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Acid-base reactions and kinetics of the halates in fused nitrates

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ACID-BASE REACTIONS AND KINETICS OF THE

HALATES IN FUSED NITRATES

by

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1962

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I. INTRODUCTION

Previous to 1900, investigations of fused salt systems had been undertaken mainly because of their novelty. At that time measurements were very approximate. Results of a higher order of accuracy were obtained between 1920 and 1950. Generalizations were made with an attempt to systematize the study of fused salt systems. After 1950 work progressed to determine exact values of the physical properties of fused electrolytes. Among these properties one might include density, conductivity, viscosity, vapor pressure, compressibility, surface tension, and transport number. Presently there are not many good direct methods to investigate the structure of fused electrolytes, although several attempts have been made through x-ray and neutron diffraction studies (1), and spectrophotometric studies (2). Consequently, the chemist has resorted to a study of the various physical properties mentioned above in hopes that correlations and relationships between these properties will be self consistent with a proposed model.

An insight into the structure of fused salts or fused electrolytes might also be gained by studying reactions carried out in this medium. The course of certain characteristic reactions is determined largely by the nature of the solvent. Excluding oxidation-reduction reactions, the structure of several nonaqueous solvents has been developed by studying

reactions carried out in these solvents (3).

The behavior of many acid-base reactions has been characterized in other solvents as well as in water. The more familiar solvents are ammonia, acetic acid, and hydrogen fluoride. Using a fused electrolyte as the solvent one can study the mechanisms of acid-base reactions beyond the one hundred degree limit imposed by water. Also, one can study these reactions in the absence of hydrolysis and solvation by the solvent, both of which usually introduce several complex reactions into the mechanism.

The increasing technological importance of high temperature processes has stirred a great interest in the field of reactions of fused electrolytes. The manufacture of glass, cement, and ceramic products, the formation of slag in blast furnaces, the use of ammonium sulfate and ammonium fluoride as fluxes in the opening of ores involve reactions at high temperatures between metal oxides, sulfides, and halides. The Lewis concept of acids and bases has been successfully applied to these reactions. In 1939 Lux (4) proposed an acid-base definition which is actually a part of the more general Lewis theory. According to Lux, an equilibrium,

$$\text{Base} \rightleftharpoons \text{Acid} + O^= \text{ , exists.}$$
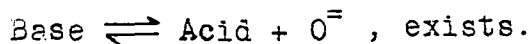
When an acid reacts with a base there is a transfer of oxide ion. The result is the familiar conjugate acid-base system. When two acids are in the presence of a base there is a

competition for oxide ion. The predominant reaction will be between the base and the stronger acid, the latter being the better oxide acceptor. Obviously this definition is limited because it excludes analogous reactions of sulfides and halides. However a great many solvent systems in use are oxides or involve oxyanions. Flood and Forland (5) compared acid strengths of oxide systems by comparing values of the equilibrium constant,

$$K = \frac{A_{acid} \, A_{O^=}}{A_{base}}$$

The research that has been done to characterize the reactions of fused salts has been the study of the decomposition of fused oxides and several pure salts. Only recently have reactions been conducted in fused electrolytes using the fused salt as a solvent. Yamamoto (6) has compared the relative acidity of the oxyanions, dichromate and pyrosulfate, and several metal ions in fused alkali nitrates. In this case, nitrate played the role of the solvent as well as the base. Studies conducted by Duke and Lawrence (7) indicate that bromate is a much stronger base than nitrate. Dichromate is a very weak acid. Perhaps the reaction between dichromate and bromate, as well as the other halates, could be studied in fused alkali nitrates. The purpose of this study is to characterize the reactions between the halates and dichromate in alkali nitrates and to compare the

relative strength and stability of the halates in the
presence of dichromate.

II. LITERATURE REVIEW

Marlowe Iverson (8) observed the reaction between nitrate and dichromate when studying lead chloride complexes in a eutectic mixture of sodium and potassium nitrate. Upon adding chloride and bromide and varying the concentration of lead nitrate, he concluded that the following equilibrium existed in fused nitrates:

$$(1) \qquad NO_3^- \rightleftharpoons NO_2^+ + O^{--}$$
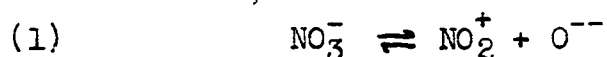
When dichromate is added, it accepts the oxide ion from nitrate and forms chromate.

$$(2) \qquad Cr_2O_7^{--} + NO_3^- \rightleftharpoons NO_2^+ + 2CrO_4^{--}$$
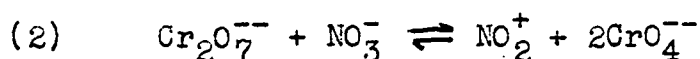
The nitryl ion then combines with a nitrate or a halide ion and decomposes to products of which nitrogen dioxide is a final product. The above equilibrium lies far to the left and no reaction is observed unless lead ion is added to precipitate the chromate. The equilibrium constant for the above reaction is very small, approximately 10^{-14}. Even when lead ion is added, the concentration of nitryl ion is not large enough to allow separation of the equilibrium constant and rate constant. That is, the reaction appears to be first order in the disappearance of dichromate and not total acid,

$$(3) \qquad T_a = Cr_2O_7^{--} + NO_2^+$$
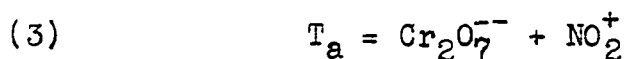
Duke and Yamamoto (9) were able to separate these two constants and evaluate the rate constant for the reaction,

$$(4) \qquad NO_3^- + NO_2^+ \longrightarrow Products$$
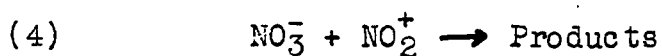
by adding a stronger acid, pyrosulfate. The same rate deter-
mining step occurs as when dichromate reacts with nitrate.
When one substitutes the rate constant obtained from the pyro-
sulfate reaction, the equilibrium constant for the dichromate
reaction can be determined. The flow rate of the gas for each
reaction must be matched carefully since it has been shown that
the rate of decomposition involving nitrate varies as the flow
rate of the carrier gas is changed. Apparently the gaseous
product, nitrogen pentoxide, is quite soluble in fused
nitrates and the rate determining step is the rate at which
gaseous nitrogen pentoxide diffuses to the surface of the
melt. By assuming that the same equilibrium exists when metal
ions are used as the acid, Yamamoto (6) evaluated their rela-
tive acidity. In this case, he obtained a product of con-
stants and used the rate constant from the pyrosulfate reaction
to determine the equilibrium constants for the metal ions.
The relative strengths of the acids in the order of increas-
ing acid strength are: $Cr_2O_7^{--}$, Zn, Cu, $S_2O_7^{--}$. When Duke
and Lawrence (7) studied the reactions of the same metal ions
with bromate in fused alkali nitrates, they found it neces-
sary to postulate a metal-bromate complex formation with sub-
sequent decomposition. Bromate is a much stronger base than
nitrate in fused nitrates, such that the reaction of bromate
with metal ions takes place before much, if any, nitrate has
reacted. Analysis has shown that no oxides of nitrogen are

present in the gases evolved. The rate of decomposition is highly dependent on the metal ion used, which is explained by a metal-chromate complex formation. The equilibrium constant of metal ions with nitrate is not obtained independently, therefore the relative acidity of zinc and copper ions to dichromate and pyrosulfate is not established.

Extensive studies of the dichromate reaction using barium as the precipitating agent have not been done. It has been shown that barium works just as successfully as lead in promoting the reaction between dichromate and nitrate. However the barium chromate precipitate does not settle very rapidly, making it difficult to extract and analyze samples from the melt during the course of a reaction. But one can follow the appearance of gaseous products and relate this to the disappearance of one of the reactants, namely that reactant which is added in limiting concentration. If one assumes that barium does not form complexes with any of the ions in solution, it would be interesting to investigate the reactions between dichromate and halates in fused nitrates.

III. EXPERIMENTAL INVESTIGATION

A. Materials and Apparatus

All the chemicals used in this study were A.C.S. Reagent Grade. They were dried at $110^{\circ}C$ in an oven and then stored in a desiccator until needed. The constant temperature bath consisted of an insulated ten quart enamel pot filled with a mixture of molten potassium and sodium nitrate. The primary heat was supplied by a ten inch Cromalox 1500 watt ring heater recessed in fire bricks and connected to a 220 volt Varaic. The auxiliary heater was an alumdum core wrapped with nichrome wire and coated with Sauereisen. This heater was connected to a Brown Electronik Temperature controller which was monitored by a chromel-alumel thermocouple. The temperature was kept well within $\pm 1^{\circ}C$ of the desired temperature. A one-half inch transite cover was fitted on top of the enamel pot to prevent radiant loss of heat.

The reactions were carried out in a reaction vessel constructed so as to continually purge the solution with an inert carrier gas, to stir the solution, and to afford easy sampling of the solution with a preheated pipet. This vessel was made of 34 mm. pyrex tubing with a 34/45 standard taper joint at one end and closed at the other end. The overall length was 24 cm. The top of the reaction vessel was a standard taper joint with a gas inlet and a gas outlet. The inlet extended

to within 1.5 cm. of the bottom of the tube. The outlet was
connected to a manifold equipped to supply six sulfite
scrubbers. The scrubbers were wide mouth erlynmeyer flasks.
A large test tube with a small hole in the bottom was inserted
into the mouth of the erlynmeyer flask. This test tube was
filled with small glass beads to afford a large surface area
contact for the halogen gases to be reduced. A schematic
drawing of the apparatus is illustrated in Figure 1.

The carrier gas, nitrogen, was dried by passing the gas
through a magnesium perchlorate tower and metered by an ori-
fice meter. The meter was calibrated with a "precision" wet
test meter. The flow rate of the carrier gas was 0.21 liters
per minute for most of the runs. Occasionally, the flow rate
was increased to 0.40 liters per minute to see what effect
this increase had on the reaction rate. The reaction rate
was independent of the flow rate for all reactions studied in
this thesis.

B. Procedure

Two methods can be used to study reaction rates in fused
salts. The concentration of a reactant can be followed with
time by sampling the melt with a preheated pipet and letting
the sample solidify on a cold porcelain plate thereby quench-
ing the reaction. Or, the disappearance of a reactant can be
measured by following the appearance of one of the product

DRYING
TOWER

ORIFICE
METER

REACTION
VESSEL

SULFITE
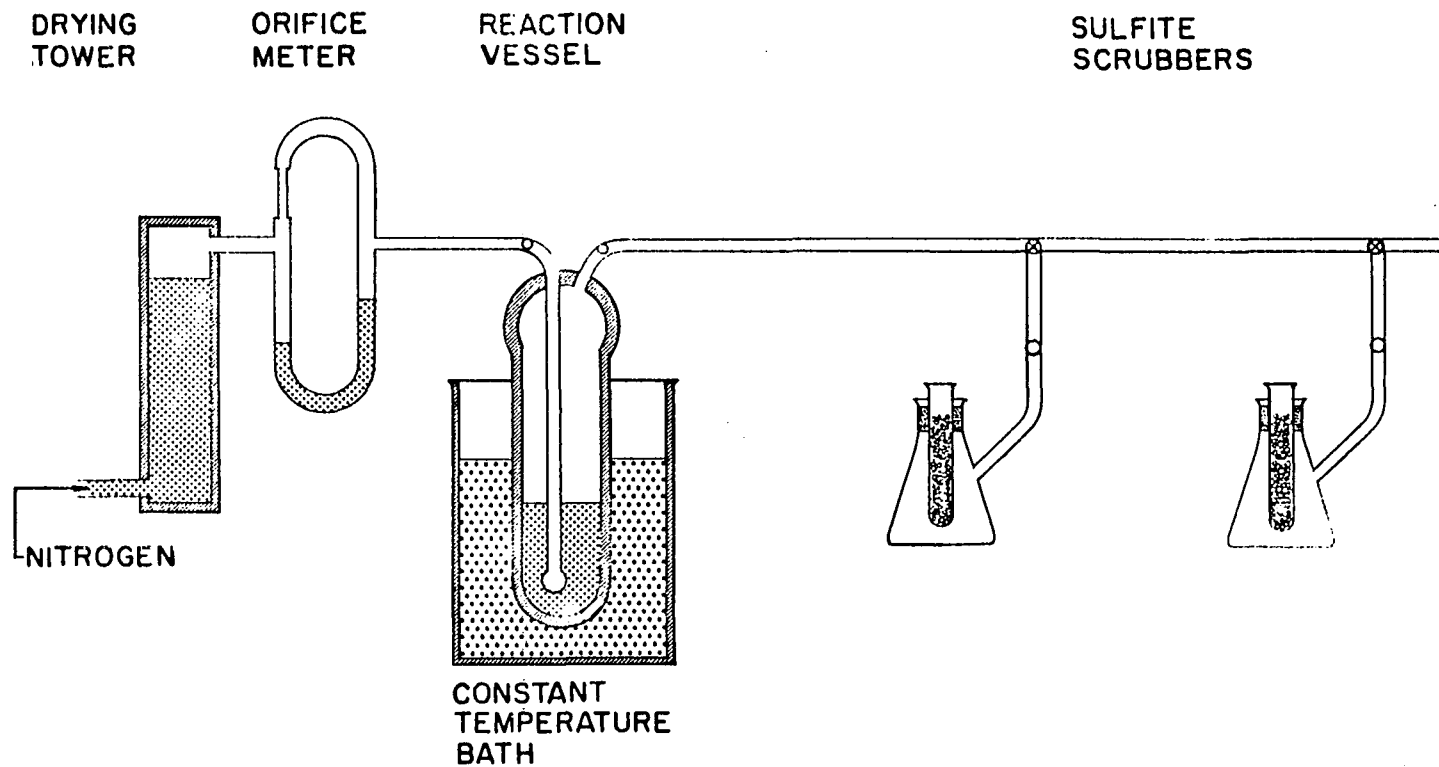SCRUBBERS

NITROGEN

CONSTANT
TEMPERATURE
BATH

Figure 1. A schematic drawing of the apparatus used to study the reactions of the halates with dichromate

gases, provided the stoichiometry is known. Since the precipitate of barium chromate is so widely dispersed and does not settle rapidly, it was found best to use the latter procedure in this study.

