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A study of the nitrate ion dissociation in fused nitrates

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A STUDY OF THE NITRATE ION DISSOCIATION

IN FUSED NITRATES

by

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INTRODUCTION

Although investigations of fused salt systems date back
to the latter part of the 19th century, no important progress
in this field of research was made until after 1950. The
appearance of numerous high temperature industrial processes
stimulated the quest for information regarding fused salt
systems. Also in recent years theoretical chemists have
shown considerable interest in the physical and chemical
properties of fused salts (4).

The structure of fused electrolytes is of prime impor-
tance, but there are few good methods presently available for
direct structural determinations. Several investigators have
reported x-ray and neutron diffraction studies (21, 28) and
spectrophotometric studies (16), but there is no generally
applicable method for direct structural investigations of
fused salts.

Some knowledge of the structure of fused electrolytes
can often be gained by the investigation of chemical re-
actions that can occur when these fused salts are used as
solvents. The structures of several non-aqueous solvents
have been characterized in this manner (1). Since many
reactions in fused salts are analogous to the acid-base
type of reaction encountered in aqueous chemistry, an
operational acid-base definition is needed for fused media.
Although the Lewis theory is applicable to solvents in

general, it is often convenient to have a more restricted
definition for particular types of solvents.

In 1939, Lux (23) proposed an acid-base definition,
applicable to solvents containing oxide ion or other oxy-
anions, which was based on the equilibrium

(1) Base = Acid + $O^=$.

A base was defined as that which could donate oxide ions and
an acid was defined as that which could accept oxide ions.
Thus a reaction of an acid with a base would result in the
transfer of an oxide ion, and a conjugate acid and a con-
jugate base would be produced. Flood and Forland (11)
suggested that acid strengths in oxide systems could be
established in a relative manner if the magnitudes of the
equilibrium constants, defined as

(2) $K = \dfrac{a_{acid} \cdot a_{O^=}}{a_{base}}$

were compared.

Acid-base reactions in fused alkali nitrates have been
studied by several workers. Duke and Iverson (8) investi-
gated the reaction between the dichromate and nitrate anions

$$Cr_2O_7^= + NO_3^- = 2CrO_4^= + NO_2^+.$$

The reaction of the pyrosulfate anion with nitrate

$$S_2O_7^= + NO_3^- = 2SO_4^= + NO_2^+$$
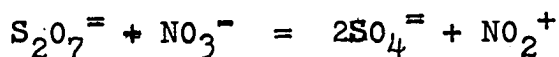
was studied by Duke and Yamamoto (10). In both of these cases
the nitrate ion provided oxide ion which was transferred to
the acids dichromate and pyrosulfate. Since nitrate acted as

a base, it would be expected to dissociate according to the Lux equilibrium

$$(3) \quad NO_3^- = NO_2^+ + O^=.$$

It is the purpose of this study to investigate this equilibrium and to determine its equilibrium constant.

If the solvent is an alkali nitrate mixture, the expression for the nitrate dissociation constant can be written

$$(4) \quad K = a_{NO_2^+} \cdot a_{O^=} .$$

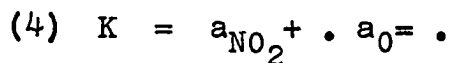Investigations on the nature of molten salt solutions have indicated that simple mixtures of molten electrolytes form almost ideal solutions with activity coefficients close to unity (29). Laity (20) has shown that if the Temkin model is used for the molten electrolyte the approximation of ion activities by ion concentrations is justified. Therefore, in this study all activity coefficients will be assumed to be unity and all activities will be replaced with concentration variables. Consequently the dissociation constant (4) can be determined by measuring the oxide and nitryl ion concentrations. Since these concentrations are expected to be very small, an electrochemical method is probably best suited to their determination.

An electrochemical investigation of a chemical equilibrium requires a reversible electrode system which will indicate the chemical activity of one of the chemical species in

the equilibrium expression. In the dissociation of the nitrate ion, an indicator electrode must be found which will respond to the nitryl or oxide ion concentration.

EXPERIMENTAL

Materials and Apparatus

Chemicals

Except for the lithium oxide, A. C. S. reagent grade chemicals were used in all of the experiments. The lithium oxide employed was obtained from the Lithium Corporation of America and was assayed as follows: 90% lithium oxide, 6.8% lithium hydroxide, 3.2% lithium carbonate, 0.0% lithium peroxide. Anhydrous lithium perchlorate was prepared by heating lithium perchlorate trihydrate under a vacuum.

The equimolar mixture of sodium nitrate and potassium nitrate used as a solvent in most of the experiments was prepared by the following procedure. The required amounts of the two salts were fused together and mechanically stirred to ensure complete mixing. The molten mixture was then filtered through a fine grade fritted glass disc and molded into small slugs of about 100 grams weight. These slugs were stored in a desiccator jar over magnesium perchlorate.

The one molal silver nitrate solution was prepared by dissolving .1 mole of silver nitrate in 100 grams of the equimolar solvent. This solution was allowed to solidify, and then milled in a ball mill to pass a 16 mesh screen.

The oxygen used was U. S. P. grade and was dried over magnesium perchlorate during use. The argon used was of the water pumped variety and was also dried over magnesium

perchlorate during use.

Electrodes

The reference electrode employed was similar to that described by Inman (17). It consisted of a nine mm. Pyrex glass tube sealed to a standard taper 14/35 inner joint. The end of the glass tube was closed off and blown to an average thickness of .1 mm. To the top of the 14/35 inner joint was sealed a standard taper 10/30 outer joint. A three inch piece of #22 silver wire (Handy and Harmon, 99.99+% pure) was welded to an eighteen inch piece of #22 platinum wire. This platinum wire was sealed in one end of a five mm. glass tube, the other end of which terminated in a standard taper 10/30 inner joint. About two grams of the one molal silver nitrate mixture were added to the outer tube and fused. The inner tube containing the silver wire was then inserted and the 10/30 joints seated. The reference electrode was then ready for use. Figure 1a. illustrates the reference electrode.

