0.12
Copper (II)[b]	177	0.16	0.0038
	190	0.155	0.024

[a]In Na-K nitrate solvent.

[b]In Na-K-Li nitrate solvent.

Table 5. (Continued)

	Temperature $^{\circ}C$	(M^{+2}) molal	k'
Copper (II)[b]	210	0.16	0.10
	210	0.04	0.033
	210	0.05	0.027
Cobalt (II)[b]	170	0.053	0.0345
	177	0.05	0.080
	195	0.06	0.25
Nickel (II)[a]	230	0.074	0.0121
	250	0.0776	0.046
	280	0.070	0.287

at $190^{\circ}C$ and $210^{\circ}C$ and the zinc system at $230^{\circ}C$ and $250^{\circ}C$ are considered, the following values for the activation energies, enthalpies and entropy were obtained:

$$E_k^{\ddagger} = 60 \text{ Kcal for } Cu^{+2}$$
$$= 66 \text{ Kcal for } Zn^{+2}$$
$$\Delta H_K = -25 \text{ Kcal for } Cu^{+2}$$
$$= -49 \text{ Kcal for } Zn^{+2}$$
$$E_{kK}^{\ddagger} = 35 \text{ Kcal for } Cu^{+2}$$
$$= 16 \text{ Kcal for } Zn^{+2}$$
$$\Delta S^{\ddagger} = 40 \pm 5 \text{ eu for } Cu^{+2}$$
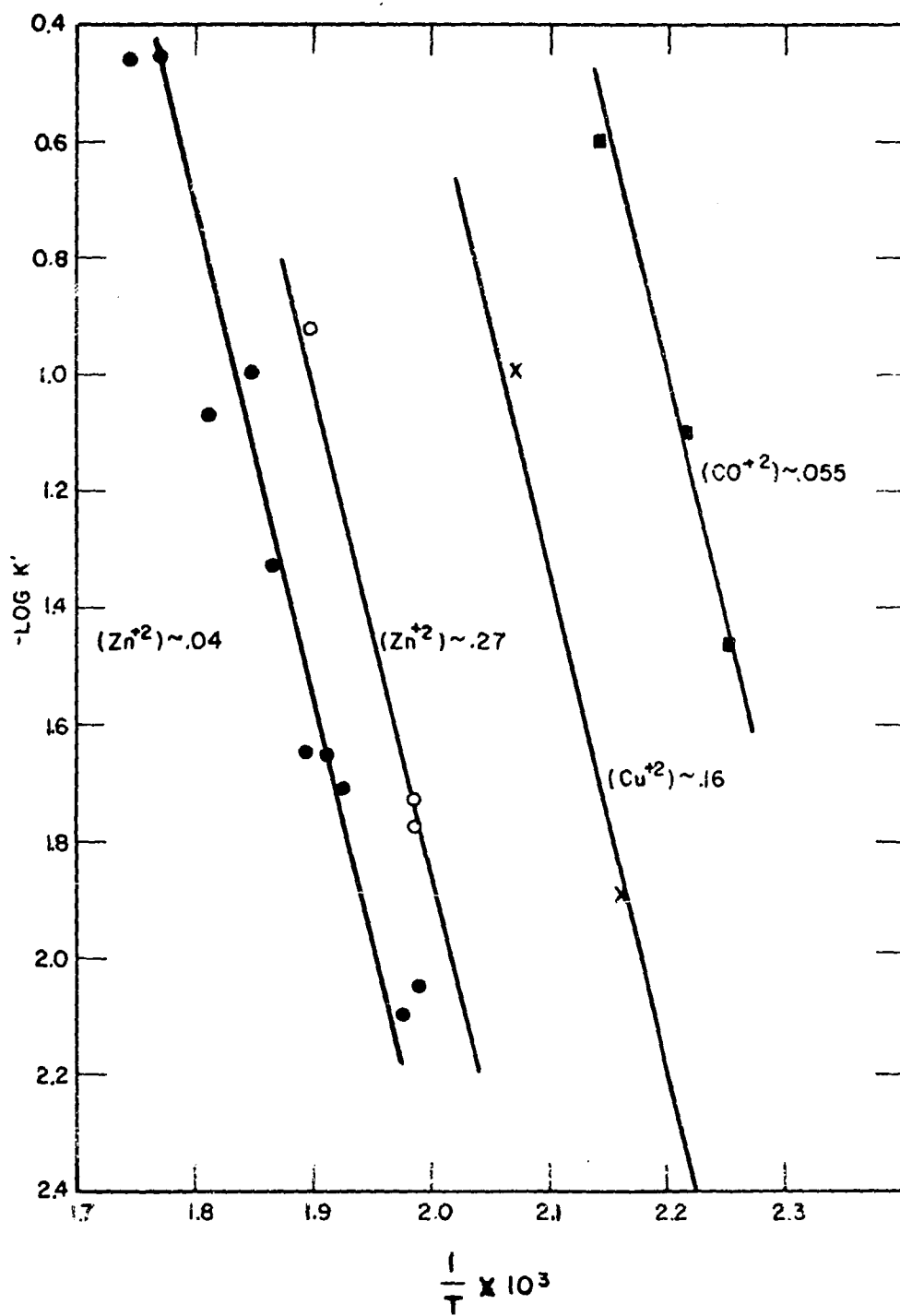
Figure 8. Determination and comparison of activation energies for metal ion-bromate reactions