The desired mixture of salts to be used as the solvent was fused and all but one of the reactants were weighed, placed in the melt and allowed to mix. This solution was purged with the inert carrier gas, nitrogen, for one-half to one hour to allow complete dissolution of the reactants and sweep out any water dissolved in the melt. When a run was to be made, the last constituent was added and halogen gases were collected in sulfite scrubbers and reduced to halide ion. The halide was then titrated with silver nitrate using either eosin or dichloroflourescein as an indicator, depending on which reaction was being studied (10). An acid solution of sulfite, prepared by bubbling sulfur dioxide through water, was used to collect bromine from the bromate reaction. These solutions could be directly titrated with silver nitrate. In the chlorate reaction a solution of sodium sulfite was used. But chloride can not be titrated in a neutral solution of sulfite because the sulfite bleaches the indicator. Therefore each solution was acidified and allowed to steam on a hot plate to drive off all of the sulfur dioxide. Base and acetate were added to neutralize the acid and to keep the solutions at approximately the same pH. A blank was run and all

samples were titrated to the same end point. The reactions were allowed to go to completion and the total amount of halogen evolved was taken as the initial amount of reactant added. Each sample was subtracted from this number to obtain the concentration of reactant at the time recorded for that sample. At first all the numbers were converted to the absolute concentration of bromate or dichromate; however one is only interested in the slope. Therefore the number of milliliters of silver nitrate was plotted directly on semi-log paper. All of the values for k' except those for the dichromate-bromate and the dichromate-nitrate reactions should be multiplied by the constant, 2.3, because the k' values reported were obtained from a common log plot. This conversion is not necessary unless one is interested in the rate of the reaction. The rate of the reaction is not of primary interest in this study and the rate is independent of the equilibrium constant. Concentrations are expressed in moles per 1000 grams of solvent unless otherwise indicated. In the chlorate reaction the number of grams of chlorate added was quite large. Consequently sodium chlorate was incorporated as part of the solvent.

C. Solubility Measurements

The solubility of barium chromate was determined in alkali nitrates and chlorates. It is necessary to know the

solubility of barium chromate in the solvents used before the
equilibrium constants of the reactions can be calculated.
The value obtained for the solubility of barium chromate in
a eutectic mixture of sodium and potassium nitrate at $250^{\circ}C$
was reproducible and was in agreement with the value obtained
by Duke and Iverson (11). However the values obtained in a
50-50 mole percent $NaClO_3-KNO_3$ mixture were not precise.
Barium chromate does not settle easily in this mixture.
After one week small amounts of suspended particles were
present in the supernatant liquid. The lower limit of the
values obtained was taken as the solubility. This number,
$K_{sp} = 2 \times 10^{-6}$, is relatively close to the value obtained
for potassium-sodium nitrate. This is apparent because sodium
chlorate-potassium nitrate forms a reciprocal salt mixture
and the solubility in sodium-potassium nitrate solvent appears
to be independent of the mole fraction of the solvent cations.

The chromate concentration was sufficiently low to deter-
mine the solubility colorimetrically. The analysis was per-
formed using the diphenylcarbizide method (12). The solutions
were prepared by fusing one hundred grams of a mixture of
sodium and potassium nitrate in a test tube and adding an
amount of barium nitrate equivalent to the concentrations used
in a typical run. Exactly 0.10 mole per 1000 gms. of solvent
of potassium chromate was added. The mixtures were stirred
for approximately thirty minutes and allowed to settle. The

mixtures were kept at the desired temperature overnight before sampling. Samples were withdrawn from the supernatant liquid with a preheated pipet and allowed to cool. The two to three gram samples were weighed and dissolved in 3N HCl. The indicator was added and the samples were diluted to 100 mls. After five minutes the chromate concentration was measured with a Junior Coleman Spectrophotometer and the concentration determined from a standard curve. Two different concentrations of barium nitrate were used and the solubility determined from $S = \sqrt{Ba^{++}\ CrO_4^{=}}$. The cation ratios were 38/62, 50/50, and 60/40 mole percent K/Na. The temperatures were $249^{\circ}C$, $259^{\circ}C$, and $239^{\circ}C$. The results are shown in Table 1.

The solubility is temperature dependent, and a plot of Log (solubility) versus 1/T gives a reasonably straight line (Figure 2). The solubility appears to be independent of the mole percent of the cations in the solvent.

Table 1. Solubilities of barium chromate at several temperatures in mixtures of sodium and potassium nitrate[a]

Temp. $^{\circ}C$	Solubility product	Solubility
259°	4.00×10^{-6}	2.00×10^{-3}
249°	3.20×10^{-6}	1.79×10^{-3}
239°	2.40×10^{-6}	1.55×10^{-3}

[a]These values are the average of values obtained at three different barium concentrations and using three different mole percent mixtures of sodium and potassium nitrate.

Figure 2.   Temperature dependence of the solubility of
            $BaCrO_4$ in KNO_3-$NaNO_3$ mistures; log (solubility)
            versus 1/T

15b
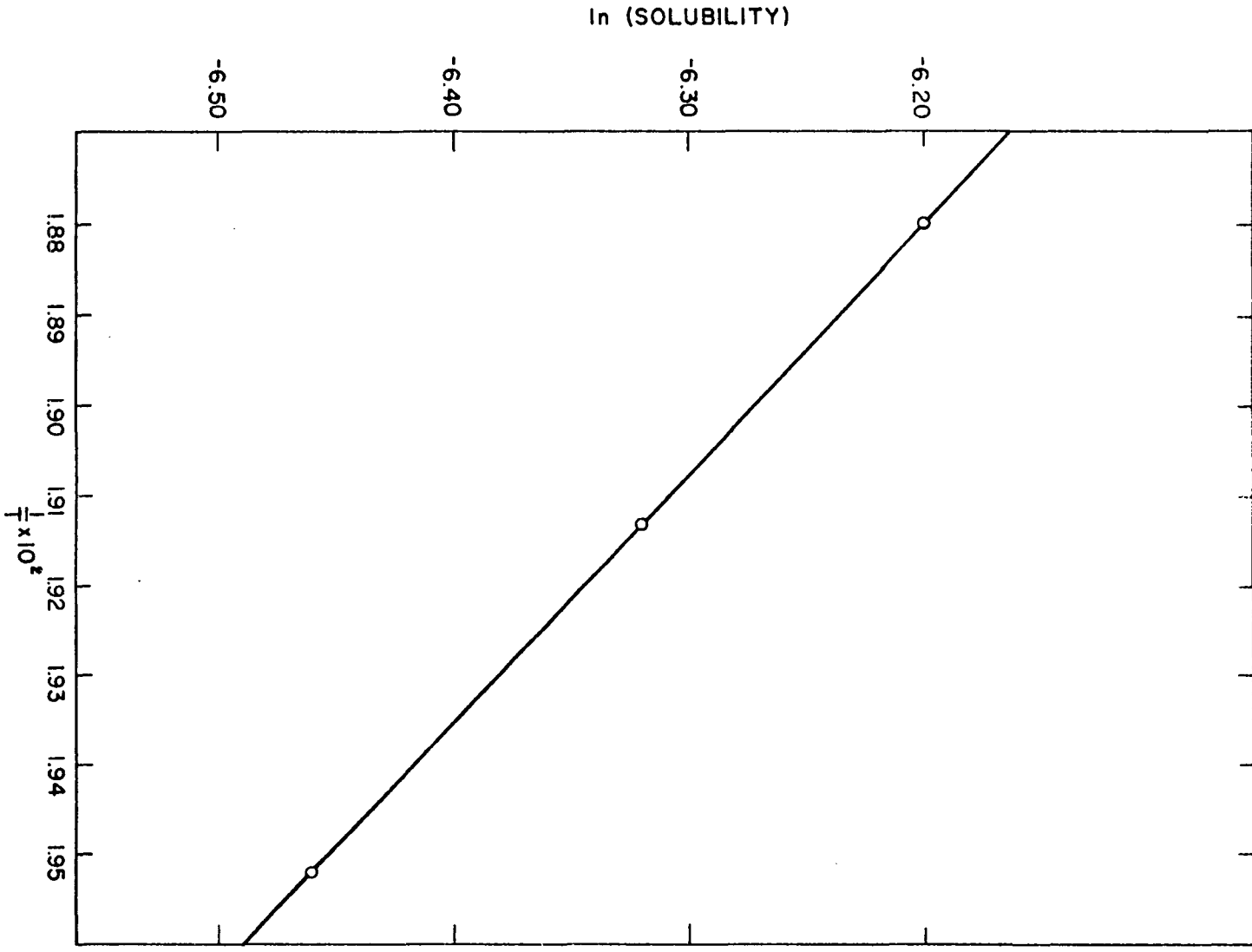
The solubility of barium chromate in $NaClO_3$-KNO_3 mixture is 0.002m ± 0.002m. The results are very close to those obtained in sodium and potassium nitrate solvent. Iverson (8) has shown that other ions present in the melt have little effect on the solubility of barium chromate. Therefore the equilibrium constants for all the reactions were evaluated using the solubility obtained in sodium-potassium nitrate mixtures.

IV. EXPERIMENTAL RESULTS
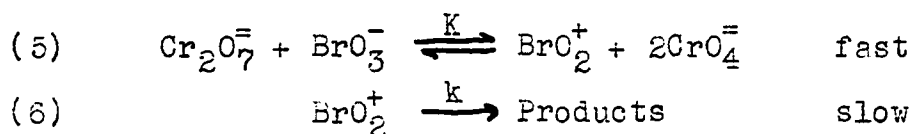
A. The Bromate Reaction

1. The reaction and mechanism

The reaction between dichromate and bromate was investigated to see if the bromyl ion, analogous to the nitryl ion, is formed in the absence of any metal ions which might form complexes. Barium nitrate was used as the precipitating agent because it was thought that barium would not likely form complexes with any of the ions in solution. Dichromate was used as the acid. Although dichromate will react with nitrate in the presence of barium, it will be shown that the equilibrium constant for the formation of nitryl ion is a factor of 10^5 times less than the equilibrium constant involving the formation of bromyl ion. Therefore the reaction between bromate and dichromate will be complete before much, if any, nitrate has reacted. Lawrence (13) observed the decomposition of bromate to bromide and oxygen if bromate was allowed to sit in fused nitrates for several days. Shute (14) has shown that this decomposition is catalyzed by bromide. The solutions used in this investigation were analyzed before and after the reaction and no bromide was found in the melt.

Preliminary runs were conducted. An immediate precipitate of barium chromate with the evolution of bromine was

observed. Analysis of the gases evolved showed no oxides of nitrogen. The reaction was complete within one-half hour to two hours depending upon the amount of barium nitrate present. This dependence of the rate on barium indicates a fast equilibrium between dichromate and bromate. When there was no detectable odor of bromine the reaction was allowed to proceed for another half-hour to insure completion of the reaction. The reaction is first order in the disappearance of total bromate. A typical plot is shown in Figure 3.

A mechanism to explain these observations involves a fast equilibrium followed by a unimolecular decomposition of the bromyl ion.

$$(5) \quad Cr_2O_7^= + BrO_3^- \underset{}{\overset{K}{\rightleftharpoons}} BrO_2^+ + 2CrO_4^= \qquad fast$$

$$(6) \quad BrO_2^+ \overset{k}{\longrightarrow} Products \qquad slow$$

When one measures the disappearance of bromate chemically, it is necessary to consider this measurement as the loss of total bromate,

$$(7) \quad T_{BrO_3} = BrO_3^- + BrO_2^+$$
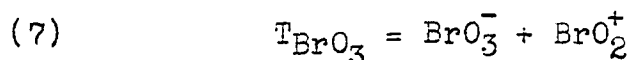
if there is an appreciable amount of BrO_2^+ present. If one uses the solubility product expression for barium chromate and equations 5, 6, and 7, and making the proper substitutions, the rate expression can be written,

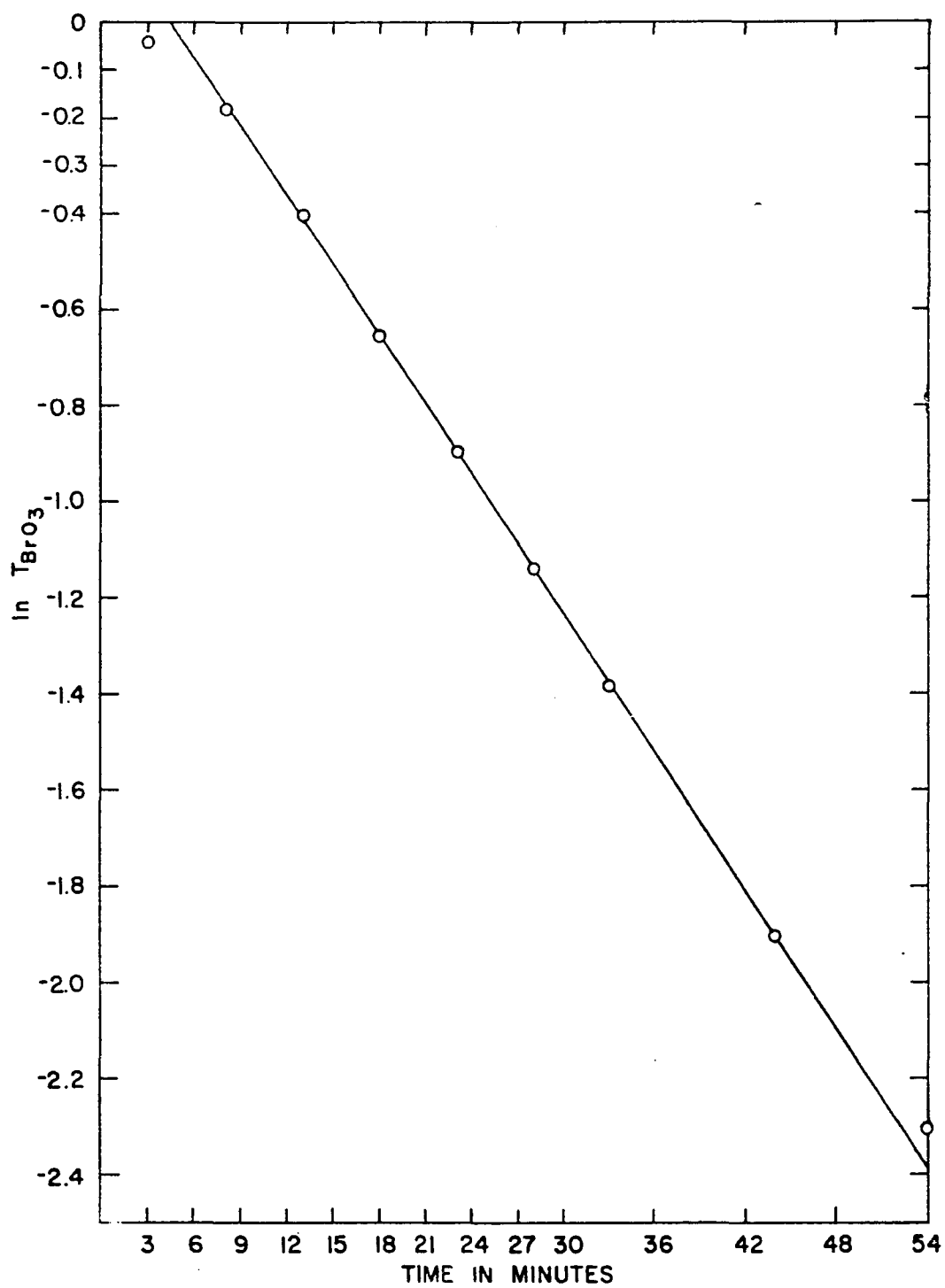$$(8) \quad R = \frac{kK[Cr_2O_7^=][Ba^{++}]^2}{K[Cr_2O_7^=][Ba^{++}]^2 + K_{sp}^2} T_{BrO_3}$$

Figure 3. Variation of log T_{BrO_3} with time for a typical run at $250^{\circ}C$ in $NaNO_3$-KNO_3 solvent

All concentrations are made large compared to bromate and are assumed to remain constant throughout a run. Thus,

$$(9) \qquad \text{Rate} = k'T_{BrO_3}$$

where the pseudo first order rate constant is,

$$(10) \qquad k' = \frac{kK[Cr_2O_7^=][Ba^{++}]^2}{K[Cr_2O_7^=][Ba^{++}]^2 + K_{sp}^2}.$$

The reciprocal of k' is,

$$(11) \qquad \frac{1}{k'} = \frac{1}{k} + \frac{K_{sp}^2}{kK[Cr_2O_7^=]} \cdot \frac{1}{[Ba^{++}]^2}.$$

A plot of $1/k'$ versus $1/[Ba^{++}]^2$, as shown in Figure 4, gives a straight line with a non-zero intercept. The ordinate intercept directly gives the rate constant. With a knowledge of the solubility of barium chromate and the concentration of dichromate, the equilibrium constant can be obtained from the abscissa intercept. The solubility of barium chromate and its temperature dependence are discussed in Section III.