The indicator electrode was an oxygen gas-platinum electrode. A nine mm. Pyrex glass tube was sealed to a standard taper 14/35 inner joint. A hole about four mm. in diameter was blown in the tube about five mm. from the end furthest away from the tapered joint. On the other end of the tube, above the tapered joint, a six inch side arm of seven mm. Pyrex glass tubing was fitted which ended in an 18/7 standard socket joint. A two inch piece of three mm.
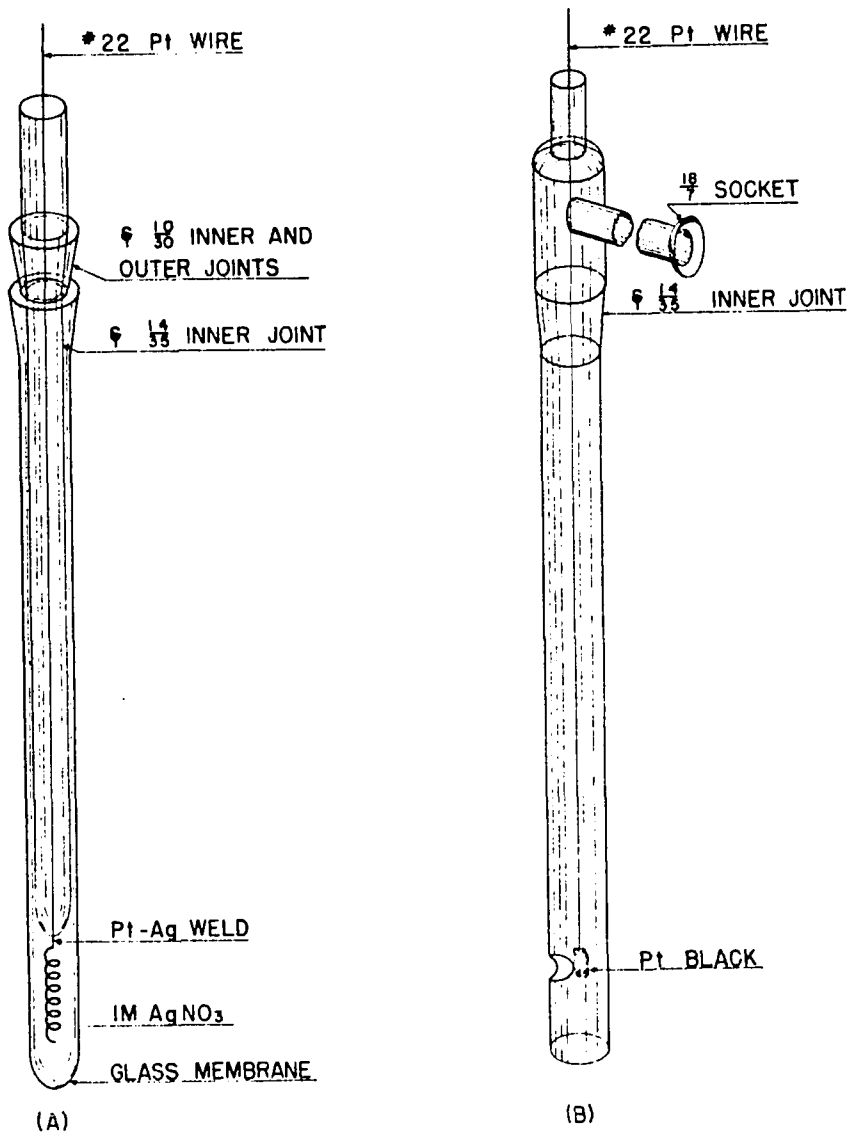
Figure 1. Electrodes:
(a) Silver-glass reference
(b) Oxygen gas-platinum indicator

Pyrex glass tubing was sealed to the tube extending above the taper. Through this smaller tube a two foot length of #22 platinum wire was passed. To the end of the wire inside the tube a square piece of platinum foil, $\frac{1}{2}$ cm. on a side, was attached and the wire adjusted so that the platinum square was opposite the hole in the side of the tube. The small tube at the top of the electrode was then collapsed around the platinum wire. Next, the square of platinum foil was platinized by cathodic reduction in a solution of platinum (IV) chloride to which a small amount of lead (II) acetate had been added (26). The electrode was then rinsed in water and dried. After drying it was soaked in a bath of fused equimolar sodium-potassium nitrate, which was saturated with sodium carbonate, for a period of thirty minutes. Then the electrode was rinsed in fused equimolar sodium-potassium nitrate three times and stored in the fused solvent until used. Figure 1b illustrates the indicator electrode.

Reaction cell

The reaction cell consisted of two parts, a top part and a bottom part. The bottom part was made from a fifty five mm. Pyrex tube which was sealed and rounded at one end and fitted to a standard taper 60/50 outer joint at the other end. The overall length of this part was twenty cm. The bottom part of the reaction vessel is illustrated in Figure 2a. The top part was made from a Pyrex standard taper 60/50 inner joint, the shank of which was sealed off about

two cm. above the taper. Onto this end were fitted two standard taper 14/35 outer joints, a thermocouple well of four mm. Pyrex tubing, a standard 12/7 socket, and a journal for a Pyrex glass stirrer. These were arranged as illustrated in Figure 2b.