2. The M^{+2}-bromide-bromate reaction

After a mechanism for the M(II)-bromate reaction had been reasonably well substantiated and the derived mathematical expression tested, it was thought this information might be useful in elucidating the mechanism for the reaction in which bromide was included. It was felt that introduction of terms involving metal-bromide complexes, which were inactive, and metal-bromate-bromide complexes, which were active might resolve the difficulty previously encountered (see discussion under Preliminary Experiments):

$$rate = \frac{kK(Zn^{+2})\ (BrO_3^-)}{1 + K\ (Zn^{+2})} \qquad \text{without } Br^- \qquad (8)$$

$$(Zn^{+2})_t = (Zn^{+2}) + (ZnBr^+) + (ZnBr_2) + \ldots$$

$$k_{01} = \frac{(ZnBr^+)}{(Zn^{+2})\ (Br^-)} \quad ; \quad (ZnBr^+) = k_{01}\ (Zn^{+2})\ (Br^-)$$

$$k_{12} = \frac{(ZnBr_2)}{(ZnBr^+)\ (Br^-)} = \frac{(ZnBr_2)}{k_{01}(Zn^{+2})\ (Br^-)^2} \quad ;$$

$$(ZnBr_2) = k_{01}\ k_{12}(Zn^{+2})\ (Br^-)^2$$

etc.

$$(Zn^{+2})_t = (Zn^{+2}) + k_{01}(Zn^{+2})\ (Br^-) + k_{01}\ k_{12}$$

$$(Zn^{+2})\ (Br^-)^2 + k_{01}\ k_{12}\ k_{23}(Zn^{+2})$$

$$(Br^-)^3 + \ldots$$

$$(Zn^{+2})_t = (Zn^{+2}) \left[1 + k_{01}(Br^-) + k_{01}k_{12}(Br^-)^2 + k_{01}k_{12}k_{23}(Br^-)^3 \right]$$

Solving for (Zn^{+2}) and substituting back into equation 8 to incorporate inactive zinc-bromide complexes:

$$rate = \cfrac{\cfrac{kK(BrO_3^-)(Zn^{+2})_t}{1 + k_{01}(Br^-) + k_{01}k_{12}(Br^-)^2 + k_{01}k_{12}k_{23}(Br^-)^3}}{1 + \cfrac{K(Zn^{+2})_t}{1 + k_{01}(Br^-) + k_{01}k_{12}(Br^-)^2 + k_{01}k_{12}k_{23}(Br^-)^3}}$$

$$= \frac{kK(BrO_3^-)(Zn^{+2})_t}{1 + k_{01}(Br^-) + k_{01}k_{12}(Br^-)^2 + k_{01}k_{12}k_{23}(Br^-)^3 + K(Zn^{+2})_t}$$

Then including active zinc (II) bromate-bromide species, the following equation was finally obtained:

$$rate = \frac{kK(BrO_3^-)(Zn^{+2})_t \left[1 + c_1(Br^-) + c_2(Br^-)^2 \right]}{1 + k_{01}(Br^-) + k_{01}k_{12}(Br^-)^2 + k_{01}k_{12}k_{23}(Br^-)^3 + K(Zn^{+2})_t + K_2}$$

$$(Zn^{+2})(Br^-) + K_3(Zn^{+2})(Br^-)^2 \qquad (10)$$

It was assumed the factors in the denominator, containing complex bromate equilibria (large K's), would be small enough to be ignored.

A series of experiments were carried out using varying high concentrations of bromide and zinc (II) in the binary eutectic at 250°C. This data, which is summarized in Table

6, was programmed for the I.B.M. 650 Magnetic Drum Calculator by Wayne Dunning[1] and the five unknown constants evaluated ($kK = 0.59$ and $K = 1.28$ had been evaluated previously for this system. The latter which is less well-known is also less important to this evaluation). The values obtained for the parameters of equation 10 were:

$$k_{01} = 250, \quad k_{12} = 40, \quad k_{23} = 10.4, \quad c_1 = 900, \quad c_2 = 300\text{-}790.$$

It will be noted that the zinc (II)-bromide complexing constants decrease in size as the number of halide ligands involved increases, as would be expected. Also they are in the range that might be expected on the basis of the values reported by Van Artsdalen (8) for some transition metal halide complexes in fused nitrate solvent (see Table 7).