The first order dependence in total bromate implies a unimolecular decomposition of bromyl ion, BrO_2^+. The final products are bromine and oxygen. There are no ions available for bromyl to react with except the solvent, nitrate. However an analysis of the product gases shows no oxides of nitrogen. Therefore a possible mode of decomposition would be,

$$(12) \qquad BrO_2^+ \longrightarrow Br^+ + O_2$$
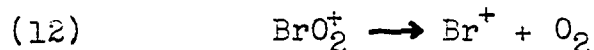
and Br^+ picks up an electron and eventually forms bromine. Work on the salts of Br^+ has been reviewed by Kleinberg (15)

Figure 4. Plot of reciprocal rate data versus $1/[Ba^{++}]^2$ at $250^\circ C$ and $260^\circ C$ to determine the equilibrium and rate constants
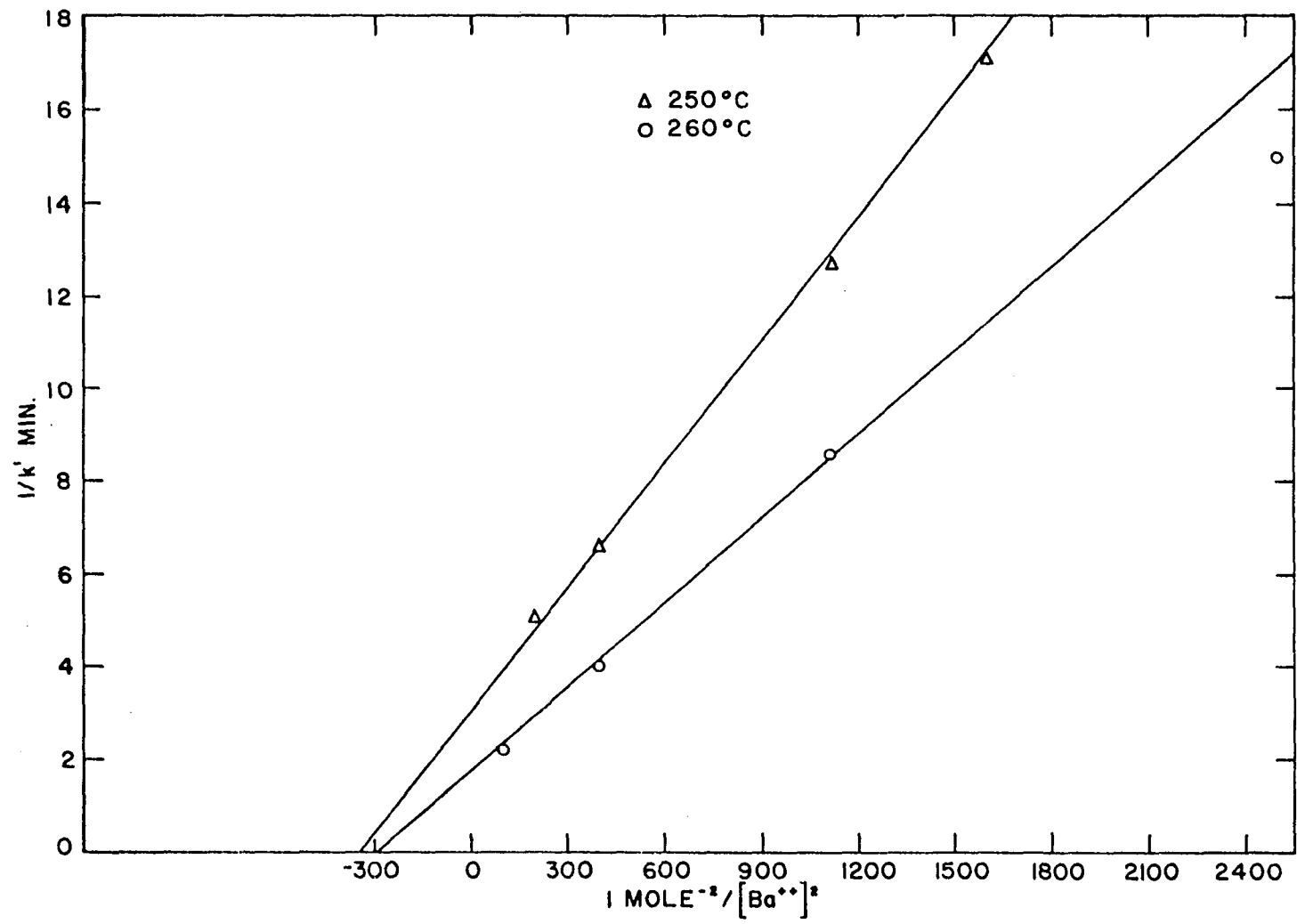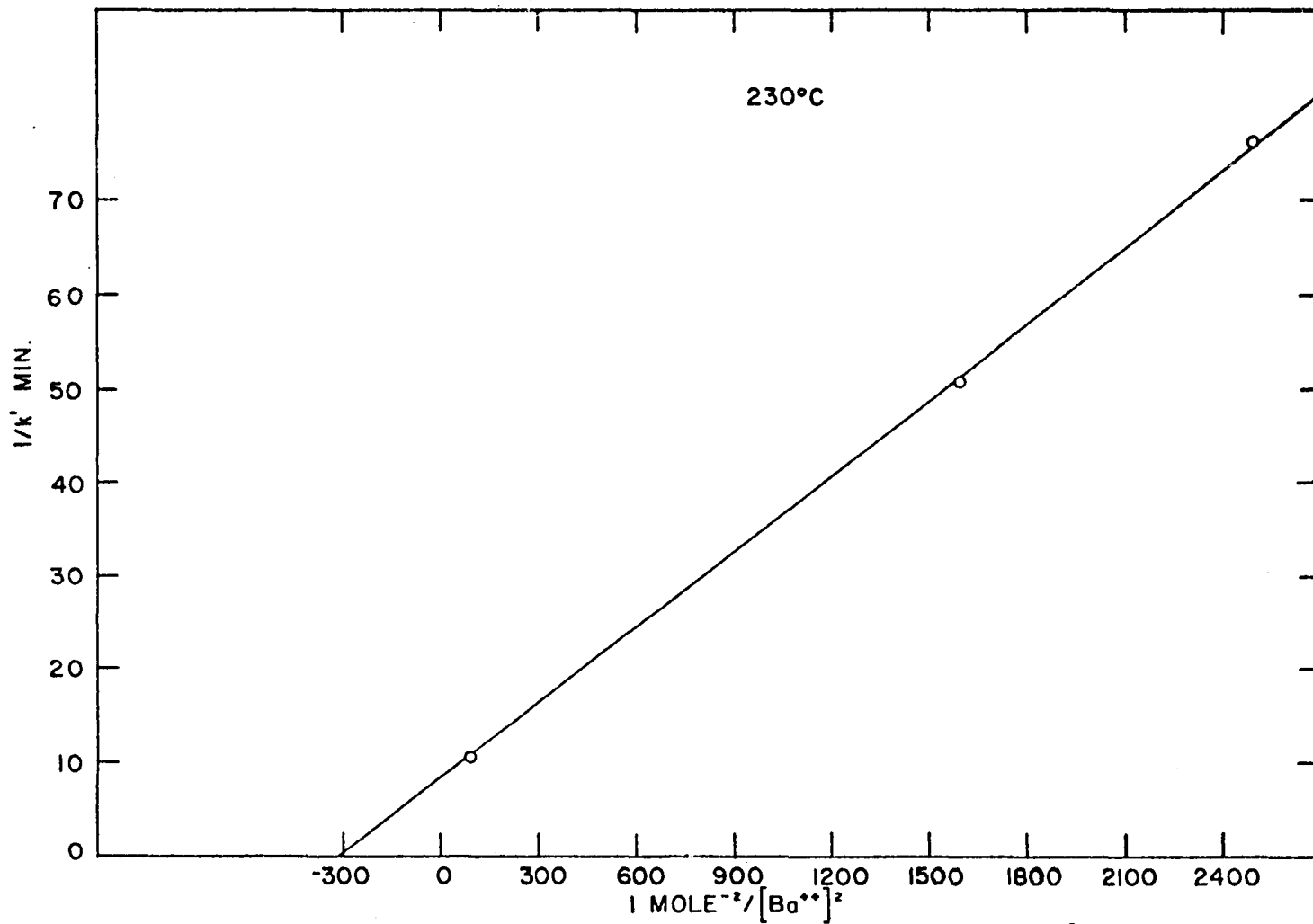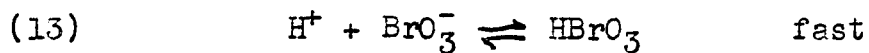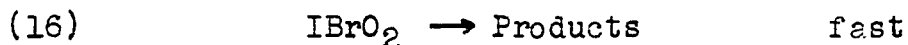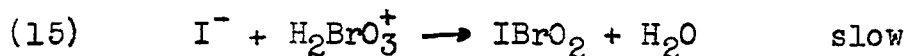
Figure 5. Plot of reciprocal rate data versus $1/[Ba^{++}]^2$ at $230^\circ C$

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Table 2. Variation of the pseudo rate constant with barium ion at 230°C, 250°C, 260°C

Ba^{++} m	$Cr_2O_7^= = 0.10$ m	$BrO_3^- = 0.01$ m	
	230°C 1/k' minutes	250°C 1/k'	260°C 1/k'
0.10	10.52	--	2.2 ± 0.1
0.07	--	5.13 ± 0.01	--
0.05	--	6.65 ± 0.30	--
0.03	--	12.7 ± 0.30	8.6 ± 0.5
0.025	50.85	17 ± 1	9.12
0.02	76	23 ± 3	14 ± 2

in a chapter of his book on unusual valence states. BrO_2^+ has been proposed as an intermediate in the mechanisms of several reactions. It is most often found in the reactions of inorganic oxyanions catalyzed by hydrogen ions and is called the electron acceptor. The order of these reactions varied from three to five. "The trend in the interpretation of rate laws greater than two has been to formulate the mechanisms of these reactions as a series of uni- bi- and ter-molecular steps." (16). Thus, the mechanism proposed for the oxidation of iodide by bromate (17) is,

$$(13) \quad H^+ + BrO_3^- \rightleftharpoons HBrO_3 \quad \text{fast}$$

$$(14) \quad HBrO_3 + H^+ \rightleftharpoons H_2BrO_3^+ \quad \text{fast}$$

(15) $I^- + H_2BrO_3^+ \longrightarrow IBrO_2 + H_2O$ slow

(16) $IBrO_2 \longrightarrow$ Products   fast

and involves the "super-acid" ion $H_2BrO_3^+$ or the anhydrous form BrO_2^+. This species is stable in an acid solution of bromate, and iodide is needed to reduce bromyl to bromine, a product of this reaction. It is interesting to find that in fused nitrates an oxide acceptor in the presence of bromate will produce the anhydrous form of this "super-acid" ion which decomposes unimolecularly to bromine at this high temperature.

Table 3. Rate constants and equilibrium constants for dichromate-bromate reaction - nitrogen flow rate 0.21 liters per minute

Temp. ^oC	$K \ 10^{+8} mole^{-1}$	k minutes
230°	1.05	0.13
250°	3.5	0.33
260°	4.8	0.58
	$E_a = 26$ kcal $\Delta H = 28$ kcal	

2. Temperature dependence

The reaction was studied at two other temperatures to determine the temperature dependence of both constants (Figures 4 and 5). Not much separation of the intercepts was obtained at these temperatures. The limits of the temperature

range are restricted because the reaction is too fast to follow above $260^{\circ}C$ and the eutectic mixture of sodium and potassium nitrate freezes below $230^{\circ}C$. From these data the activation energy and heat of reaction can be calculated. The activation energy for the decomposition of bromyl ion was obtained from the slope of the Arrhenius plot shown in Figure 6.