Auxiliary equipment

An equimolar mixture of fused sodium and potassium nitrates in a ten quart enameled pot was used as a constant temperature bath. This mixture melted at about 220 deg. C. and had a high thermal conductivity. This binary mixture was used in preference to a ternary mixture of lithium, sodium, and potassium nitrates because of the corrosive action of the latter mixture on Pyrex glass (22). The primary source of heat for the bath was a 1500 watt, 220 volt "Chromalux" ring heater. An auxiliary heater, made from ten feet of #18 nichrome wire wound on an alundum core, was enclosed in a 38x200 mm. test tube and immersed in the bath. This heater was operated by an on-off controller (Minneapolis-Honeywell Brown Model 156C16PS-21 Temperature Controller). The bath was insulated by wrapping successive layers of glass wool, aluminum foil, asbestos paper and asbestos tape around it. Temperature measurements were made with a chromel-alumel thermocouple in conjunction with a Minneapolis-Honeywell Rubicon Thermocouple Potentiometer. The temperature of the reaction vessel could be controlled to within $\pm$ .5 C. deg. up to 375 deg. C. with this system.

Because of the high impedance of the glass membrane of the reference electrode, about 500K ohms, it was necessary to use an e.m.f. measuring circuit which had an impedance on the order of 100 megohms or greater. For this purpose, a potentiometer circuit, incorporating an electrometer for a null point indicator, was used. The potentiometer was a Leeds and Northrup Type K-3 Universal model, and the null point indicator was a Keithley Model 603 Electrometer-Amplifier. The electrometer was placed in series with the reference electrode and the impedance was set at 100 pico ohms.

Three flow meters were needed to measure the flow rate of oxygen, argon, and carbon dioxide. These were of the orifice type and were made in the shape of two opposed U-tubes. The upper bend was constructed from one mm. bore capillary tubing and the lower bend and side arms were made from six mm. Pyrex tubing. Increased sensitivity was obtained from constrictions placed in the capillary tubes. n-Butyl phthalate served as the indicating fluid. The calibration of the oxygen and argon flow meters was accomplished through direct displacement of water from a large reservoir. The water in the reservoir was saturated with the gas used for calibration by bubbling the gas through a fritted glass "bubbler" for a minimum of five hours. The flow rate was varied from about twenty ml./min. to about 100 ml./min. The average deviation for five readings at each calibration
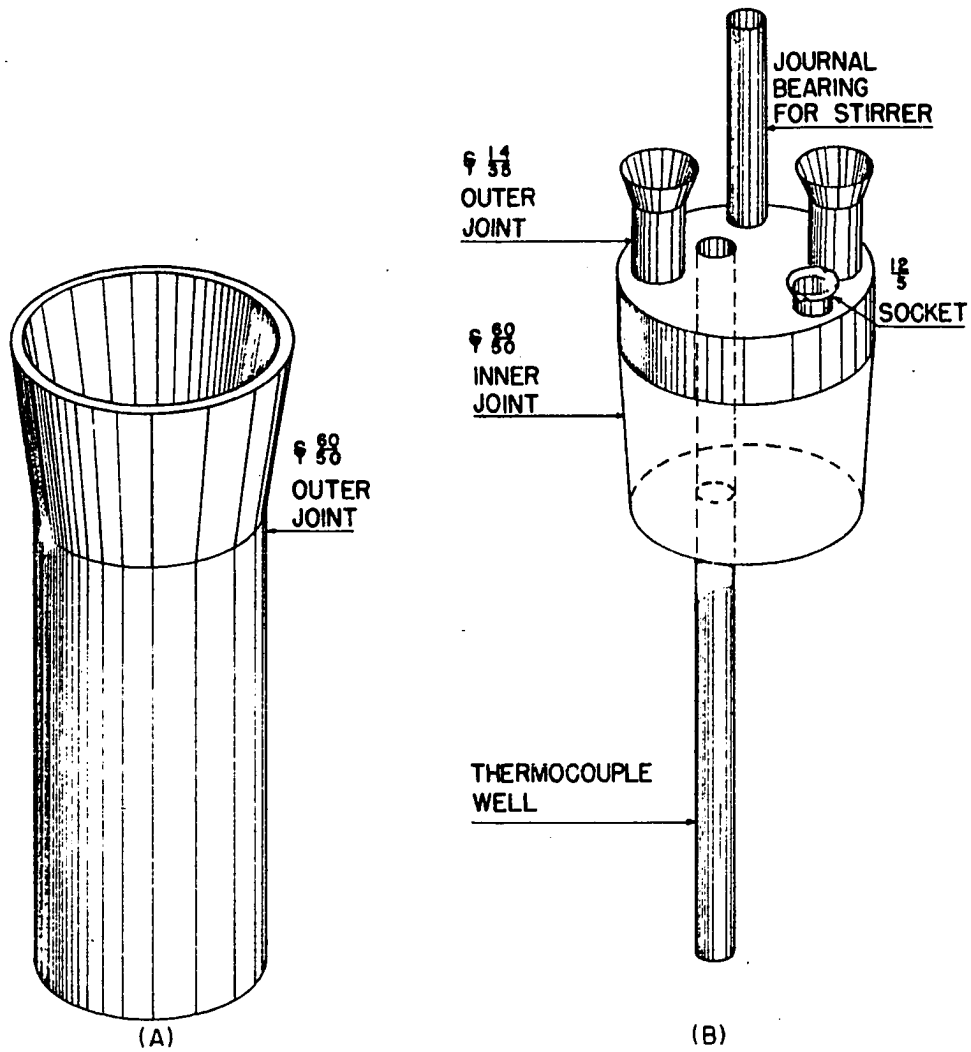
Figure 2. Reaction cell:
(a) bottom part
(b) top part

point was .1 ml./min. or less. A gas burette filled with n-butyl phthalate was used to calibrate the carbon dioxide flow meter.

The chromel-alumel thermocouple used in measuring the reaction cell temperature was calibrated in the range 220 deg. C. to 420 deg. C. with the freezing points of tin, 231.9 deg. C., lead, 327.3 deg. C. and zinc, 419.5 deg. C. These freezing points were listed by the National Bureau of Standards as secondary fixed points on the international temperature scale (1948) (27).