C. Miscellaneous Experiments

Iverson (9) and Yamamoto (10) found the rate of stirring to be a factor for reactions in fused nitrate in which nitronium ion, NO_2^+, is assumed as reaction intermediate in the rate controlling step. It was assumed that the dependence involved the formation of N_2O_5, which was removed from solution in a diffusion controlled step. Since BrO_2^+ is assumed to be one of the initial product intermediates of

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[1]Iowa State University, Ames, Iowa. 1959.

Table 6

Kinetic data for divalent zinc-bromide-bromate
in binary eutectic at 250°C

(Zn^{+2}) molal	(Br^-) molal	$t_{\frac{1}{2}}$ min
0.079	0.135	47
0.073	0.124	36
0.067	0.114	33
0.040	0.069	72
0.036	0.063	28
0.066	0.049	23.5
0.062	0.045	20.5
0.0505	0.019	13.5
0.0488	0.0156	10.0
0.0455	0.010	9.5
0.0432	0.105	72
0.081	0.061	10.3
0.078	0.056	16.0
0.05	0.014	7

the decomposition of the $MOBrO_2^+$ complex it is possible that
this also might form an adduct with the nitrate of the
solvent to form BrO_2NO_3. Therefore a pair of runs were made
at 188-190°C with 0.46M copper in the ternary solvent. In

one case the flow rate for the inert purge gas was 0.11

l/min and in the other it was 0.27 l/min. The rate of the

reaction was not noticeably altered by this change in

stirring rate by the purge gas. These data can be

identified in the list in Table 4.

The experiments previously mentioned, which were

designed to determine whether there were nitrogen gases in

the product stream, indicate also that if BrO_2NO_3 is formed

during the course of reaction it must dissociate again to

form NO_3^-, which stays in solution. This would mean that

BrO_2^+ is very much less an oxide acceptor than NO_2^+, which is

reasonable considering the fact that the decomposition of

the dissolved metal nitrates is imperceptible at the

temperature of this study.

In order to find out whether the reaction of bromate

with these divalent metals has any extension to other

halates in the fused nitrate, some attempt was made to

investigate reaction with chlorate and iodate. It was found

that all of the metal iodates are very insoluble in the

fused nitrate solvents. They also seem to be thermally

stable at $250^\circ C$ since very little in the way of decomposition

products could be detected either in the melt or in the

purge gas stream.

The metal chlorates were found to decompose slowly to

form Cl_2 and Cl^-, with the latter being the major product.

The rate of reaction was affected by the metal ion present

but there was also an uncatalyzod decomposition of the chlorate itself. This reaction was not studied extensively since there seemed to be no connection with the bromate decomposition.

Attempts were made to determine zinc bromide complexing constants in the fused alkali nitrate by use of solubility studies. In this method an insoluble salt of the metal is used. The complexing anion is added and increase in solubility of the salt determined. This increase is then interpreted on the basis of various possible complexes of the metal with the anion being added. For this purpose three zinc compounds were found to be insoluble and also stable in the fused nitrate melt. These were zinc chromate, zinc oxide and zinc oxalate. When bromide was added to the chromate solution a vigorous reaction took place causing the solution to foam. Zinc oxide was found to be so insoluble that addition of large quantities of bromide did not increase the solubility measurably. The zinc oxalate stayed in colloidal suspension in the solvent and therefore analysis of the solubility was impossible.

D. Discussion

1. Complexing constants

The relative reactivities of the metal ions studied do not fit any of the previously established orders. The so-called "natural order" of Irving and Williams (11) for

divalent transition element complexing strengths (Co Ni Cu Zn) with many ligands would allow for nickel (II) and zinc (II) to have the same complexing constant with bromate, but cobalt (II) would be lower and copper (II) higher. Most of the data that has been compiled to establish this "order" are for organic complexes in aqueous solution at 25°C (11,12,13). Extension of the argument to relatively small inorganic complexes in a fused nitrate solvent at 200°C or higher would be expecting a great deal. Davies (13) in his table of pK diss of ion pairs in aqueous solution shows these values for sulfate to decrease uniformly from cobaltous through zinc in a periodic arrangement. Even in Irving and Williams' table of constants (11) this latter order shows up when four ammonia ligands are coordinating.

The enthalpies obtained in this study for the metal-bromate complexes must be taken to be very crude since only two points are used to evaluate them. This is also the case for the activation energies and entropy of the separated rate constants. Enthalpies for most other complexes reported in the literature (9,11,12,14,15) seem to range from a few to about ten or fifteen kilocalories, therefore the present values seem a bit high. Nevertheless, Flengas and Ingraham (16) report activation enthalpies of divalent cobalt, nickel and zinc chloride complexes in molten 1:1 Na-KCl in the range of 14 to 54.5 Kcal.