Thermodynamic quantities such as entropy of activation, free energy of activation, and etc. can be calculated from Boltzman's constant, Planck's constant, the rate constant and the corresponding temperature. The relationship,

$$(17) \qquad k = \frac{k_B T}{n} K$$

used for these calculations is defined by Frost and Pearson (18). However, the more recent custom is to list the activation energy and the pre-exponential term, A, defined by the Arrhenius equation,

$$(18) \qquad k = Ae^{-E_a/RT}$$

The only direct information one can obtain from the activation energy is the temperature dependence of the rate constant. The pre-exponential term, A, gives a qualitative picture of the magnitude of the entropy of activation. A large value of A indicates a large positive entropy and small value indicates a negative entropy. Several theories of reaction kinetics have been proposed and in most cases only one or two reactions fit the theory quantitatively. However the
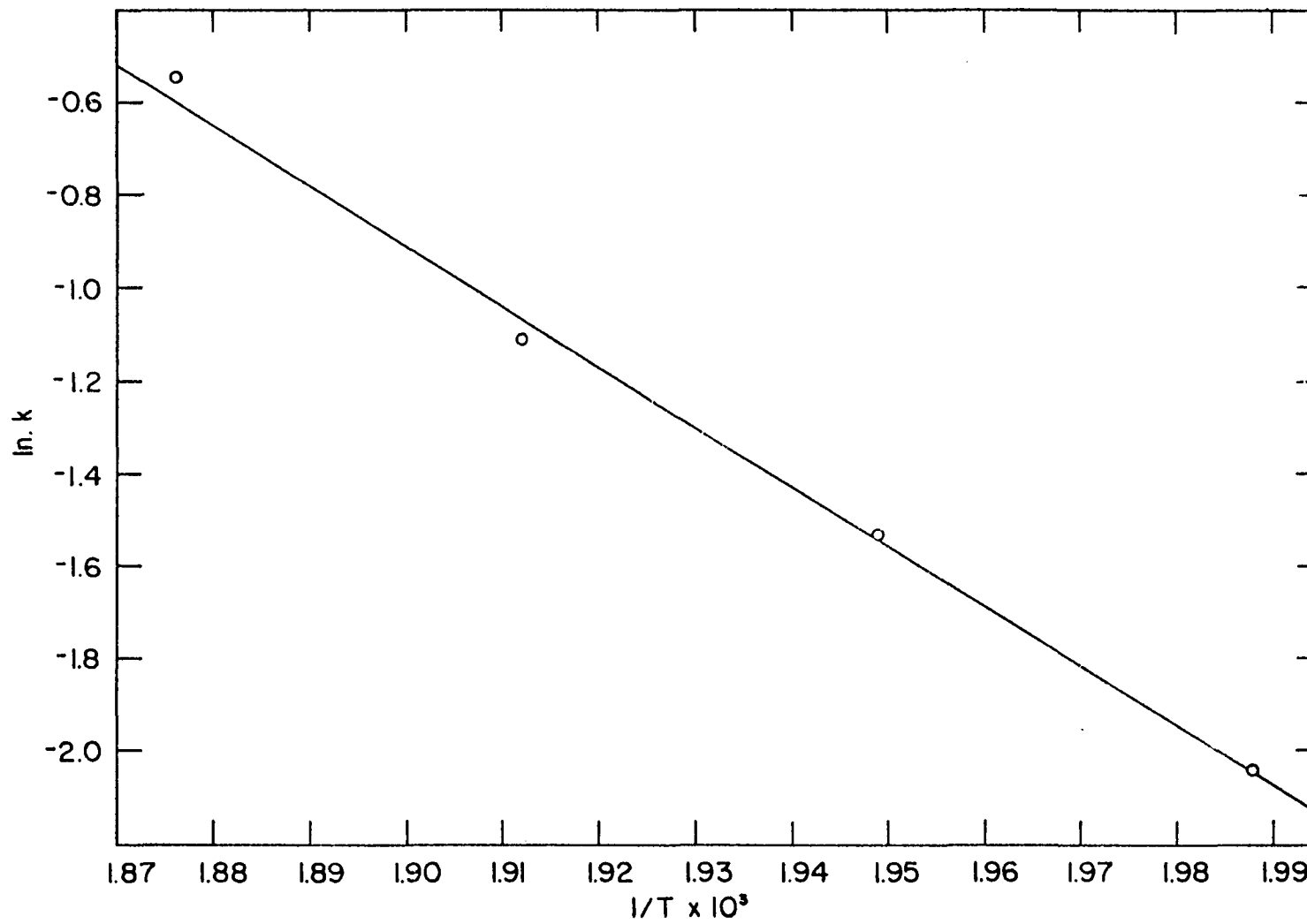
Figure 6.   Temperature dependence of the rate constant in eutectic mixture of $NaNO_3$-KNO_3

theoretical values and experimental values of A have been
compared for many reactions and arguments have been proposed
to explain the deviations. The theoretical value of A pre-
dicted by collision theory for reactions carried out in
aqueous solutions is 10^{11}. This value is considered to
be the norm (18). Table 4 lists calculated experimental
values of A for the reactions studied in fused salts. The
pre-exponential term calculated from Duke and Yamamoto's
(9) data is extremely low. This is due to the small

Table 4. Pre-exponential terms calculated from activation
energies and rate constants reported by the
authors cited

Reference	E_a cal.	k	T ^{o}K	A
Schlegel[a]	26,000	0.13 min^{-1}	503	$10^{10.5}$
Schlegel[a]	26,000	2.95 min^{-1}mole^{-1}	503	10^{11}
Shute (14)	43,000	0.022 min^{-1}mole^{-1}	643	$10^{12.4}$
Yamamoto (9)	12,000	0.038 min^{-1}mole^{-1}	508	$10^{3.8}$

[a]For the dichromate-bromate and dichromate-chlorate
reactions respectively.

activation energy. A small activation energy is related to
a small temperature dependence of the rate of reaction. If
the rate measured is the rate of diffusion of gaseous N_2O_5
to the surface of the melt, this rate of diffusion would have

a very small temperature dependence and would give rise to a small activation energy. The other values lie close to the norm stated above. The activation energy for the dichromate-bromate reaction was calculated to be 26 kcal. The heat of reaction for the decomposition of dichromate was determined from,

$$(19) \qquad \frac{d(\ln K)}{d(1/T)} = - \frac{\Delta H}{R} .$$

The value for ΔH was found to be 28 kcal.

3. Solvent effects

The mole ratio of the cations was varied to see if there were any solvent effects on the reaction rate. The solvent effect has been measured in several reactions carried out in alkali nitrates. In most cases an effect has been observed. Shute (14) found that a change in the cation ratio of sodium-potassium nitrate solvent changed the rate of oxidation of bromide by bromate. Other observations included are:

(1) The reaction is autocatalytic and first order with respect to both bromate and bromide.

(2) The reaction products are bromide and oxygen in sodium-potassium nitrate mixtures; but are bromine gas and lithium oxide in lithium nitrate.

The rate of this reaction increased as the concentration of sodium ion was increased. Shute (14) attributed this observation to a larger polarizing power of the sodium ion on

bromate. The polarizing effect facilitates the approach of the two negative ions, bromate and bromide, to form the activated complex. Therefore the postulated mechanism is,
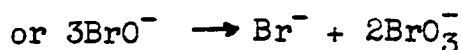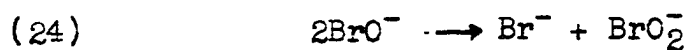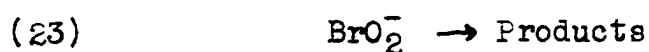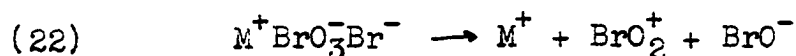
$$(20) \quad M^+ + BrO_3^- \rightarrow M^+BrO_3^-$$

$$(21) \quad M^+BrO_3^- + Br^- \rightarrow M^+BrO_3^-Br^-$$

$$(22) \quad M^+BrO_3^-Br^- \rightarrow M^+ + BrO_2^+ + BrO^-$$

$$(23) \quad BrO_2^- \rightarrow Products$$

$$(24) \quad 2BrO^- \rightarrow Br^- + BrO_2^-$$

$$\text{or } 3BrO^- \rightarrow Br^- + 2BrO_3^-$$
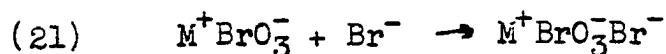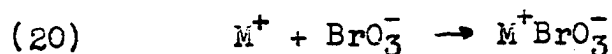
Table 5. Effects due to cation ration of sodium and potassium nitrate at 250°C

K/Na	I	$K \times 10^{-8} mole^{-1}$	1/k minutes
60/40	330	3.2	3.4
50/50	352	3.5	3.0
38/62	520	4.8	2.7

Both the equilibrium constant and rate constant for the dichromate-bromate reaction is increased as the solvent becomes richer in sodium ion. The increase in the equilibrium constant could be explained by postulating that the oxide ion transfer from bromate to dichromate proceeds via the solvent cations, or that the more polarizing solvent cation polarizes the bromate ion and thus reduces the apparent charge seen by
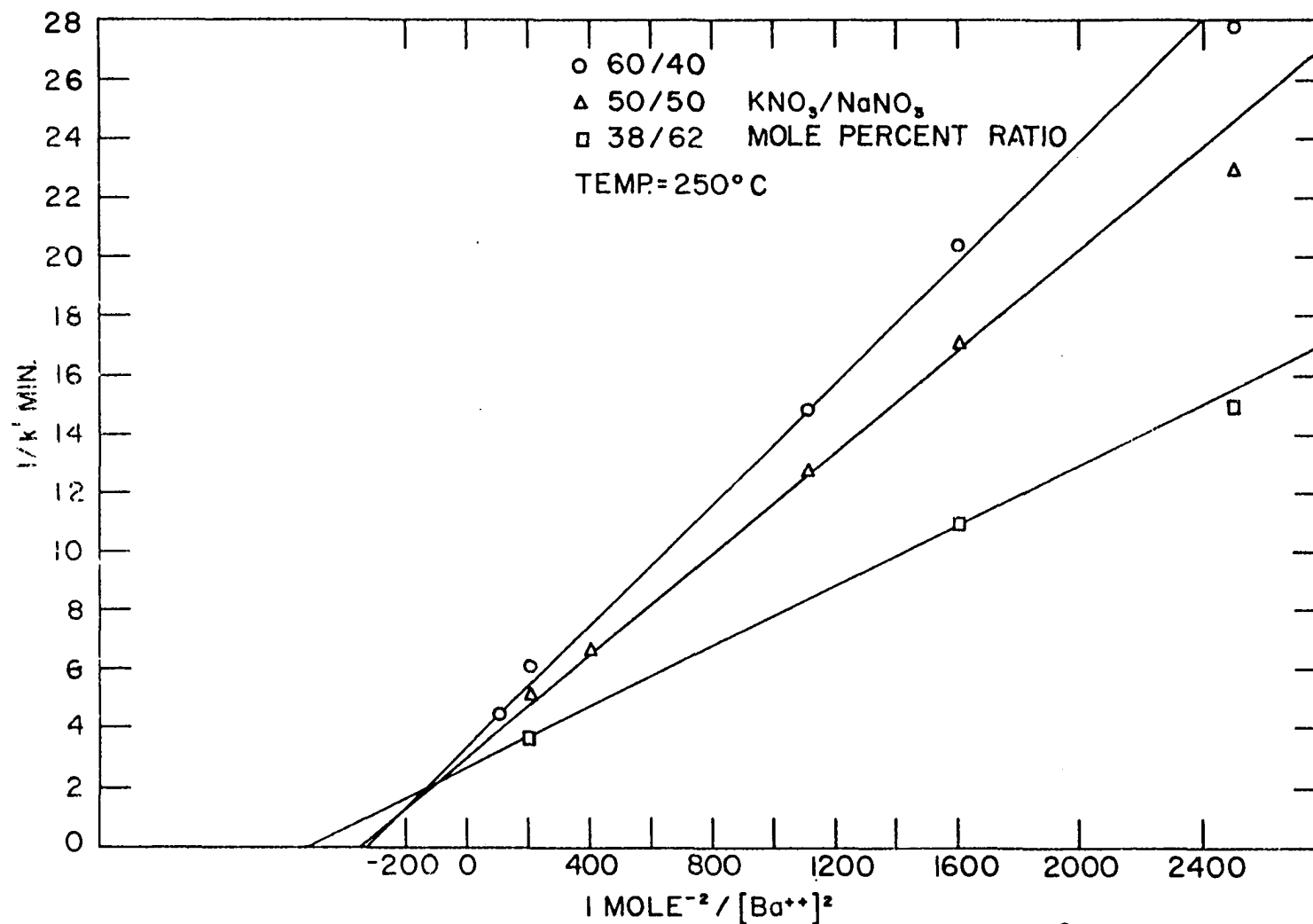
Figure 7. Plot of reciprocal rate data versus $1/[Ba^{++}]^2$ at $250°C$ in different mixtures of $NaNO_3$-KNO_3 solvent

the dichromate ion shifting the equilibrium to the right.
Polarizing the bromyl ion to favor its decomposition could
explain the increase in the rate constant. It is interest-
ing to note that Lawrence (13) observed no change in the
rate upon using different mixtures of the alkali nitrates.
It is difficult to offer any reasonable explanations for these
effects. In all cases, if an effect were observed, this
effect was to enhance the reactivity of the ions participating
in the reaction as the concentration of the smaller alkali
cations was increased.

B. The Chlorate Reaction

1. The reaction and mechanism

Results of the reaction between bromate and dichromate
has shown the presence of bromyl ion as an intermediate which
then decomposes to bromine and oxygen. It was thought that
perhaps chlorate and also iodate might behave in a similar
manner. If they are stronger bases than nitrate, one could
follow their behavior with dichromate in fused nitrates.