The introduction of oxide ion into the reaction cell was accomplished through electrolysis. To accurately determine the amount of oxide ion generated, a constant current genera-tor was built with an electronic circuit similar to that given by Bair (2). A D. C. power supply was built capable of delivering 120 ma. at 300 volts. With this power supply and with special modifications to the constant current generator, it was possible to produce currents of from two μa. to eighty ma. The current fluctuations were less than .5% at ten μa. output.

<center>Experimental Procedure</center>

The experimental procedure did not vary significantly in the different phases of this investigation. The amount of solvent used in each of the experiments varied between 200 and 500 grams. The solvent was weighed out and placed

in the lower part of the reaction cell. This part of the
cell was then placed in the constant temperature bath. As
soon as the solvent was fused, the top portion of the reaction
cell with a glass stirrer was fitted into place. The oxygen
electrode was put in place and the oxygen flow started. The
oxygen was allowed to bubble through the solvent for at
least three hours to insure dryness of the solvent and the
attainment of equilibrium between the dissolved and undis-
solved oxygen. It has been reported that the solubility of
oxygen gas in molten nitrates is less than 10^{-4} moles per
mole of salt (14).

In the experiments on the decomposition of pyrosulfate
ion, the required sodium sulfate was first added to the
solvent and allowed to dissolve. Then the potassium pyro-
sulfate was added and the reference electrode immediately
inserted. Potential measurements began within a minute after
the start of a reaction.

The electrolysis to produce oxide ion was usually
carried out with a current of $10-20 \mu a$. A different
reference electrode from that previously described was used
for the electrolysis. This electrode contained an asbestos
wick junction which greatly lowered the internal resistance
of the cell. The voltage at which the electrolysis was
carried out never exceeded .05 volts and was usually much
less.

RESULTS AND DISCUSSION

The Nitrogen Dioxide Electrode

Preliminary investigation

Attempts to obtain an electrode reversible to the nitryl, NO_2^+, ion were first made. Nitrogen dioxide was bubbled over a piece of platinum foil which was dipping into a tube containing fused equimolar sodium-potassium nitrate. For a reference electrode a silver-silver chloride electrode was first used. This consisted of a silver wire, coated at one end with silver chloride, placed in a ten mm. sealing tube with a fine grade fritted glass disc. The tube was filled part way with the equimolar solvent and sufficient potassium chloride was added to give a chloride ion concentration of .01 molal. This sealing tube dipped into the reaction vessel and completed the electro-chemical cell. The voltage between the two electrodes was about +.7 volts with the NO_2 gas electrode functioning as the cathode. The reduction which occurred could have been due either to the reduction of NO_2^+ according to the reaction

$$NO_2^+ + e^- = NO_2$$
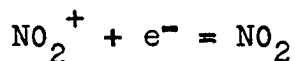
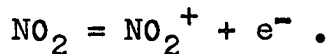or to the reduction of NO_2 according to the reaction

$$NO_2 + e^- = NO_2^- .$$
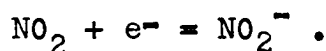
In an effort to simplify this situation, an attempt was made to find a reference electrode which utilized a sufficiently strong oxidizing agent to oxidize NO_2 gas to

NO_2^+. This would make the NO_2 gas electrode the anode with the only feasible reaction being

$$NO_2 = NO_2^+ + e^- .$$

The only reference electrode found which would meet this requirement was one involving the ceric-cerous couple

$$Ce^{+4} + e^- = Ce^{+3} .$$
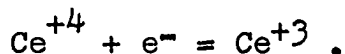
A saturated solution of ceric and cerous sulfates in the equimolar sodium-potassium was placed in the sealing tube and the potential between it and the NO_2 gas electrode measured. A potential of about +.4 volts was obtained, the gas electrode functioning as the anode. However, the ceric sulfate in the reference electrode was found to be unstable, being converted to ceric oxide in about an hour at 250 deg. C. In an effort to stabilize the ceric sulfate, the nitrate solvent in the reference electrode was replaced by potassium hydrogen sulfate. To prevent interdiffusion of the two solvents, the sealing tube was replaced by a thin glass bulb. Some stabilization of the ceric sulfate did occur but decomposition still took place over a period of several hours.

In order to determine the response of the indicator electrode to the nitryl ion, some potassium pyrosulfate was added which reacted with the nitrate solvent according to the reaction

$$(5) \qquad S_2O_7^= + NO_3^- = 2 SO_4^= + NO_2^+ .$$
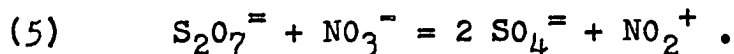
Immediately upon the addition of the pyrosulfate, the

voltage of the cell was observed to decrease rapidly by several hundred millivolts. After several minutes the voltage began to increase slowly.

These observations are explained with the aid of the Nernst expression for the cell reaction,

$$(6) \qquad E = E^O - \frac{RT}{F} \ln \frac{a_{Ce^{+3}} \cdot a_{NO_2^{+}}}{a_{Ce^{+4}} \cdot a_{NO_2}} \cdot$$

An increase in the activity of the nitryl ion will lower the voltage. As NO_2^{+} is removed by the reaction

$$(7) \qquad NO_2^{+} + NO_3^{-} = 2\ NO_2 + \tfrac{1}{2}\ O_2$$
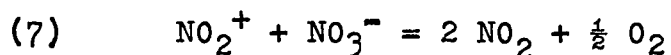
postulated by Duke and Yamamoto (10), the voltage will increase.

Although this electrode system apparently responded to the changes in the activity of the nitryl ion, the voltage depended considerably on the rate of flow of the NO_2 gas. Also the voltage obtained for a given set of initial conditions was irreproducible. However, the change in voltage with time during the decomposition of the pyrosulfate appeared to be the same for experiments having the same initial concentration of the pyrosulfate ion. Therefore it seemed possible that the kinetics of the pyrosulfate decomposition could be followed with this electrode system.