In comparing the constants reported for lead and
cadmium nitrates with their corresponding halides in
water at 25°C, it is seen that the former are smaller by a
factor of about 20-60. See Table 7 (Ref. 17-20). If the
same sort of relationship holds for bromate, which might be
expected to be similar to nitrate, then the values obtained
in this study are in a reasonable order of magnitude. Just
the fact that the data allow one to postulate a metal-bromate
complex in the fused nitrate solvent would indicate that the
complex with bromate is somewhat stronger than with nitrate.
A reversal of this may explain the non-reactivity of cadmium,
lead, mercury, the rare earths, and other metal ions toward
decomposition of bromate in this reaction.

Stranks and Wilkins note that there is no a priori
reason for a correlation between thermodynamic stability
and exchange lability, i.e. reaction rate (21,22). Part
of a table from their review is reproduced in Table 8,
which illustrates this (23-26).

In studies of exchange of an atom of the ligand such
as the hydrogens of metal-ammonia complexes it was shown
that the more inert the complex is to substitution of the
ligand the easier it is to exchange the hydrogens.
This was explained in terms of the greater orbital overlap
in the metal-nitrogen σ bond, lowering the electron
distribution on the nitrogen and resulting in greater

Table 7

Stability constants of complex ions in water and fused nitrate

$$K_n = \frac{(MX_n^{2-n})}{(M^{+2})\,(X^-)^n}$$

Solvent	Complex	K_n(mol/l)$^{-1}$	Temp (°C)	Ref
Water	$PbCl^+$	38	25	15
	$PbBr^+$	70,59	25	15
	PbI^+	83	25	15
	$CdCl^+$	91 ± 5	25	15
	$CdBr^+$	142 ± 7	21	15
	CdI^+	300 ± 15	20	15
	$AgNO_3$	0.67	25	19
	$CdNO_3^+$	1.3	25	19
	$HgNO_3^+$	1.2	25	19
	$Hg(NO_3)_2$	1.0	25	19
	$PbNO_3^+$	2.5	25	19
	$Pb(NO_3)_2$	0.8	25	19
Alkali nitrate	$PbCl^+$	18	250	20
	$PbCl_2$	36	250	20
	$PbBr^+$	18	250	20
	$PbBr_2$	90	250	20
	$CdCl^+$	20	250	20

Table 7. (Continued)

$$K_n = \frac{(MX_n^{2-n})}{(M^{+2})(X^-)^n}$$

Solvent	Complex	$K_n(mol/l)^{-1}$	Temp (^oC)	Ref
Alkali nitrate	$CdCl_2$	100	250	20
	$CdBr^+$	20	250	20
	$CdBr_2$	100	250	20
	$PbCl_2$	30 ± 5	300	8
	$CdCl_2$	320 ± 40	300	8
	$ZnCl_2$	380 ± 30	300	8
	$CdBr_2$	2900 ± 1000	300	8
1:1 K-NaCl	$PbCl_2$	3.5	682	17
	$ZnCl_2$	68	684	17
	$NiCl_2$	3.3	705	17
	$CoCl_2$	23	710	16
	$CdCl_2$	82	680	18

probability of acid dissociation.

2. Magnetic catalysis

Other types of electronic disturbances in the complex can result from the non-bonding, unpaired electrons from the metal ion involved in the complex. A magnetic catalysis of this sort was demonstrated by Calvin (27,28), in the

Table 8

Exchange rates of metal complexes of
bis-salicylaldehyde-ethylene diimine
Stranks and Wilkins (21)

Metal	Conc (m)	Temp ($^{\circ}$C)	Rate	Ref
Cu	0.015	25	$t_{\frac{1}{2}}$ = 2.1 hr	23
Ni	0.01	room	none after 40 hr	24
Co	0.017	30	complete in 6 min	25
Zn	0.01	25	complete in 0.5 min	26

oxidation of some metal tetra phenyl chlorins with quinone
and light. He postulated the necessity of reaching an
activated triplet state in the chlorin with sufficient half-
life for reaction to take place. In the presence of the
heavy metal nucleus of zinc or magnesium this can occur, but
in the presence of copper with its unpaired electron the
electronic transition from ground singlet to activated
triplet by way of activated singlet and back is too fast.
Thus the time the complex is in the "reactive" state is much
shorter than the time needed for effective collision to
occur.

Much of the catalysis in homogeneous reactions by metal
ions has been demonstrated to involve metal-substrate
complexes. It has been assumed that withdrawal of electrons

from the reactive center is a primary effect, facilitating reaction. This effect involves not only the degree of interaction of the metal ion on the substrate in the ground state but also in the activated or transition state. Some metal-ligand complex catalyses involve electron transfer (29-36).