Preliminary studies with chlorate showed that no
observable reaction occurs unless the concentration of
chlorate is quite large, 2.0m to 5.0m. Therefore runs were
conducted using fifty grams of potassium nitrate and fifty
grams of sodium chlorate. This mixture is close to 50-50
mole percent sodium-potassium, and the concentration of

Figure 8. Plot of reciprocal rate constant versus $1/[Ba^{++}]^2$ at
several chlorate constants; initial chloride is zero;
the rate constants were obtained from plots on semi-log
paper and therefore should be multiplied by 2.3

(

32b
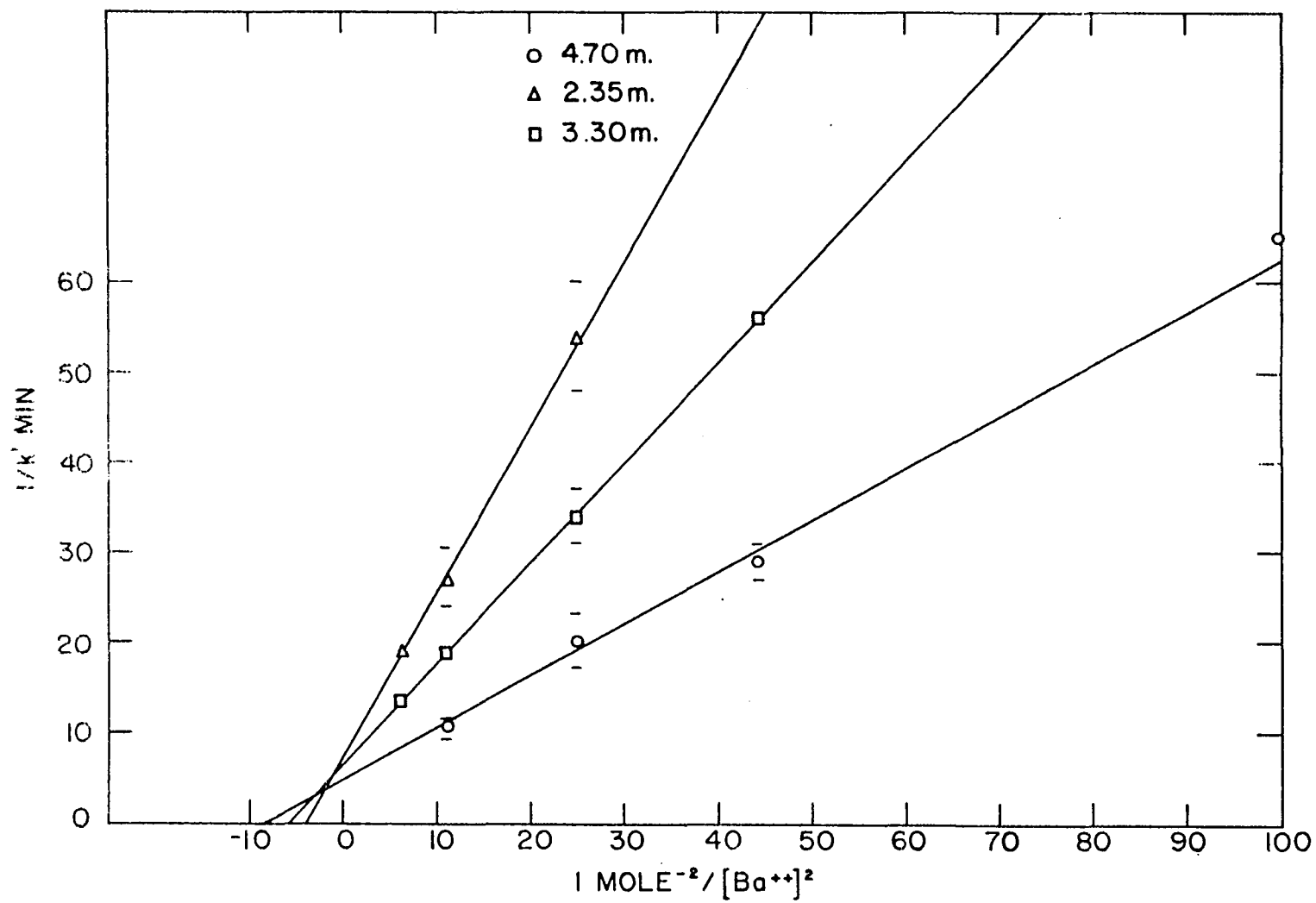
chlorate is almost 5.0m. When the concentration of chlorate
was lowered, an appropriate amount of sodium nitrate was
added to keep the mole ratio of sodium and potassium 50-50.
The addition of dichromate causes an immediate precipitate of
barium chromate followed by the evolution of chlorine or
oxides of chlorine. The halogen gas was reduced with 0.33M
sodium sulfite. Chloride was determined using the technique
described in Section III B. It was found that no chloride
was lost by the evaporation of HCl while the samples steamed
on a hot plate. The samples were neutralized and titrated
with silver nitrate. The end point is not very clear, however
a blank was run and all samples were titrated to the same
end point. With practice, reproducible results were obtained
using this method. Dichromate is the only reactant whose
concentration can be limited and followed with time.
Dichromate was added and the reaction was allowed to go to
completion. The reaction is complete when the precipitate
is a very lemon yellow and there is no odor of halogen
gases.

In all preliminary runs, two gram equivalent weights of
chlorine were recovered for every gram equivalent weight of
dichromate. Therefore the disappearance of dichromate can
be calculated by following the appearance of chlorine. At
this time it was assumed that the rate determining step was,

(25) $ClO_3^- + ClO_2^+ \longrightarrow$ Products
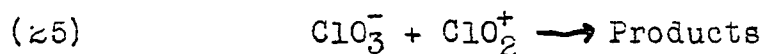
because of the observed stoichiometry. The rate would be,

$$(26) \qquad R = \frac{kK\,[ClO_3^-][Ba^{++}]^2}{K\,[ClO_3^-][Ba^{++}]^2 + K_{sp}^2}\, T_A$$

where (28), $T_A = Cr_2O_7^= + ClO_2^+$. The reaction was first

order in dichromate after a rather long induction period.

This induction period was ignored because reproducible

results were obtained within a reasonable experimental

error. Also, $1/k'$ plotted against $1/[Ba^{++}]^2$ gave a good

straight line. The data are recorded in Table 6 and a graph-

ical representation is presented in Figure 8. Different con-

centrations of chlorate were used and the results gave an

order less than one in chlorate instead of an expected second

Table 6. Variation of the pseudo first order rate constant
with barium ion at different chlorate concentra-
tions (temperature is 250°C)

ClO_3^-	Ba^{++}	$1/k'$ min. mole	ClO_3^-	Ba^{++}	$1/k'$ a min. mole
4.70m	0.30m	10.5 ± 1.3	2.35m	0.40m	19
	0.20	20 ± 3		0.30m	27 ± 4
	0.15	29 ± 2		0.20	54 ± 6
	0.10	65		0.15	68
3.30m	0.40	13.4	1.41m	0.40	43
	0.30	19		0.30	63 ± 3
	0.20	34 ± 3		0.20	96 ± 8
	0.15	56 ± 1			

order. The temperature was lowered by twenty degrees and a much longer induction period was observed, too long to be ignored.

2. The chloride effect

Frost and Pearson (18) state that a long induction period indicates the presence of a more complex mechanism. Perhaps chlorate is decomposing. The reaction was allowed to go to completion and was analyzed for chloride. A considerable amount of chloride was found in the solution. Therefore the chloride content was determined at different concentrations of reactants, and the following observations were made:

(1) Chloride is produced in the melt only when all of the reactants are present; that is, when the reaction evolving chlorine and oxygen takes place.

(2) The amount of chloride found in the melt after completion of the reaction is mainly dependent on chlorate, dichromate, and the initial amount of chloride added, and is not dependent on barium. Chloride added to the melt before starting the reaction will be called initial chloride.

(3) One millimole of dichromate produces approximately 6.5 millimoles of chloride, which we shall call excess chloride. When chloride is added initially,

less excess chloride is produced. See Table 7.

(4) A small amount of initial chloride decreases the induction period to a negligible amount. See Figure 9.

(5) A low order in chloride at low concentrations of initial chloride is observed. See Figure 9.

(6) A positive test for perchlorate is observed using methylene blue as an indicator (12).

Observations (1) and (5) indicate the disproportionation of chlorate to perchlorate and chloride. The disproportionation is possibly induced by the chloryl ion. This sort of decomposition has been observed by Harvey (19), Bosch and Aten (20), and Glasner and Weidenfeld (21), when they studied the thermal decomposition of perchlorate and chlorate. Observations (1) and (3) indicate that chloride is needed for the chlorate-dichromate reaction to proceed. The rate determining step becomes,

$$(27) \qquad ClO_2^+ + Cl^- \longrightarrow Products$$
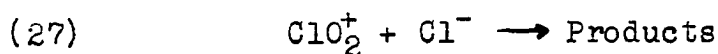
at high concentrations of chloride. A plot of $\log Cl^-$ versus $\log k'$ gives a slope of 0.77 at high concentrations of chloride. If the chloride concentration found in the melt at the end of the reaction is used in this plot, the slope is true for all chloride concentrations. The point at which the curve deviates from a straight line is where the initial chloride equals 0.08m. This concentration is not far from

Table 7. Chloride concentration at different concentrations of reactants and the observed rate constants

| ClO_3^- m	Ba^{++} m	$Cr_2O_7^=$ m	Cl^- initial	Cl^- final	Cl^- excess	$1/k'$ min.mole	k' min^{-1}mole^{-1}
4.70	0.20	0.01	0.04	0.082	0.042	17.4	0.0575
4.70	0.20	0.01	0.08	0.108	0.028	14.0	0.0714
4.70	0.20	0.01	0.02	0.071	0.051	18.5	0.0540
4.70	0.20	0.02	0.00	0.087	0.087	20.0	0.0500
4.70	0.20	0.015	0.00	0.078	0.078	18.0	0.0555
4.70	0.20	0.01	0.00	0.065	0.065	20.0	0.0500
4.70	0.20	0.01	0.30	0.298	0.002	6.0	0.1667
4.70	0.20	0.01	0.20	0.202	0.000	8.3	0.1205
4.70	0.20	0.01	0.15	0.16	0.01	8.5	0.1177
4.70	0.20	0.01	0.082	0.111	0.029	12.5	0.0800
4.70	0.20	0.01	0.08	0.108	0.028	14.0	0.0714
4.70	0.20	0.01	0.05	0.086	0.036	15.0	0.0667
4.70	0.20	0.01	0.10	--	--	13.0	0.0770
4.70	0.10	0.01	0.30	--	--	18.2	0.0550
4.70	0.15	0.01	0.30	--	--	8.3	0.1205
4.70	0.12	0.01	0.30	--	--	12.0	0.0833
4.70	0.30	0.01	0.30	--	--	3.7	0.2700
1.414	0.20	0.01	0.00	0.039	0.039	--	--
4.70	0.30	0.01	0.00	0.061	0.061	--	--
4.70	0.15	0.01	0.00	0.068	0.068	--	--
4.70	0.20	0.01	0.40	0.40	0.000	4.6	0.2170

37
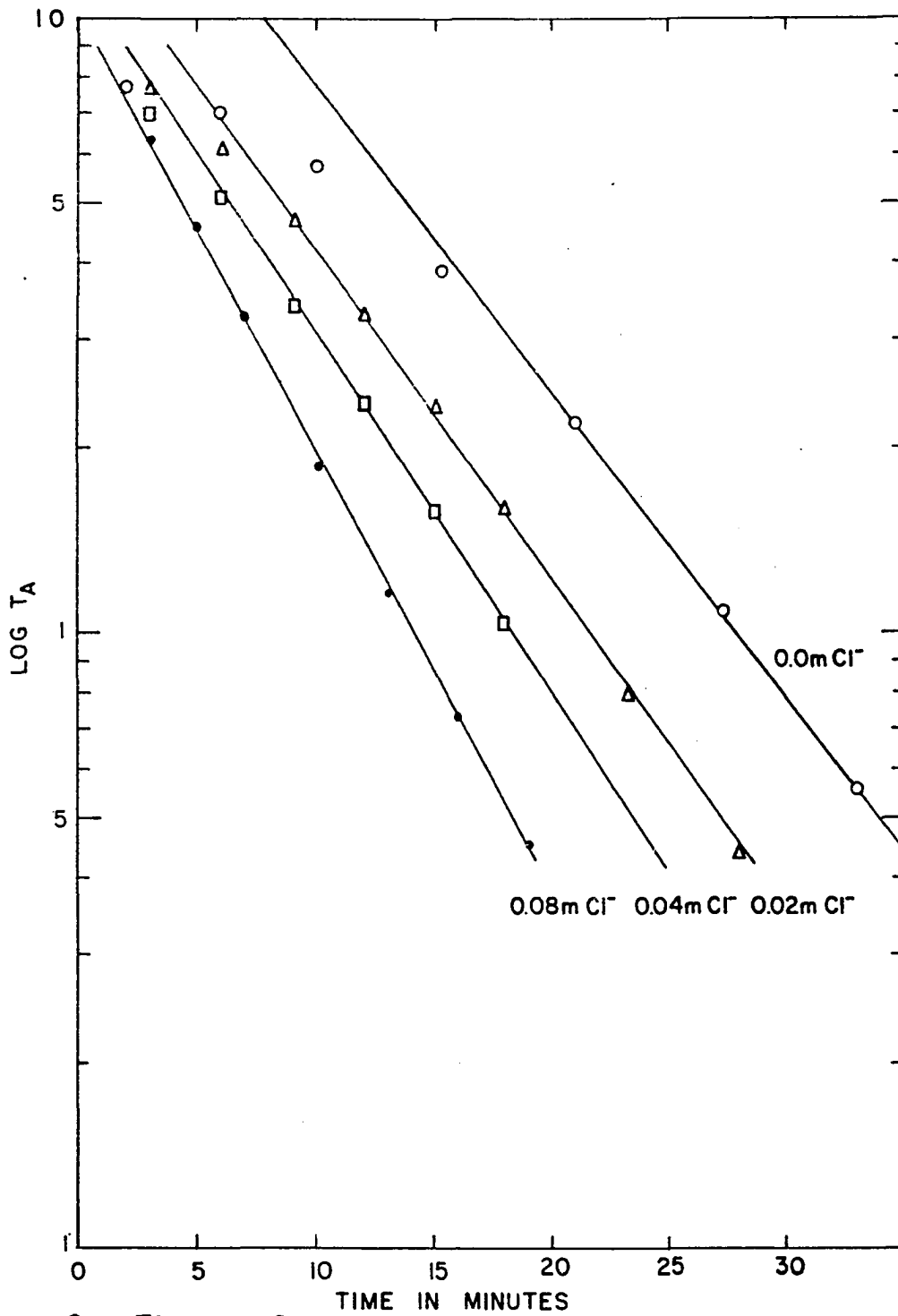
Figure 9. First order plots of total acid with time at different initial chloride concentrations
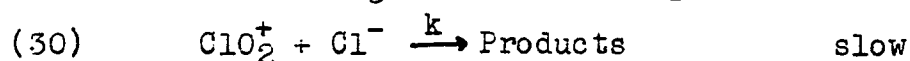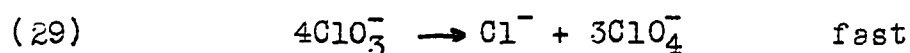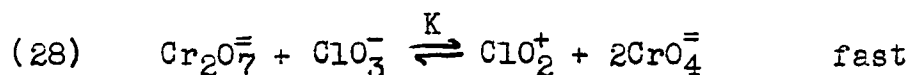
Figure 10. Plot to determine order in chloride; both
          initial chloride and chloride analyzed in the
          solution are plotted; rate constants obtained
          from semi-log plots and should be multiplied
          by 2.3
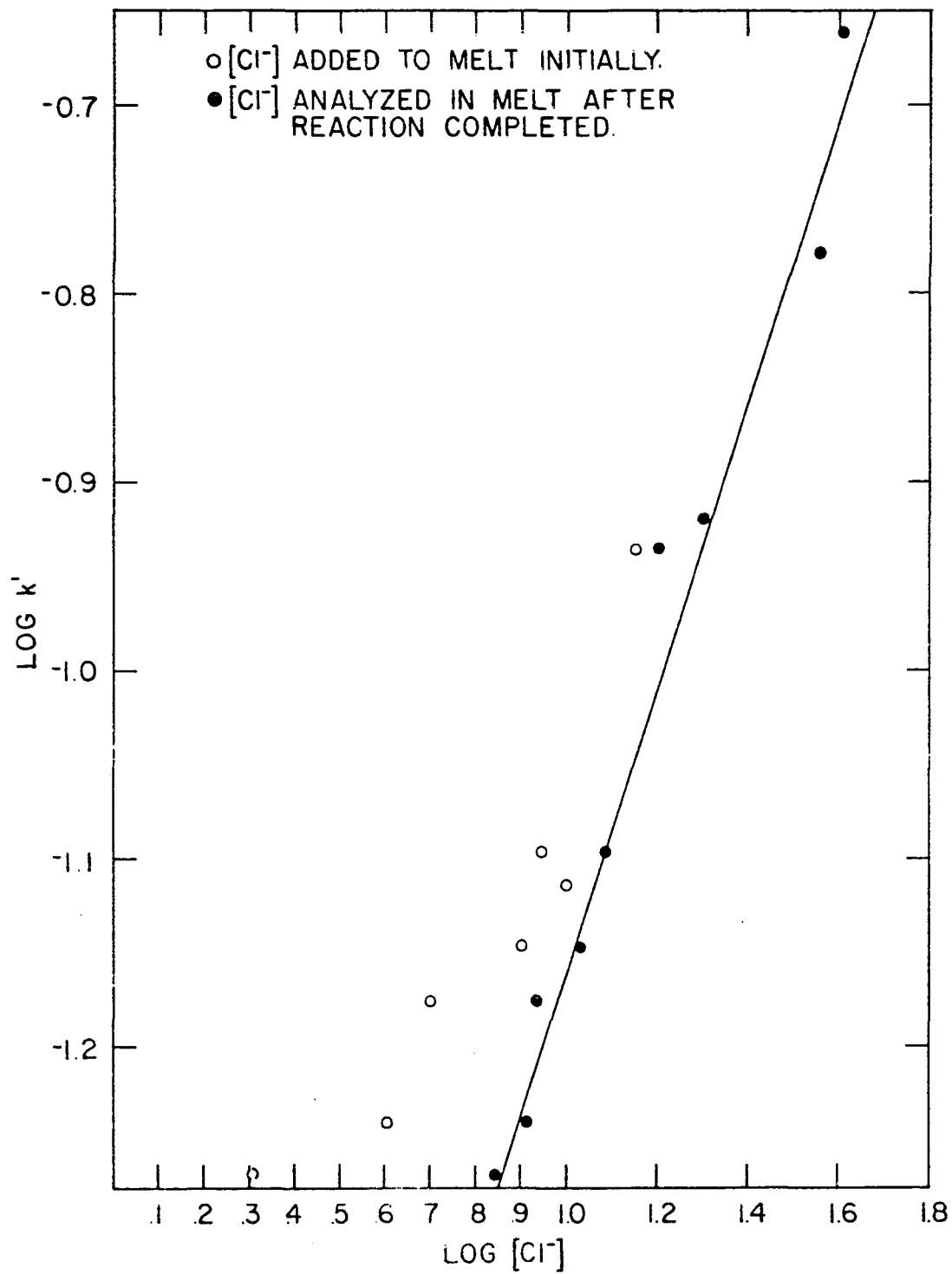
the concentration of chloride found in the melt at the end of a reaction which contained no initial chloride. This observation would partially justify the extrapolation procedure used to evaluate the pseudo rate constant when a long induction period was present.