Pyrosulfate decomposition kinetics

Duke and Yamamoto (10) developed a rate expression for the pyrosulfate decomposition in alkali nitrate solvents which indicated that the rate controlling step was reaction

(7) above. The rate expression, verified by chemical methods, was

$$(8) \qquad -\frac{dT}{dt} = \frac{kKT}{K + (SO_4^=)^2} = k'T$$

where T was the total acid and was equal to $(S_2O_7^=) + (NO_2^+)$, k was the specific rate constant for reaction (7), k' was a pseudo-first order rate constant equal to

$$(9) \qquad \frac{kK}{K + (SO_4^=)^2},$$

and K was the equilibrium constant for reaction (5). The rate constant k and the equilibrium constant K were separated by plotting $\frac{1}{k'}$, vs. $(SO_4^=)^2$, the ordinate intercept being equal to $\frac{1}{k}$ and the abscissa intercept being equal to -K.

A series of experiments was performed in which the rate of the pyrosulfate decomposition was followed with the NO_2 gas electrode. The experiments were carried out at 290 deg. C. with a constant gas flow. The concentration of sodium sulfate was varied from .103 to .242 molal. The results are indicated in Table 1 and a graphical presentation is given in Figure 3.

The rate constant obtained from this data was .086 min.$^{-1}$ and the equilibrium constant $37.8 \pm .4$. A satis-factory measurement of the flow rate of NO_2 gas was not made. Since very slow flow rates were needed, it seemed that an orifice type flow gauge would work the best. However, NO_2 gas was extremely soluble in water and almost all organic fluids and no satisfactory meter fluid was
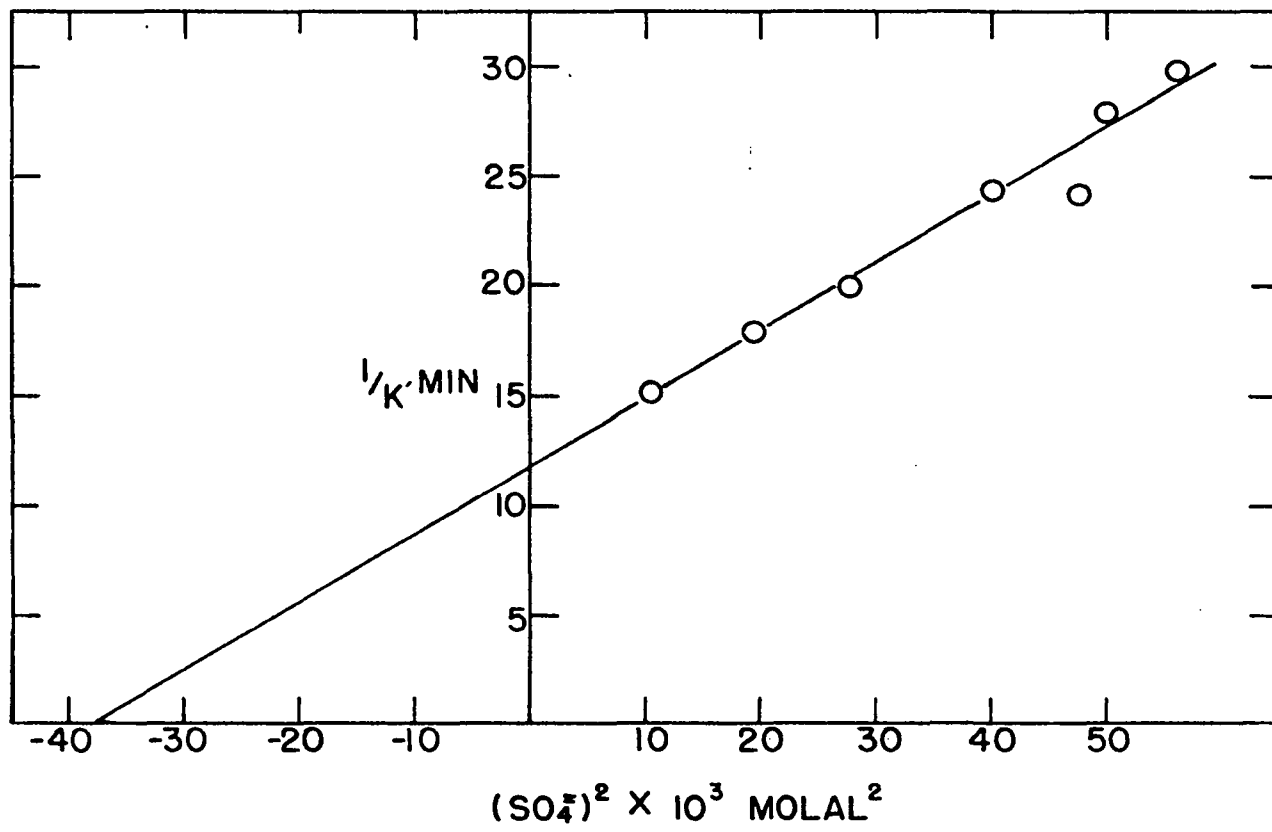
Figure 3. Plot of reciprocal rate data vs. $(SO_4^=)^2$ at 290° C. to determine k and K.

found. Since the rate constant was dependent on the flow rate, the value obtained for the rate constant was of no comparative significance. The equilibrium constant should be independent of the flow rate and should have comparative value.

Because of the irreproducibility of the e.m.f. values and the dependence of the e.m.f. on the flow rate of the gas, this electrode system was abandoned.

Table 1. The variation of the pseudo-first order rate constant with $(SO_4^=)$ at 290 deg. C.