Withdrawal of electrons from the reaction center has been shown in the metal-ion catalyzed hydrolysis of certain organic esters, the halogenation of oxo-esters and the decarboxylation of β-oxo-carboxylic acids (37,38,39). In the latter case it was proposed (37,38) that the metal ion is linked to the keto and the carboxylate groups of dimethyl oxaloacetic acid, increasing electron displacement toward the keto group and thus leaving the carboxyl bond less stable. Furthermore, in the mono ethyl ester (esterified at the carboxyl adjacent to the keto group) decarboxylation is reduced. The assumption was made that the complex linked the keto group and ionized carboxyl through the metal ion, stabilizing the molecule.

Working with oxaloacetic acid, Pederson (39) obtained the following results from the equilibrium and rate constants involved when Cu^{+2} and Zn^{+2} were used to catalyze the decarboxylation of oxaloacetic acid:

	k_3K_3	k_4K_4	k_3	K_3	$\dfrac{(CuO_x)}{(Cu^{+2})(O_x^{--})}$
Cu^{+2}	1.96	0.50	1.63	1.20	0.67×10^4
Zn^{+2}	0.027	0.063	--	--	--

In extending this work to the rare earth and related ions Gelles et al. (40,41,42,43,44,45) measured the rate of decarboxylation of oxaloacetic acid in the presence of La^{+3}, Gd^{+3}, Y^{+3}, Dy^{+3}, and Lu^{+3}. A large acceleration in rate was observed over the uncatalyzed decomposition. This again was attributed to specific association, leading to withdrawal of electrons from the decomposing carboxyl group.

It was assumed that if no electronic transitions or change in type of bonding are involved in the transition state of decarboxylation, the energy of activation for decarboxylation would be expected to be a constant fraction of the free energy of association. In other words, a linear free-energy relationship between the logarithm of rate constant, k_c, (or k_cK_1) and logarithm of association constant, K, would exist. Therefore the rate data were compared with some complexing data and a line placed through the points for La^{+3}, Y^{+3}, and Lu^{+3}. The points for Gd^{+3} and Dy^{+3} were displaced, indicating a further acceleration for the decarboxylation over that expected for simple catalysis. Also the difference for Gd^{+3} was larger than for Dy^{+3}. This was therefore attributed to the number of unpaired electrons,

showing that the effect is a function of electronic spin
properties of the ions (44).

When the same decarboxylation was coupled with carbon
isotope studies it was found that Dy^{+3} catalyzes the fission
of $C^{12}-C^{12}$ bonds about four per cent more strongly than
$C^{12}-C^{13}$ bonds. This was interpreted as a "magnetic" isotope
effect in that carbon-13 nuclear spin-electron spin inter-
actions might be in the same order of magnitude as the
electron spin-electron spin interactions produced at a
greater distance by the paramagnetic ion. The "magnetic
catalytic" effect of Dy^{+3} would then be greater on $C^{12}-C^{12}$
than on $C^{12}-C^{13}$ bonds, where the C-13 nuclear spin effect
would already be operative (46,47,48).

This also explains the large discrepancy, arising from
explanations based on mass considerations alone, in the rate
of substitution of C^{14} for C^{12} over that for C^{13}, since C^{14}
again has zero nuclear spin and magnetic moment (46).

Harman and Eyring (49) have suggested that paramagnetic
substances might increase the probability of transition from
singlet to triplet state by producing a non-homogeneous
magnetic field which will act differently on the two
magnetic dipoles arising from the spin of the two electrons in
the π-bond. Alternatively, McConnell (50) has suggested that
the catalyst in an electronic state other than singlet inter-
acts with the singlet and triplet states of the ligand
resulting in formation of two doublet states together with a

quartet state. The minimum of separation of these doublet states will then be determined by the bond strength between catalyst and ligand. A minimum of separation of the order of kT could make the alternative non-adiabatic path 10^4-10^7 times more probable. Thus even weak catalyst-ligand chemical interactions could account for the catalytic effect of paramagnetic molecules. No corresponding mechanism exists for catalysts in singlet states.

Considering these and other arguments, it is possible to hypothesize that the decomposition of bromate is catalyzed not only by the presence of a heavy metal nucleus in the activated complex, but also by the presence of unpaired electrons in the complex. The increasing rate follows the increase in paramagnetic character normally expected in going through the divalent ions from zinc through cobalt, except for nickel, and that also can at times be expected to have its pair of d-electrons coupled up by strong enough ligand interaction. This effect would leave Ni^{+2} and Zn^{+2} with much the same properties, enough so as to give essentially the same observed kinetics.

Little is known about the nature of the solvent-metal complexes in the fused nitrates. Gruen (51,52) claims that the spectra he has observed for nickel (II) in Li-K nitrate indicated the same octahedral coordination as shown in water.