3. A new mechanism

Chloride remains constant throughout a run when the initial chloride concentration is 0.30m. Therefore pseudo rate constants were obtained at three barium concentrations with 0.30m initial chloride. The results are plotted in Figure 11. The abscissa intercept is the same as that obtained earlier when no initial chloride was added. It appears that the equilibrium constant is unaffected by the amount of chloride present in the melt. A mechanism would then be,

$$(28) \quad Cr_2O_7^= + ClO_3^- \overset{K}{\rightleftharpoons} ClO_2^+ + 2CrO_4^= \qquad \text{fast}$$

$$(29) \quad 4ClO_3^- \longrightarrow Cl^- + 3ClO_4^- \qquad \text{fast}$$

$$(30) \quad ClO_2^+ + Cl^- \overset{k}{\longrightarrow} \text{Products} \qquad \text{slow}$$

Equation 29 is just a way of representing the production of chloride from chlorate. There is a suspicion that chloryl ion promotes the decomposition of chlorate to chloride. However the decomposition of chlorate to chloride takes place quite fast compared to reaction 30 and consequently, reaction 29 does not appear in the rate expression at high concentrations of chloride. Thus,
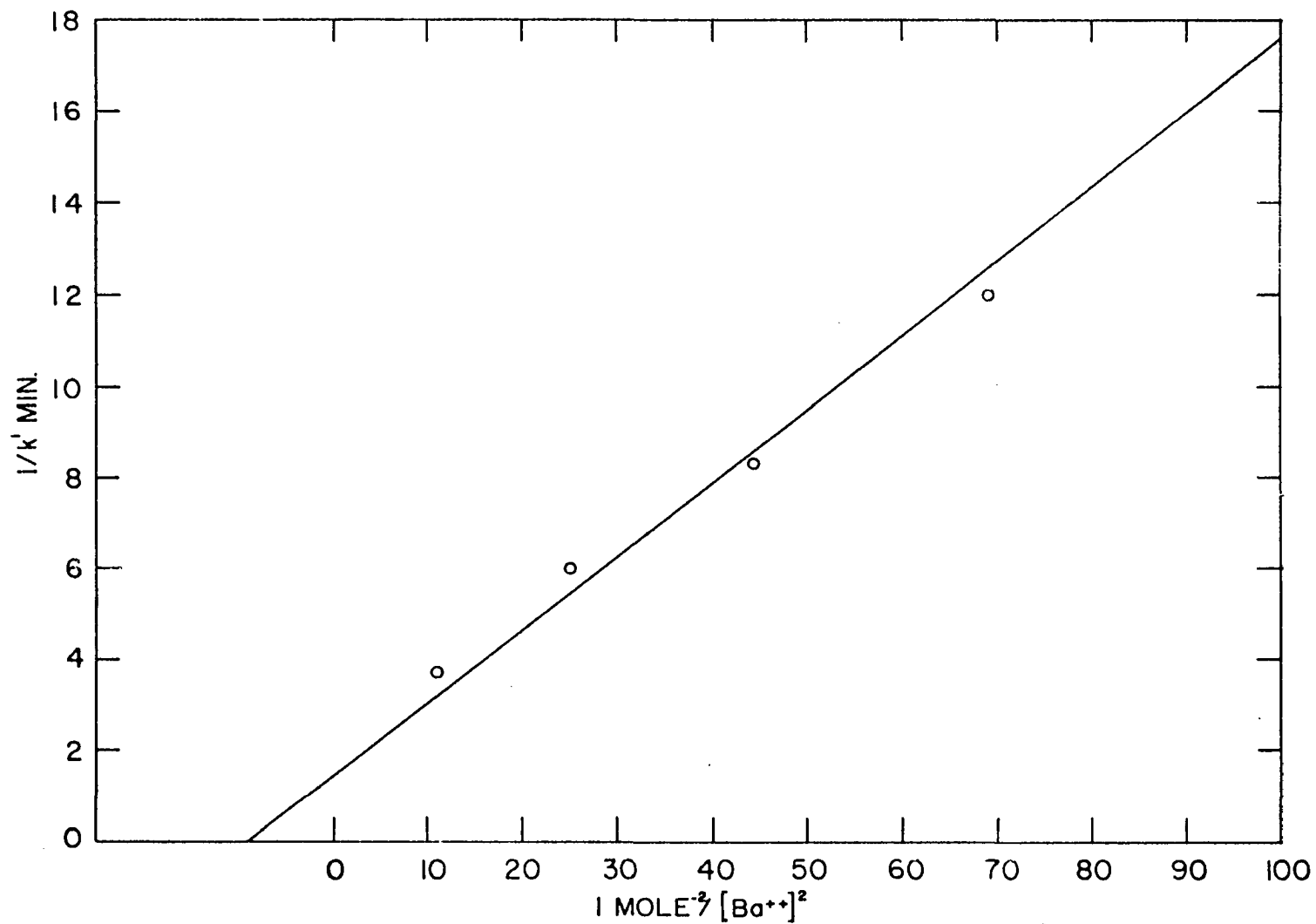
Figure 11. Plot of reciprocal rate constant versus $1/[Ba^{++}]^2$ for the dichromate-chlorate reaction when 0.30m initial chloride is used

(31) $$\text{Rate} = k[ClO_2^+][Cl^-] = -\frac{dT_A}{dt}$$

where,

(32) $$T_A = Cr_2O_7^= + ClO_2^+ .$$

From the equilibrium expression and the solubility product of barium chromate,

(33) $$[Cr_2O_7^=] = \frac{K_{sp}^2}{K[ClO_3^-][Ba^{++}]^2 + K_{sp}^2} T_A .$$

Differentiate with time,

$$\frac{d[Cr_2O_7^=]}{dt} = \frac{K_{sp}^2}{K[ClO_3^-][Ba^{++}]^2 + K_{sp}^2} \cdot \frac{dT}{dt} ,$$

and substitute (31) into this expression to obtain,

$$\frac{d[Cr_2O_7^=]}{dt} = - k[ClO_2^+][Cl^-] \frac{K_{sp}^2}{K[ClO_3^-][Ba^{++}]^2 + K_{sp}^2} .$$

Substitute for $[ClO_2^+]$,

$$\frac{d[Cr_2O_7^=]}{dt} = \frac{kK[ClO_3^-][Cl^-][Ba^{++}]^2}{K[ClO_3^-][Ba^{++}]^2 + K_{sp}^2} [Cr_2O_7^=] = k'[Cr_2O_7^=] .$$

The reciprocal of k' is,

(34) $$\frac{1}{k'} = \frac{1}{k[Cl^-]} + \frac{K_{sp}^2}{kK[ClO_3^-][Cl^-]} \cdot \frac{1}{[Ba^{++}]^2} .$$

If one sets 1/k' equal to zero, the equilibrium constant is related to the abscissa intercept, I, by,

(35) $$K = \frac{K_{sp}^2 I}{[ClO_3^-]} .$$

It was found that the production of chloride, that is, the chloride found in the melt at the end of a run, is nearly independent of the barium concentration. The relationship (35) shows that the intercept is directly proportional to the concentration of chlorate,

$$(36) \qquad \frac{K}{[ClO_3^-]} = \frac{K}{K_{sp}^2} = constant$$

This was observed in Figure 8. The value obtained for the equilibrium constant was $8 \times 10^{-11} mole^{-1}$. The ordinate intercept is related to the rate constant and the chloride concentration. Analysis of the melt shows that the chloride concentration produced is not in direct proportion to the amount of chlorate present. When the chlorate concentration was decreased by more than one-third, the chloride found in the melt was only decreased by one-sixth. This information in addition to equation 34 would explain the small change in the ordinate intercept in Figure 8. The low order in chloride at small concentrations of initial chloride suggests that there is some decomposition taking place which is independent of chloride, or, $k' = k_1' + k_2'[Cl^-]$. To check this, k' was plotted against $[Cl^-]$, Figure 12. A straight line can be drawn through these points and $k_1' = .046$ and $k_2' = 1.15$. The predominant rate step is the one involving chloride. However at low initial chloride the other rate step would be noticeable.
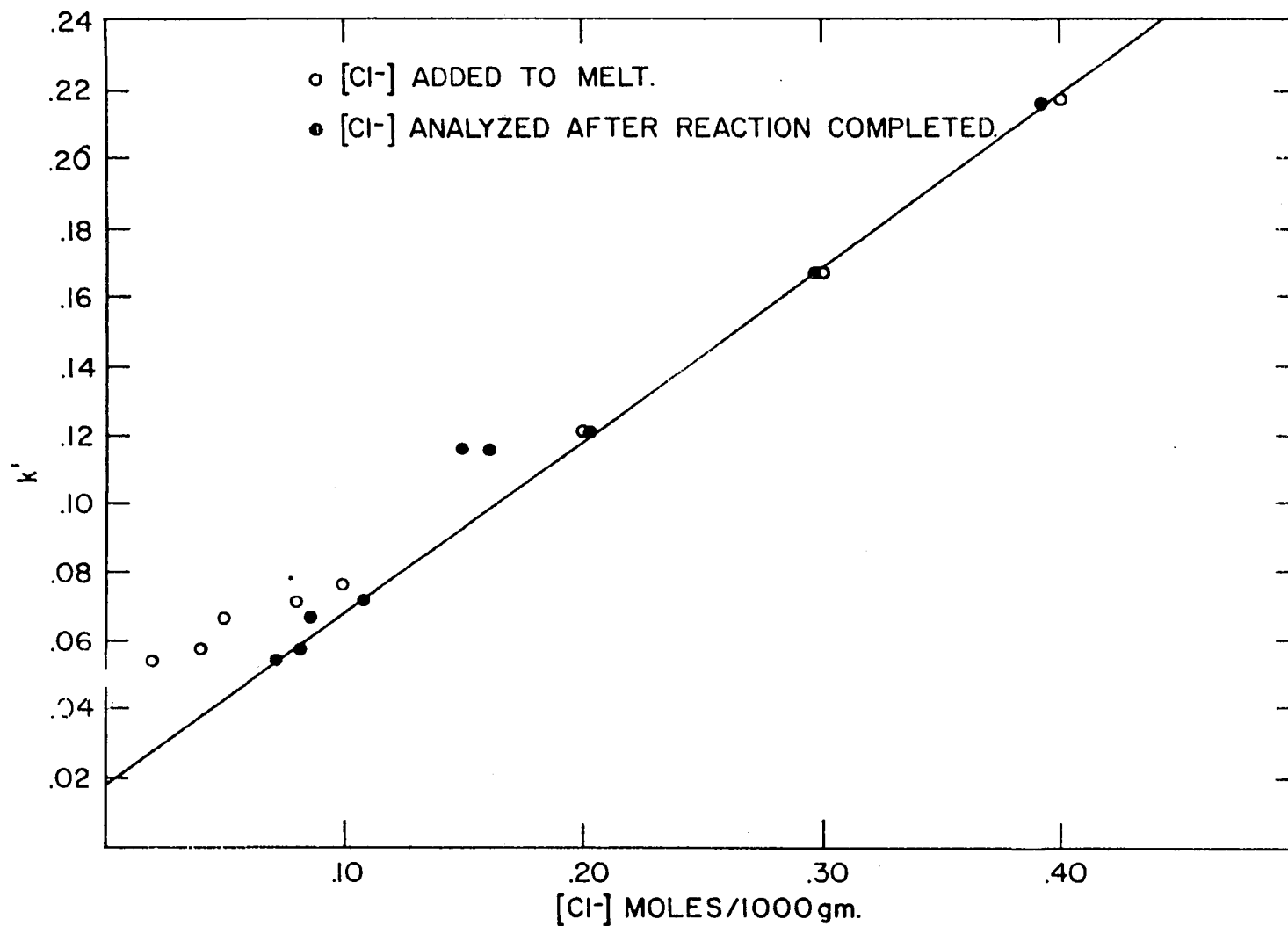
Figure 12. A plot of k' versus chloride concentration at 250°C; the chlorate concentration is 4.7m