$(SO_4^=)$ m.	$(SO_4^=)^2$ m.^{2} x 10^2	k' min^{-1}
.103	1.06	.151
.140	1.96	.129
.167	2.79	.115
.201	4.04	.094
.218	4.75	.094
.224	5.02	.082
.238	5.66	.077
.242	5.86	.064

The Oxygen Electrode

Preliminary investigation

Next an attempt was made to obtain an oxygen electrode which would be reversible to the oxide ion.

In aqueous electrochemistry, oxygen is notorious for its irreversibility when used as an electrode, large overvoltages with all metals being displayed in almost all situations (15). Such is not the case when some fused electrolytes are substituted for water as the solvent. This is probably due to the increase in temperature necessitated by the higher melting points of these solvents. The reversibility of an electrode depends in large part upon the velocities of the electrode processes and consequently upon the magnitude of the exchange current. Since the rates of all reactions are accelerated by an increase in temperature, the exchange currents also increase. Thus, reversibility is enhanced in molten electrolytes.

Numerous examples of oxygen gas electrodes in fused electrolytes have appeared in the literature. The first attempt to make such an electrode was that of Baur (3) who used molten silver metal saturated with dissolved oxygen, and also platinum with gaseous oxygen in solvents of fused sodium hydroxide and fused sodium carbonate. Flood and Forland (12) and Flood, Forland, and Motzfeldt (13) used an oxygen gas-platinum electrode in phosphate melts, and an oxygen-carbon dioxide-platinum electrode in fused carbonates. However, most reports of reversible oxygen electrodes were in the temperature range of from 400 to 1100 deg. C. It seemed possible that an oxygen electrode might be reversible at temperatures as low as 250 deg. C. in a fused alkali

nitrate solvent.

Preliminary experiments with an oxygen gas-platinum electrode and a silver-silver ion- glass reference electrode were carried out. The electrodes were inserted into the equimolar sodium-potassium solvent and after equilibrium had been reached indicated a potential of about +.2 volts with the oxygen electrode as anode. Upon addition of potassium pyrosulfate the potential decreased to about -.5 volts. After several minutes the voltage began to increase slowly. Upon the addition of sodium carbonate, a strong base in nitrate solvents, the potential increased to about +.4 volts.

This behavior can be explained if the cell reaction is written

$$(10) \qquad 2\ Ag^+ + 0^= = 2\ Ag + \tfrac{1}{2}0_2 .$$
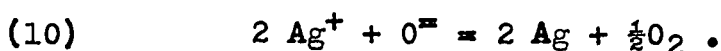
The Nernst equation for this cell would be

$$(11) \qquad E = E^O - \frac{RT}{2F}\ ln\ \frac{P_{0_2}^{\frac{1}{2}} \cdot a_{Ag}^2}{a_{Ag^+2}^2 \cdot a_0^=} .$$

If equilibrium (3) existed, then addition of the pyrosulfate would increase the concentration of NO_2^+ and consequently decrease the concentration of the oxide ion which, in turn, would decrease the potential. Addition of carbonate would increase the oxide ion concentration according to the dissociation

$$(12) \qquad CO_3^= = CO_2 + 0^= .$$
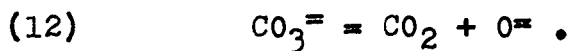
These observations indicated that the electrode system was sensitive to the oxide ion concentration and that the

equilibria involved were rapidly attained.

Reversibility and the standard e.m.f.

To evaluate the variation of the e.m.f. with the pressure of the oxygen gas, the oxygen was mixed with varying amounts of argon. The partial pressure of the oxygen was varied from about .1 atm. to about .7 atm. The potentials first obtained were somewhat erratic and depended slightly on the rate of flow of gas. However, this was not too surprising since the solvent was unbuffered. To buffer the solution a basic buffer was needed since acids tended to decompose the solvent. Also a buffer was needed which did not produce a gaseous product. It was found that sodium orthosilicate, Na_4SiO_4 met these requirements.

The potentials obtained after the solvent was buffered with $1.74x10^{-4}$ molal sodium orthosilicate were plotted against the log of the partial pressure of the oxygen. The graph is illustrated in Figure 4 and the data are listed in Table 2. The theoretical slope obtained from the Nernst equation was -.0260 volts at 250 deg. C. The observed slope was -.0276 volts.

To further test the reversibility of the oxygen electrode and to establish the standard e.m.f. for the cell reaction, it was necessary to devise a method to introduce known amounts of oxide ion into the system. The addition of a metal oxide was not considered satisfactory for several reasons:

Table 2. The variation of e.m.f. with oxygen pressure in a
1.74x10^{-4} molal silicate buffered nitrate solvent
at 250 deg. C.

Pressure O_2 atm.	E. M. F. volts
.151	.3450
.175	.3421
.206	.3408
.288	.3380
.342	.3345
.468	.3309
.602	.3274
.342	.3348
.274	.3380

Theoretical slope = -.0260 v.
Observed slope = (-.0276 ± .0008) v.[a]

[a]Slope obtained from least squares analysis

(1) metal oxides in general exhibited low solubilities
in nitrate melts,

(2) there was no guarantee that the small amount of
metal oxide which in some cases would dissolve
would dissociate completely into metallic cations
and oxide ions,

(3) the introduction of metals not in groups IA or IIA
of the periodic table could possibly complicate the
electrochemical processes,