The nitrate solutions of Ni^{+2} used in this study had a definite brownish color when fused, which turned to bright

green on cooling. This could indicate a change in bonding
of the solvation sphere of the transition metal ion. The
color of a compound or its solution may not necessarily be
indicative of its magnetic properties, as is pointed out by
Zelentsov et al. (53), but many people have noted that
paramagnetic nickel compounds are usually green to blue
while those that are diamagnetic are yellow to brown (54,55).

In an attempt to study the magnetic character of the
solution a hot sample was placed between the poles of a
strong electro-magnet. Care was taken to eliminate as much
nickel oxide, which is ferromagnetic, as possible, but this
is not easy since it is a product of reaction of nickel
nitrate decomposition. At first the sample was neither
strongly drawn into nor pushed out of the field but on
cooling it was drawn strongly into the field of the
magnet and against one of the poles. No provision was taken
to heat the sample while in the magnetic field.

3. Role of the solvent

It was thought that the question of solvation effect
could be resolved by using a less complexing solvent.
Therefore a melt of lithium perchlorate was prepared and the
reaction studied at $250^{\circ}C$. As before, samples containing
high metal ion concentration (zinc or nickel) were prepared
and bromate added. In all cases the resulting reaction was
too fast to follow kinetically.

In an attempt to study the reaction in a perchlorate

containing solvent at lower temperatures an equal molar mixture of lithium nitrate and lithium perchlorate was prepared. The freezing point of the solvent was found to be about 177°C. It was thought that the activity of nitrate in this mixture might be lowered sufficiently to allow separation of zinc and nickel reactivities. A sample of this solvent was then prepared containing 0.075 m (BrO_3^-). Small amounts of nickel nitrate and zinc nitrate were added to the melt at 215°C as before. Half-lives of about 11 minutes were obtained for both. It was found that the bromate reacted with perchlorate in this melt at a slow rate at 215°C and very vigorously at 255°C. Products of the reaction are bromine and chloride. This solvent system was therefore abandoned, although the latter reaction might be of interest at a future date.

Several combinations of alkali nitrates were used as solvents in the study of bromate decomposition. Differences in reactivities in other reactions have been reported in the presence of different alkali cations[1] (11). No variations in rate for zinc (II) and nickel (II) could be detected in the lithium-potassium-sodium or sodium-potassium nitrate solvents cf. Tables 1 and 4 for zinc data. In pure lithium nitrate an

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[1]Senderoff, Seymour, National Carbon Laboratory, Union Carbide Corporation, Parma, Ohio. Discussions on fused salts. Private communication. 1959.

acceleration of about 3-fold was observed for zinc (II) and about 6-fold was observed for nickel (II). The experiments were repeated several times, giving the same results. The effect of separating the rates for zinc and nickel in this solvent may be real or may reflect inaccuracies in the experimental procedure, since the difference is not great. Nevertheless, the results can be rationalized on the basis of previously proffered arguments[1] (11), concerning the stronger coordination of the nitrate by lithium than that for sodium or potassium. Thus the nitrates free for coordination with the transition metal ions will be at a much lower activity. Along this line, it may be significant to note that the color of the nickel-perchlorate melt was bright green.

4. Free-energy correlation to rate

If an equilibrium involving the metal ion and its oxide is involved in the reaction one of the factors which would be expected to play a role in the rate of reaction is the free-energy change in going from the solvated metal ion to the metal oxide. Since no thermodynamic data were available for the system or temperatures investigated in this study, it was thought that some idea of the relative magnitudes of the free-energy changes might be evaluated from data at room temperature for aqueous ions, since solvation by nitrate might

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[1]Senderoff, Seymour, National Carbon Laboratory, Union Carbide Corporation, Parma, Ohio. Discussions on Fused salts. Private communication. 1959.

be comparable and the relative effect might be essentially the same for similar ions (56). Therefore the data for Table 9 were assembled (57,58). It did not seem at first that much correlation could be made from this information since the values obtained for ions, which were known not to react, seemed about as favorable as the energies for those that do.

After the relative rates of reaction for the four metal ions had been evaluated it was noted that the free energies from Table 9 fit the experimental data very well, i.e. the most negative free-energy change is indicated for cobalt with copper intermediate and zinc and nickel about the same at the least negative end in the list of these four ions. It should be noted that RT ln 800 gives a value of 6.7 Kcal, whereas the difference in the free-energy changes involving cobalt and zinc is 6.6 Kcal. Therefore this fits the relative reactivity obtained from Figure 8. The values comparing copper with zinc give RT ln 50 = 3.9 Kcal while the table gives 5 Kcal. In order to get such good agreement it was necessary to use the free-energy value for Co_3O_4 rather than CoO. This is not unreasonable in view of the X-ray experiment mentioned on page 14 of this thesis.