The mechanism of the dichromate-chlorate reaction has been established well enough to determine the constant of the first equilibrium involving the formation of chloryl ion. Subsequent steps which finally lead to barium chromate, chloride, chlorine, and oxygen are not so well understood. However the data indicate the predominant slow step to be,

$$(37) \qquad ClO_2^+ + Cl^- \longrightarrow Products$$
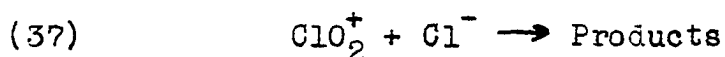
In aqueous solution studies of the chlorate-chloride reaction, the nucleus of all the rate laws is the complex Cl_2O_2, whose concentration is given by the expression,

$$(38) \qquad [Cl_2O_2] = K[ClO_3^-][Cl^-][H^+]^2$$

A discrepancy in the order of reactants is found when the studies of Sand (22), Hirade (23), and Luther and MacDougall (24, 25) are compared. Sand (22) and Hirade (23) observed the rate law,

$$(39) \qquad R = k[ClO_3^-][Cl^-][H^+]^2,$$

while Luther and MacDougall (24) found,

$$(40) \qquad R = k[ClO_3^-]^2[Cl^-]^2[H^+]^4$$

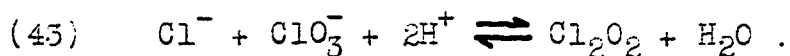In the presence of iodide ion and bromide ion respectively, Brag (26) and Hirade (23) observed the equation,

$$(41) \qquad R = k[ClO_3^-][Cl^-][H^+]^2$$

Edwards (16) points out that the reaction of chlorate with water takes place through the equilibrium,

$$(42) \qquad ClO_3^- + 2H^+ \rightleftharpoons H_2ClO_3^+ \rightleftharpoons ClO_2^+ + H_2O$$

With chloride present the equilibrium expression becomes,

$$(43) \quad Cl^- + ClO_3^- + 2H^+ \rightleftharpoons Cl_2O_2 + H_2O \ .$$

It appears that the complex Cl_2O_2 decomposes by collision with a nucleophilic particle. This complex could be in equilibrium with ClO_2^+ and Cl^- in fused nitrates, however the rate should decrease as the chloride concentration is increased. The opposite effect in fact was observed.

4. Temperature dependence

It was mentioned earlier that the dichromate-chlorate reaction was followed at a lower temperature of $230^o C$. However these data were obtained when no initial chloride was added. Three points, which gave a straight line, were obtained at 4.70m chlorate, and two points were obtained at a lower chlorate concentration. If one assumes that a temperature change does not affect the production of chloride, these data can be used to evaluate an approximate activation energy for the dichromate-chlorate reaction. The concentration of chloride was assumed to be 0.065m at 4.70m chlorate and 0.400m for 1.414m chlorate and the rate constants were determined from the ordinate intercept. A value of 26 kcal. was found using the data from 4.70m chlorate and 31 kcal. from 1.414m chlorate. More points were obtained for the data at 4.70m chlorate, therefore the activation energy 26 kcal. is used to calculate the pre-exponential term recorded in Table 4. It was shown that the equilibrium constant of the abscissa

intercept is independent of chloride. Therefore this observation was assumed to be true at $230^{\circ}C$ and the heat of reaction was determined. This value, 27 kcal., is very close to the heat of reaction for the dichromate-bromate reaction.

C. The Iodate Reaction

1. Preliminary studies

The bromate reaction has been characterized quite thoroughly. No halide ion is needed to catalyze this reaction so that it may be followed. However chloride is necessary for the chlorate reaction to proceed at a measurable rate. In fact, it is impossible to study the chlorate reaction in the absence of chloride because chloride is a product of this reaction. Intuitively one would expect the chlorate ion to be the weaker base. But one would also expect the iodate ion to be the strongest base and the reaction between iodate and dichromate to take place at a more rapid rate.

Preliminary runs have shown that no reaction occurs at low concentrations of iodate. This reaction cannot be studied at very high concentrations of iodate because of its limited solubility in fused nitrates. Therefore sodium bromide was added to increase the rate of reaction using low concentrations of iodate. The following concentrations were used: 0.10m $Cr_2O_7^=$, 0.01m IO_3^-, 0.10m Br^-. At these concentrations of reactants, nitrate also oxidized bromide and thus inter-

fered with the iodate reaction. Therefore the oxidation of
bromide by nitrate and dichromate was studied in the absence
of iodate.

2. The nitrate reaction

The reaction between dichromate and a base can be repre-
sented in some cases as,

$$Cr_2O_7^= + BO_3^- \rightleftharpoons BO_2^+ + 2CrO_4^=.$$
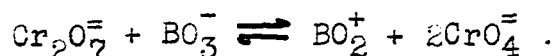
If the intermediate, BO_2^+, formed in the equilibrium, is a
strong enough acid compared to the acid reactant, $Cr_2O_7^=$, a plot
of $1/k'$ versus $1/[Ba^{++}]^2$ will give a straight line that lies
so close to the origin that it is impossible to evaluate an
intercept. Such is the case when Duke and Iverson (27)
studied the decomposition of dichromate in a fused alkali
nitrate mixture. They obtained values for the product of the
equilibrium constant and the rate constant but were unable to
separate the two quantities. However they used lead ion as
the precipitating agent which forms complexes with dichromate
and possibly bromide. This complexing phenomenon decreases
the activity of the dichromate and the bromide, and also
decreases the activity of the lead ion which drives the equi-
librium. If one uses barium in place of lead and follows the
appearance of bromine with time, it is possible to separate
the equilibrium and rate constants.

A small amount of dichromate was used and its concentra-

tion was followed by observing the appearance of bromine gas.
Duke and Iverson (27) had found this reaction to be first
order in bromide. At high concentrations of barium one gram
equivalent weight of bromine was recovered for every gram
equivalent weight of dichromate; this indicates that the rate
is first order in bromide. At low concentrations of barium
the rate was too slow to allow the reaction to go to comple-
tion. Therefore it was assumed that the initial concentration
of dichromate, 0.01m, was the amount added to the melt.
Barium nitrate was varied from 0.10m to 0.30m. The data are
listed in Table 8 and an appropriate plot is shown in Figure
13.

Table 8. Variation of the pseudo first order rate constant
with barium ion in the dichromate-nitrate reaction
at 250°C

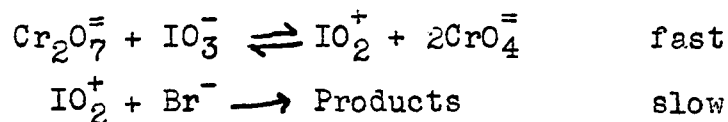| $Cr_2O_7^{--}$ = 0.01m	Br^- = 0.10m
Ba^{++}m	1/k' min.mole
0.15	340
0.17	292
0.20	213
0.25	141
0.30	114

Figure 13. Variation in pseudo first order rate constant with
barium for the dichromate-nitrate reaction

DICHROMATE-NITRATE

50b
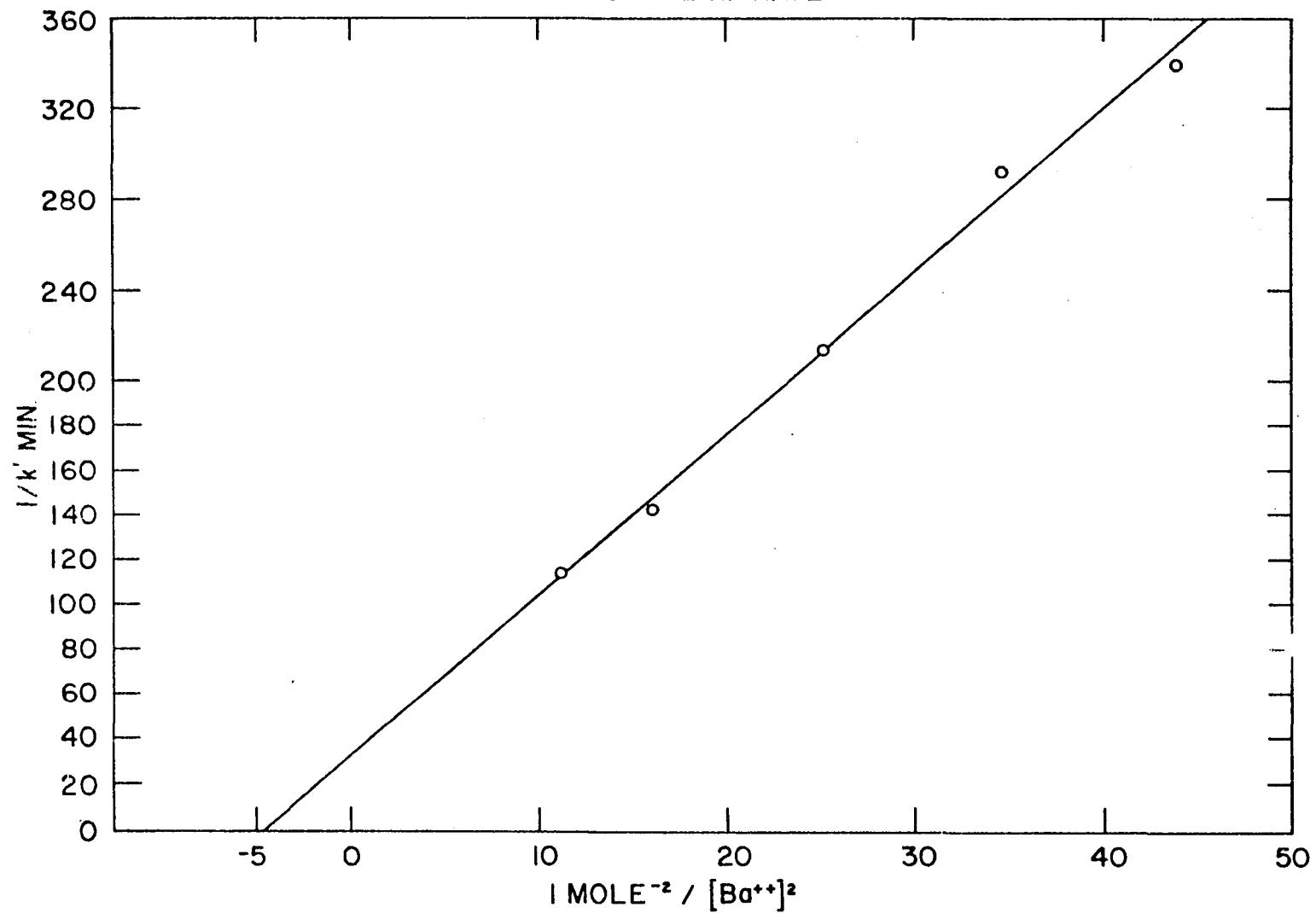
3. The mechanism

The oxidation of bromide by dichromate and nitrate proceeds at a measurable rate if a large concentration of barium is added. This reaction is easily suppressed by keeping the concentrations of barium and dichromate low. A very small amount of iodate increases this rate considerably. Therefore the following concentrations were used: $0.01m$ Cr_2O_7, $0.10m$ IO_3^-, $0.10m$ Br^-. Dichromate is the limiting concentration. Iodate reacts completely with dichromate before any observable amount of nitrate does. These conditions make it possible to follow the reaction to completion because no reaction occurs after all the dichromate has reacted. The gases formed from the reaction contain both iodine and bromine. For every gram equivalent weight of dichromate two gram equivalent weights of halogen were recovered. The reaction is first order in the disappearance of total acid. The concentrations of barium and bromide were varied and the results are listed in Table 9. The temperature was $250^\circ C$ for all runs. A plot of $\log Br^-$ versus $\log k'$ is shown in Figure 14. The slope of this line indicates a first order dependence in bromide. The simplest mechanism to explain these observations would be,

$$Cr_2O_7^= + IO_3^- \rightleftharpoons IO_2^+ + 2CrO_4^= \qquad \text{fast}$$
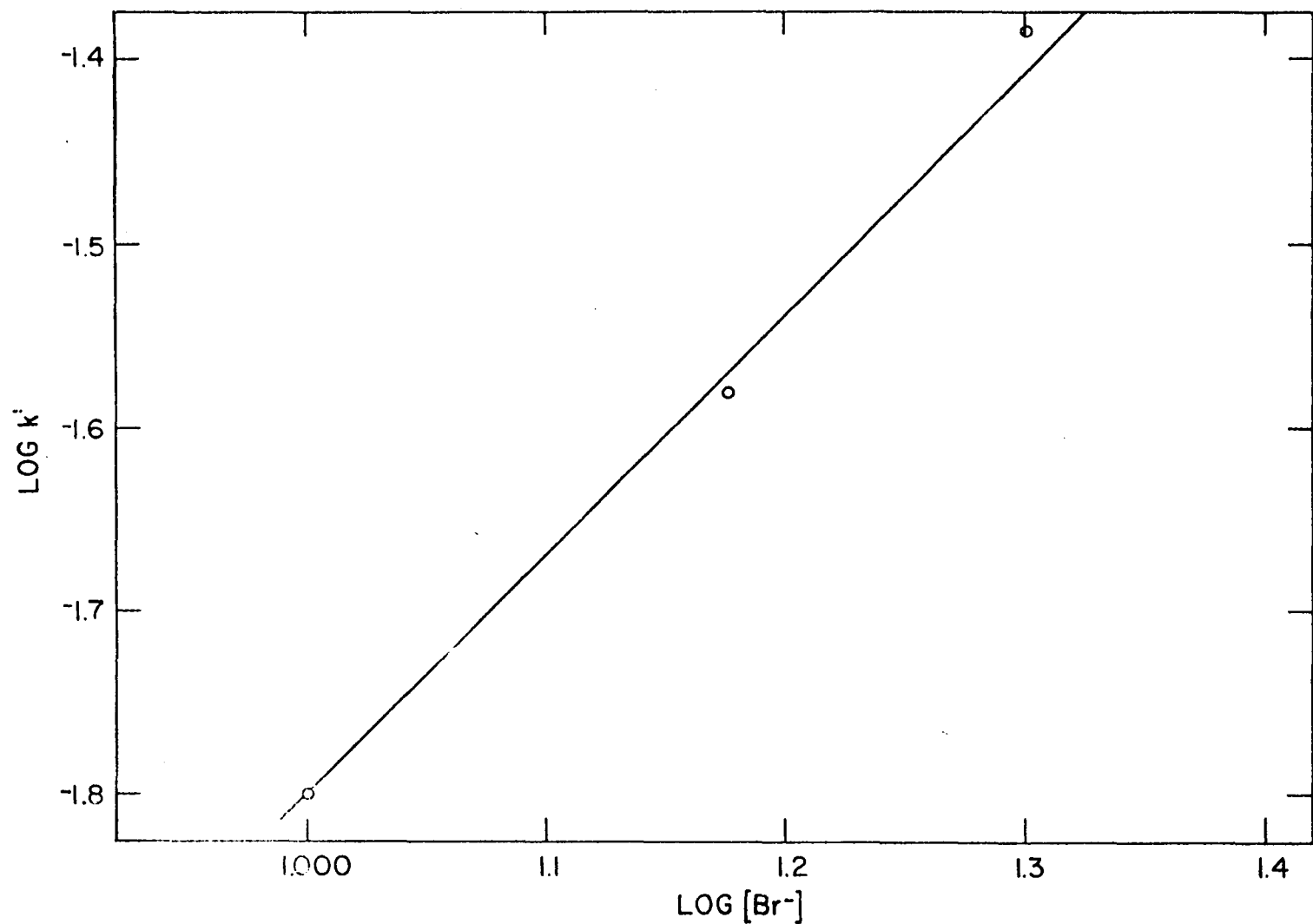
$$IO_2^+ + Br^- \longrightarrow \text{Products} \qquad \text{slow}$$