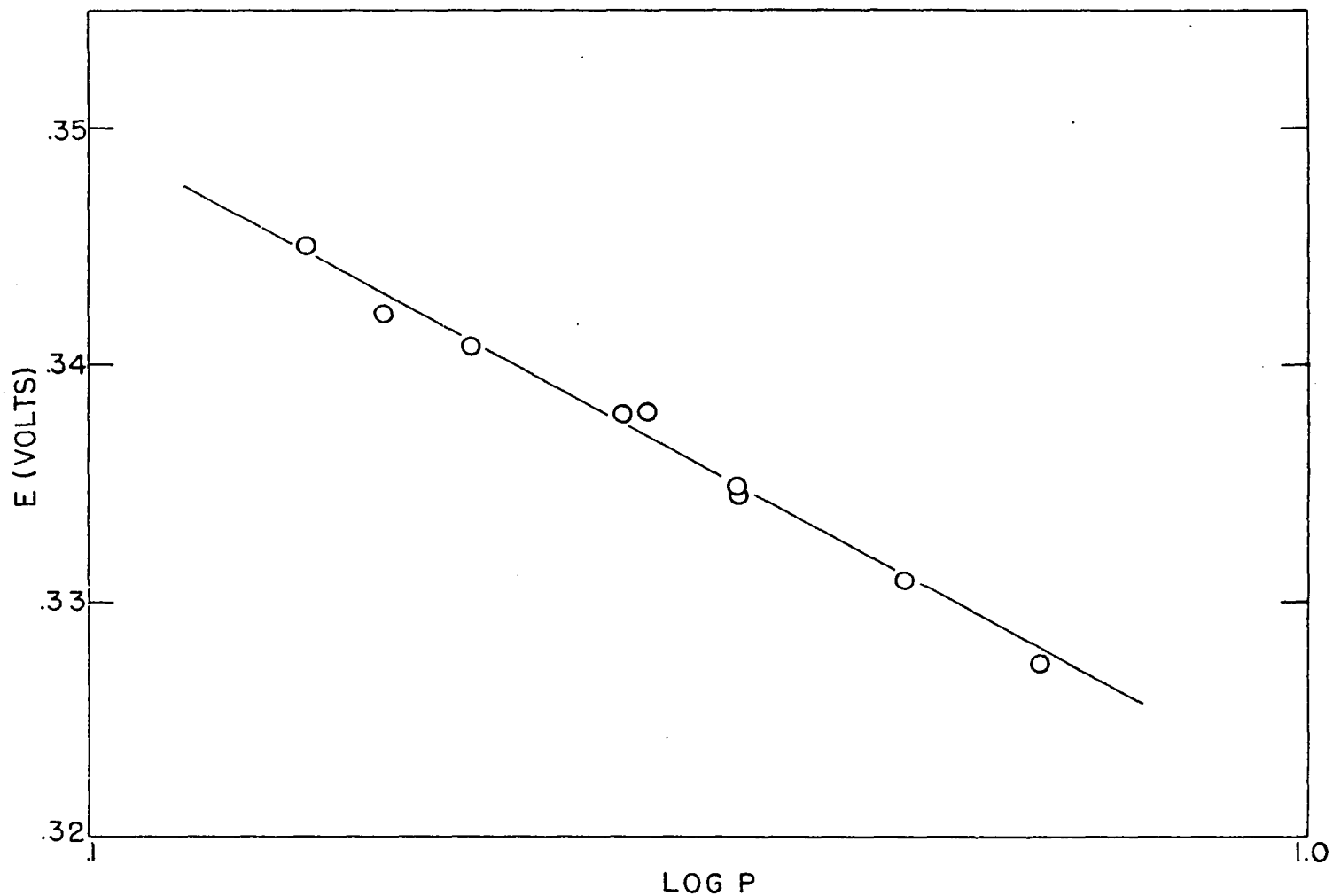Figure 4. Plot of E vs log P_{O_2} at 250° C. to determine reversibility of electrode system.

(4) introduction of lithium oxide, which was the only

alkali oxide available in sufficiently pure form,

would cause attack on the reaction vessel.

Since the oxygen- silver electrode system appeared to

be reversible, it should be possible to form oxide ion

electrochemically by reversing the cell reaction with an

applied voltage. If this procedure worked, there would be

several advantages derived from it:

(1) no additional cations would be added to the solvent,

(2) further evidence for reversibility would be

establi shed,

(3) small concentration changes in oxide ion could be

obtained,

(4) the standard e.m.f. could be established from data

obtained in the oxide ion concentration range of

primary interest, i.e. 10^{-8} to 10^{-5} molal.

This method of producing oxide ion was tried success-

fully. The constant current generator previously described

was used for the electrolysis. The current was ascertained

by measuring the voltage drop across a precision ten ohm

resistor. During the electrolysis the reference electrode

was replaced by the silver electrode with the asbestos wick

junction. The electrolysis was conducted in an equimolar

sodium-potassium nitrate solvent at 273 deg. C. Three

different experiments were performed, each using a different

oxygen electrode. The data are listed in Table 3 and a

graphical representation is given in Figure 5.

The close agreement among the three electrodes indicates the reproducibility of the oxygen gas-platinum electrode. Comparison of the theoretical Nernst slope and the observed slope indicates that the use of molality in the Nernst expression in place of activity is justified. The standard e.m.f. for the cell at 273 deg. C. was calculated from this data and is .6390 $\pm$ .0014 volts.

Additional thermodynamic information for the overall cell reaction was obtained from the variation of the standard e.m.f. with temperature. If the thermodynamic relation $\Delta G^O = -nFE^O$ is substituted into the Gibbs-Helmholts equation

$$(13) \qquad \frac{d(\Delta G^O/T)}{dT} = -\frac{\Delta H^O}{T^2}$$

the following equation is obtained.

$$nF \frac{d(E^O/T)}{dT} = \frac{\Delta H^O}{T^2} .$$

This can be written

$$\frac{nF}{T} \frac{dE^O}{dT} - \frac{nFE^O}{T^2} = \frac{\Delta H^O}{T^2}$$

or

$$\Delta H^O = -nF \left(E^O - T \frac{dE^O}{dT} \right) .$$

From this, the expression

$$\Delta S^O = nF \left(\frac{dE^O}{dT} \right)$$

can be derived.