5. Concluding remarks

The inability to predict reactivities from free-energy data alone probably reflects in part the ability of the metal ion to form the bromate complex. Also it is not

Table 9

Thermodynamic free-energy data for aqueous metal
ions and their solid oxides

		$\Delta \bar{F}^o$	
Element	M^{+2} (aq) Kcal	MO (s) Kcal	(MO - M^{+2}) Kcal
Zn	-35.18	-76.050	-40.86
Ni	-11.1	-51.7	-40.60
Cu	15.53	-30.4	-45.9
Co	-12.3	-59.8[a]	-47.5
Cd	-18.58	-53.79	-35.21
Pb	- 5.81	-45.05	-39.24
Pd	38.3	-14.4	-52.7
Mn	-53.4	-86.80	-33.4
Hg	39.38	-13.99	-53.37

[a]Value for Co_3O_4 per cobalt.

unreasonable to presume that some of the data listed are not
applicable for the system under consideration since solvation
and temperature effects may be considerable. It is not known
whether the free-energy argument or the magnetic-catalytic
argument should be given more weight in explaining the
results of this study. Some interpretation may be available
based on the activation energies obtained. One would

probably expect the activation energies to decrease as reactivity increased if thermodynamic energies are the main consideration in establishing relative reactivities. Furthermore, a combination of exothermic reaction and high activation energy does not necessarily lead to a regular tendency for the most stable products to be produced the most rapidly (59). On the other hand, the effect of a magnetic perturbation might be evident in the frequency factor of the absolute rate theory of Eyring (60). If a triplet or some such electronic state must necessarily be reached for reaction to occur the frequency that this state is reached would be a considerable factor. Certainly the thermodynamic situation would be important in that case also. Therefore, one must conclude that there are probably three main factors involved:

1. The ability to form a metal-bromate complex,

2. A favorable free-energy change,

3. The ability of the reactive intermediate to get into the best electronic state for dissociation to occur rapidly.

IV. SUMMARY

The decomposition of bromate in fused alkali nitrates was found to be catalyzed by the presence of certain divalent metals, such as cobalt, nickel, copper and zinc. This decomposition involves a mechanism in which a metal-bromate complex is formed in a fast equilibrium followed by a slow rate-controlling decomposition. The products of the reaction are the metal oxide, bromine and oxygen. This mechanism can be expressed in the following manner:

$$M^{+2} + BrO_3^- \underset{fast}{\overset{K}{\rightleftharpoons}} MBrO_3^+$$

$$MBrO_3^+ \underset{slow}{\overset{k}{\longrightarrow}} products$$
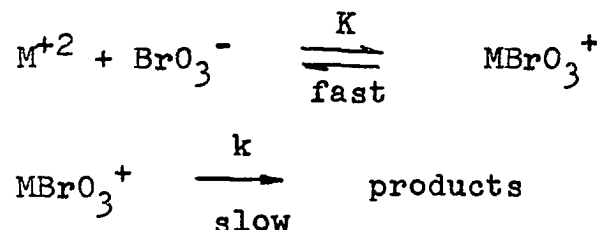
The decomposition is not only catalyzed by the presence of the heavy metal nucleus in the activated complex but also by the presence of unpaired electrons from the d-orbital of the transition metal involved in complex formation. The normally unpaired d-electrons of nickel are probably paired up in the nitrate solvent making it diamagnetic and reducing the reactivity from what would normally be expected. The resultant reactivities of the metal ions studied are:

$$Zn : Ni : Cu : Co$$
$$1 : 1 : 50 : 800$$
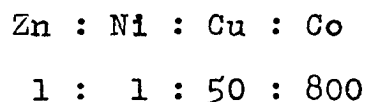
The rate equation derived for the above mechanism involves both the equilibrium and rate constants:

$$\text{rate} = \frac{kK(M^{+2})(BrO_3^-)}{1 + K(M^{+2})} = k'(BrO_3^-) \text{ when } (M^{+2}) >> (BrO_3^-)$$

The constants were evaluated for several variations of reactants and temperature. Estimates of activation energies, enthalpies, and entropy were made. A summary of constants is presented in Table 10.

Other metals were tested but not studied extensively. It was found that Mn^{+2} and BiO^+ seemed to be reactive in the decomposition but that the rare earths, lead, cadmium, strontium, mercury, and silver were not reactive. It was hypothesized that bromate might not fit readily into the nitrate solvation spheres of these ions.

The rate of stirring of the reaction mixture was not a factor and no nitrogen gases were produced in the product stream therefore stable mixed bromine-nitrogen oxides are not involved in the reaction mechanism.