Figure 14. Plot of log Br⁻ versus log k' to determine order in Br⁻; $[Ba^{++}]$ = 0.20m (the rate constants should be multiplied by 2.3)

Table 9. Variation of the pseudo first order rate constant with concentrations of reactants

Ba^{++} m	IO_3^- m	$Cr_2O_7^=$ m	Br^- m	$1/k'$ min.mole
0.10	0.10	0.01	0.10	63
0.08	0.10	0.01	0.10	90
0.07	0.10	0.01	0.10	116
0.10	0.10	0.01	0.15	38
0.10	0.10	0.01	0.20	26
0.10	0.20	0.01	0.10	70
0.10	0.10	0.02	0.10	64

$$K = 2.2 \times 10^{-9} \text{ mole}^{-1}$$

$$k = 0.870 \text{ min}^{-1}\text{mole}^{-1}$$

The rate expression,

$$\text{Rate} = -\frac{dT_A}{dt} = \frac{kK[IO_3^-][Ba^{++}]^2[Br^-]}{K[IO_3^-][Ba^{++}]^2 + K_{sp}^2} T_A = kT_A \ ,$$

where $T_A = Cr_2O_7^= + IO_2^+$, is analogous to the other reactions that were studied. The reciprocal of the pseudo first order rate constant becomes,

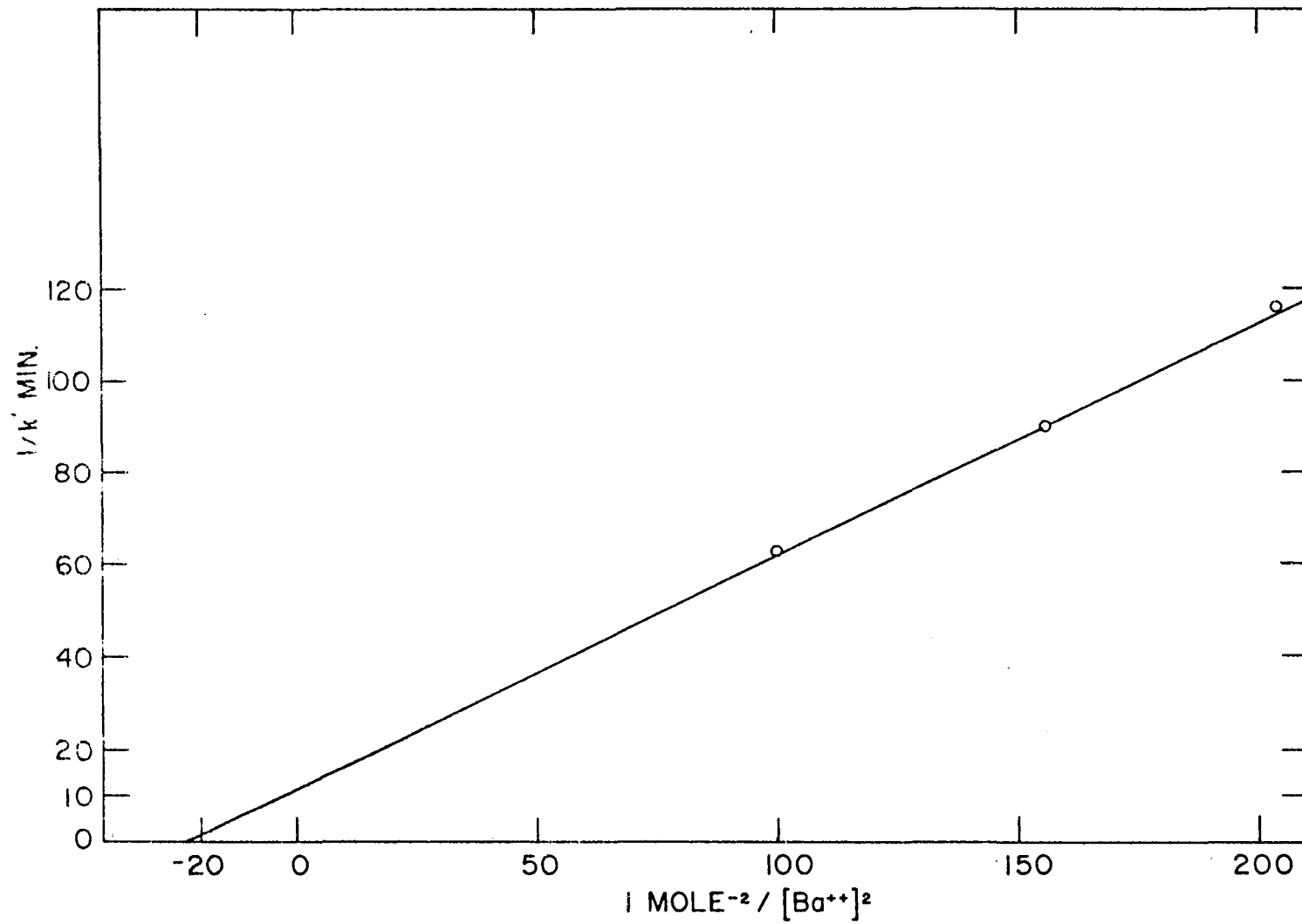$$\frac{1}{k'} = \frac{1}{k[Br^-]} + \frac{K_{sp}^2}{kK[Br^-][IO_3^-]} \cdot \frac{1}{[Ba^{++}]^2}$$

A plot of k/kI versus $1/[Ba^{++}]^2$ is shown in Figure 15.

The oxidation of iodide by iodate has been studied in aqueous solutions. The fifth order rate law,

Figure 15. Variation of pseudo first order rate constant with barium for the dichromate-iodate reaction (the rate constants should be multiplied by 2.3)
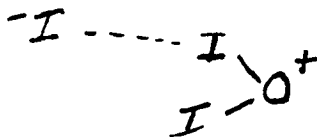
DICHROMATE-IODATE

54b

$$R = k_3 [IO_3^-][I^-]^2[H^+]^2$$

was observed by Abel and Stadler (28), Dushman (29), and Skrabel and Zahorka (30). Abel and Hilferding (31) found a fourth-order law which is probably related to the others with water as the nucleophilic particle. Connick and Hugus (32) repeated the work of Abel and Hilferding (31) using a different procedure. In perchlorate medium of constant ionic strength they found,

$$R = k [IO_3^-][I^-][H^+]^2$$

An article on the iodate-iodide reaction introduces a mechanism involving the intermediate IO_2^+ and a complex (32). The postulated complex of the fourth order rate law was

and that for the fifth order law (with a second-order dependence on iodide concentration) was similar, with one iodide ion on each oxygen of IO_2^+.

V. CONCLUSIONS AND SUMMARY

The reactions of nitrate and all three halates with
dichromate have been studied in fused alkali nitrates. It
appears that the halates behave similarly insofar as an equi-
librium is established before decomposition occurs. However
the path of decomposition of XO_2^+ to products was different
for each intermediate, XO_2^+. When one represents the halate
ion isn general as XO_3^-,

$$Cr_2O_7^= + XO_3^- \rightleftharpoons XO_2^+ + 2CrO_4^=$$
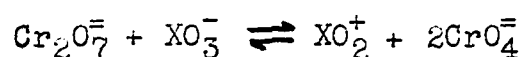
is the general equilibrium expression. The equilibrium con-
stants for the above reaction would serve as a measure of the
relative acidity of XO_2^+. Equilibrium constants were obtained
for all four acids at $250^\circ C$. These constants are tabulated.
A problem arises when the equilibrium constant was evaluated
for nitrate and chlorate because both of these ions were in-
corporated as all or part of the solvent. In the case of
nitrate, nitrate is the solvent and therefore its concentra-
tion does not appear in the equilibrium expression. In the
case of chlorate, chlorate served as half of the solvent.
All concentrations are expressed as moles of reactant per
1000 grams of solvent. Instead of reporting the chlorate
concentration as 4.7 moles per 1000 grams of solvent, and
stating that the chlorate is part of the solvent, one should
report this as 4.7 moles per 500 grams of nitrate solvent.

Perhaps a better way of representing the equilibrium constants of chlorate and nitrate would be by mole fraction of the halate and nitrate. The mole fraction of chlorate corresponding to 4.7 moles per 1000 grams of solvent is 0.488, and the mole fraction of nitrate in a sodium-potassium nitrate mixture is one. The equilibrium and rate constants for these reactions at 250°C are recorded in Table 10.

Table 10. The equilibrium constants and rate constants for all of the reactions studied, $Cr_2O_7^= + XO_3^-$ $XO_2^+ + 2CrO_4^=$ (temperature is 250°C)

XO_2^+	k	K
BrO_2^+	0.33 min^{-1}	3.5x10^{-8} mole^{-1}
ClO_2^+	5.68 $min^{-1}mole^{-1}$	4.0x10^{-11}
NO_2^+	0.312 $min^{-1}mole^{-1}$	4.5x10^{-11}
IO_2^+	2.00 $min^{-1}mole^{-1}$	2.2x10^{-9} mole^{-1}

The equilibrium constant obtained for the dichromate-nitrate reaction is lower than the value, 8.5x10^{-14}, calculated by Duke and Yamamoto (9). However several assumptions were made by Duke and Yamamoto to obtain this value.

(1) The product of constants obtained from Duke and
Iverson's (11) studies which Duke and Yamamoto used
to determine the equilibrium constant did not include
the complexing of dichromate by lead.

(2) The rate step for the dichromate-nitrate reaction
was the same as the rate step for the pyrosulfate-
nitrate reaction.

(3) The temperature dependence was assumed to be linear
and the rate constants were extrapolated to the
desired temperature. The rate constants for the
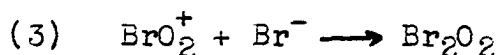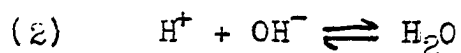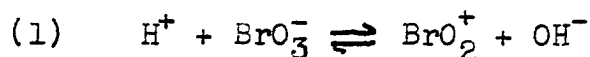pyrosulfate-nitrate reaction were determined at
two temperatures only.

The first assumption would introduce a sizeable error, and
would explain why Duke and Yamamoto's equilibrium constant
is less than the value obtained in this study.

The equilibrium constants for nitrate and chlorate are
nearly the same. The explanation of the chlorate reaction
being carried out without interference of the nitrate reaction
is that different halide ions were used to reduce the inter-
mediate to gases. The nitryl ion does not react with chloride
to any measurable extent during the dichromate-chlorate
reaction.

From the data in Table 10, one can arrange the relative
acidity of the intermediate acid ions as $BrO_2^+ < IO_2^+ < ClO_2^+ \approx NO_2^+$, going from weakest to strongest. The stability of these
intermediates can only be roughly compared. Bromyl decomposes
unimolecularly at a sizeable rate, therefore it would be the
least stable. A nucleophilic particle is needed to measure
the decomposition of the other intermediates. Iodyl and

nitryl can be compared because the same nucleophilic ion, bromide, is used to follow their reaction rates. The rate constants indicate that iodyl is less stable than nitryl. Chloryl has the largest rate constant. However this ion cannot be compared to the others because chloride is the nucleophilic ion and chloride is much more difficult to oxidize than bromide.

The intermediate acid ions, XO_2^+, which are postulated in this thesis have also been postulated as participating in the mechanism of oxidation-reduction reactions conducted in aqueous systems (6, 32, 34). Duke (35) proposed a hypothesis which explains the general pattern emerging from the studies of oxidation-reduction reactions carried out in aqueous systems. Stated simply, the hypothesis is this: "An oxidation reduction reaction is preceded by, or is simultaneous with a generalized acid-base reaction." An example is the reaction between the anions bromide and bromate, which proceeds only in acid solution (34),

$$(1) \quad H^+ + BrO_3^- \rightleftharpoons BrO_2^+ + OH^-$$

$$(2) \quad H^+ + OH^- \rightleftharpoons H_2O$$

$$(3) \quad BrO_2^+ + Br^- \longrightarrow Br_2O_2$$

Many authors cited in this thesis combine the equilibrium steps 1 and 2 and write BrO_2^+ in the hydrated form to exemplify the second order dependence in hydrogen ion. A similar equilibrium occurs in the dichromate-nitrate reaction carried out

in fused nitrates. Shute (14) observed totally different products in lithium nitrate than in sodium-potassium nitrate solvent when she studied the oxidation of bromide by bromate in fused nitrates. The products in lithium nitrate solvent were lithium oxide and bromine. Lithium ion is very polarizing and is the only ion that approaches a polarizing power equivalent to hydrogen. It would be interesting to study this reaction varying the lithium concentration to see if a second order dependence occurs as found in the analogous reaction carried out in water and acid.

The alkali nitrates are the only solvents in which acid-base reactions have been studied. There are three outstanding reasons why the alkali nitrates were chosen as a solvent.

(1) Mixtures of alkali nitrates melt at a low temperature and are easily thermostated.

(2) They are quite stable thermally.

(3) The conjugate acid of nitrate, NO_2^+, is stronger than the conjugate acid of other bases which makes it possible to study the reaction of these other bases with several acids.

The reactions of nitrate with Lewis acids have been studied at high concentrations of nitrate simply because nitrate was the solvent. Chemical observations of perchlorate indicate that its conjugate acid is much stronger than NO_2^+. The slow

reaction of aqueous perchlorate ion as an oxidant is a good example. Therefore lithium perchlorate could be used as a solvent to study the reaction of many acids with a limited concentration of nitrate. Also, the gaseous product, N_2O_5, formed in the dichromate-nitrate and pyrosulfate-nitrate reactions, may not be soluble in lithium perchlorate and a meaningful rate constant for the decomposition of nitryl ion could be evaluated.

VI. BIBLIOGRAPHY

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