When bromide is added to the reaction mixture metal-bromide complexes are formed which are inactive toward bromate decomposition and metal-bromate-bromide complexes are formed which are more reactive than the simple metal-bromate complexes:

$$M^{+2} + BrO_3^- \xrightleftharpoons{K} MBrO_3^+ \xrightarrow{k} \text{products}$$

$$MBrO_3^+ + Br^- \xrightleftharpoons{K_2} MBrO_3Br \xrightarrow{c} \text{products}$$

$$MBrO_3Br + Br^- \xrightleftharpoons{K_3} MBrO_3Br_2^- \xrightarrow{c'} \text{products}$$

$$M^{+2} + Br^- \xrightleftharpoons{k_{01}} MBr^+$$

$$MBr^+ + Br^- \xrightleftharpoons{k_{12}} MBr_2$$

$$MBr_2 + Br^- \xrightleftharpoons{k_{23}} MBr_3^-$$
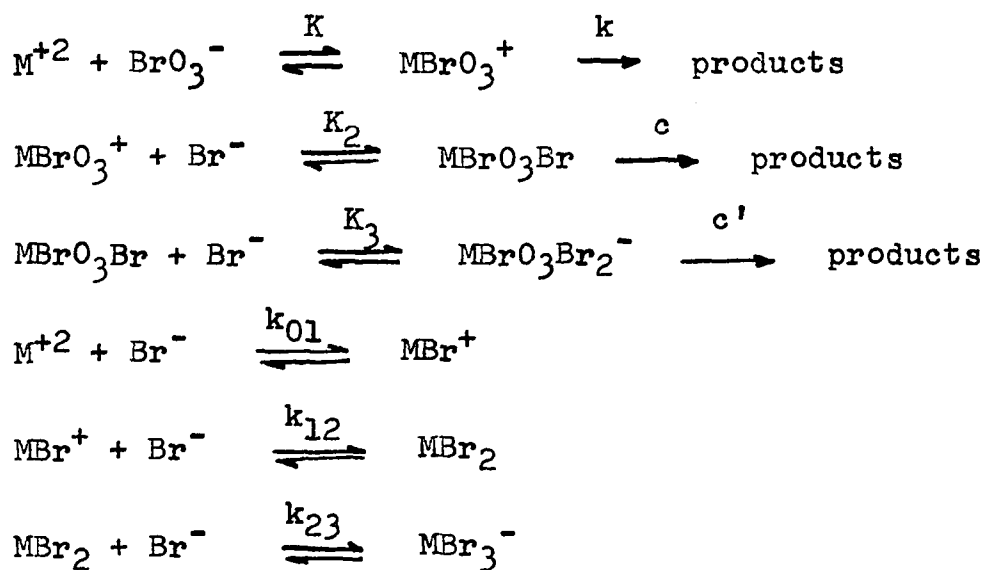
Table 10

Summary of constants evaluated in this study

Ion	Temp °C	Rate const k, min^{-1}	E_k Kcal	Equil const K, m^{-1}	H_K Kcal
		Reaction: M^{+2}-bromate			
Zn^{+2}	230	0.025	66	12	-49
	250	0.46	66	1.28	-49
Ni^{+2}	230	0.025	-	12	-
	250	0.46	-	1.28	-
Cu^{+2}	190	0.022	60	9.3	-25
	210	0.33	60	3	-25
Co^{+2}	180	0.15	-	45	-

Table 10. (Continued)

Reaction: M^{+2}-Br^--bromate				
			Rate constants	
Ion	Temp ^oC	k, min^{-1}	kc_1, min^{-1}	kc_2, min^{-1}
Zn^{+2}	250	0.46	410	140-360

Complex species		Stability constants
$ZnBr^+$	250	$k_{01} = 250\ m^{-1}$
$ZnBr_2$	250	$k_{12} = 40$
$ZnBr_3^-$	250	$k_{23} = 10.4$

$$\text{rate} = \frac{kK(M^{+2})(BrO_3^-)\ 1+c_1(Br^-)+c_2(Br^-)^2}{1+k_{01}(Br^-)+k_{01}k_{12}(Br^-)^2+k_{01}k_{12}k_{23}(Br^-)^3+K(M^{+2})+etc.}$$

The constants involved in this rate expression for the case in which (M^{+2}) is zinc at 250^oC were evaluated assuming the terms in the denominator encompassed by the notation "etc." were small enough to be ignored.

Studies were made with various combinations of alkali cations in the solvent but little effect on the reaction rate was observed. The use of lithium perchlorate as a less complexing solvent led to faster reaction as was expected but also involved a different type of reaction to add

complications.

A further study could be made on the effect of adding another halide such as Cl^- to the reaction mixture along with the bromide. In the aqueous studies (1) mixtures of this sort were found to be more active than with chloride or bromide alone. The complexing effect of many other ligands could be studied by observing their affect on the decomposition of bromate in these fused nitrate solvents.

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