Table 3. Variation in e.m.f. with change in the oxide ion
concentration. P_{O_2} = 1 atm., T = 273 deg. C.

Electrode	$(O^=)$ x 10^7 m.	E volts
#1	4.2	.2959
	6.54	.3037
	9.65	.3140
	12.76	.3207
	16.18	.3260
	22.40	.3338
#2	2.90	.2823
	6.00	.3000
	8.38	.3070
	14.94	.3166
#3	3.38	.2867
	5.86	.3003
	10.06	.3133
	13.94	.3205
	17.50	.3265
	20.60	.3298

Theoretical slope = .0541 Observed slope = .0543 $\pm$ .0013[a]
E^0_{273} = .6390 $\pm$ .0014[a]

[a]Obtained from least squares analysis

To measure the temperature dependence of the e.m.f., a
known amount of oxide ion was introduced into the reaction
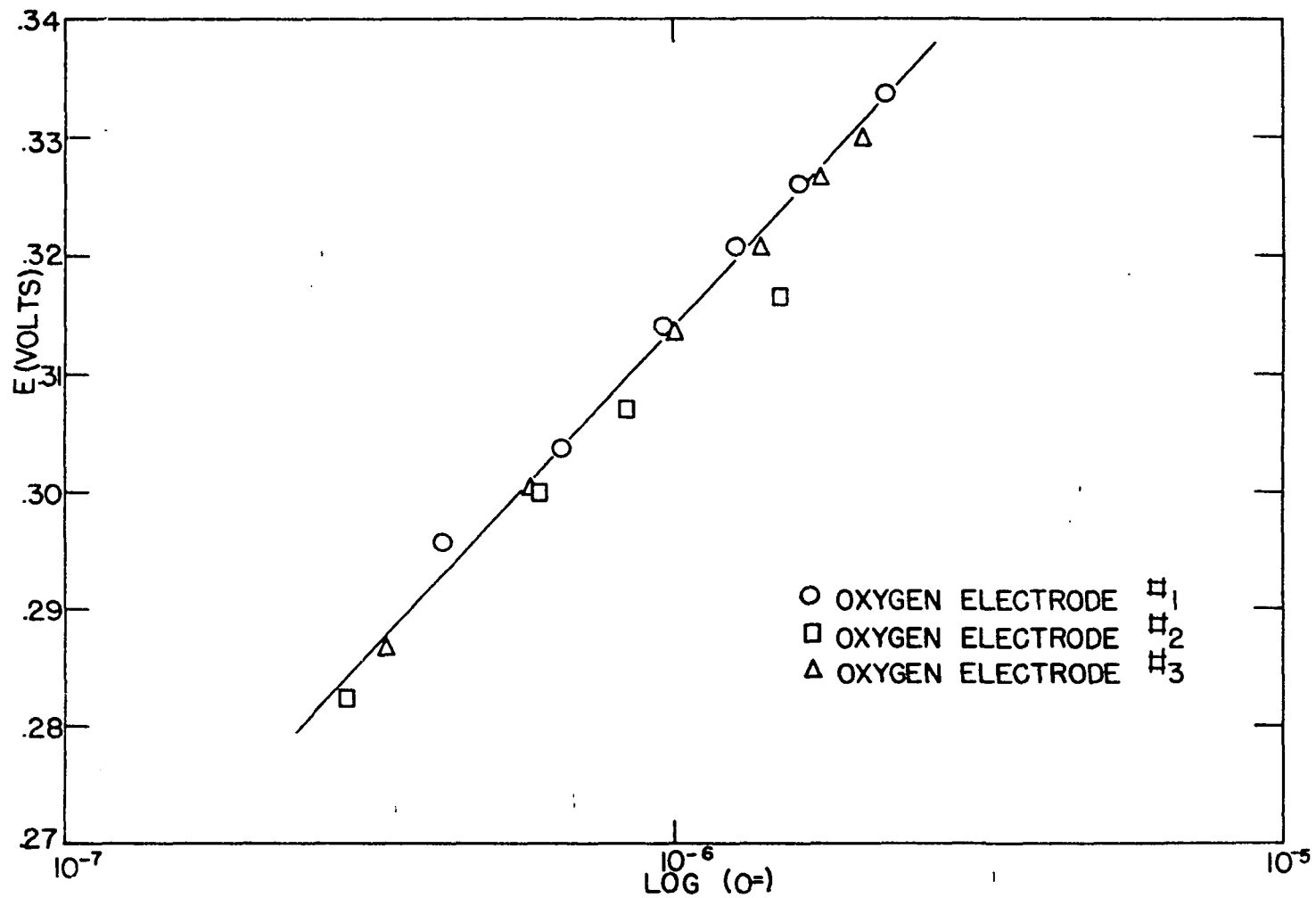vessel by electrolysis at 273 deg. C. The temperature was

Figure 5. Plot of E vs. log (0=) at 273° C. for three different
electrodes to determine reversibility and reproducibility
of the electrode system.

then varied between about 316 and 250 deg. C. Potential measurements were made at several temperatures and the standard e.m.f. values were calculated. The data are listed in Table 4 and illustrated graphically in Figure 6.

Table 4. Variation of E^O with temperature. $(0^=) = 1.49 \times 10^{-6}$ m.

Temp. ^OK	E volts	E^O volts
546.5	.3298	.6373
5-56.2	.3198	.6338
573.2	.3000	.6225
589.5	.2938	.6256
582.5	.2929	.6259
567.0	.3104	.6304
534.5	.3381	.6386

Slope = $-(2.56 \pm .10) \times 10^{-4}$ v/deg.[a]

[a]Obtained from least squares analysis

The approximation to a straight line is made under the assumption that ΔH^O and ΔS^O are nearly constant over the range of temperatures considered. The values of ΔG^O, ΔH^O, and ΔS^O for the cell reaction at 273 deg. C. were calculated to be:
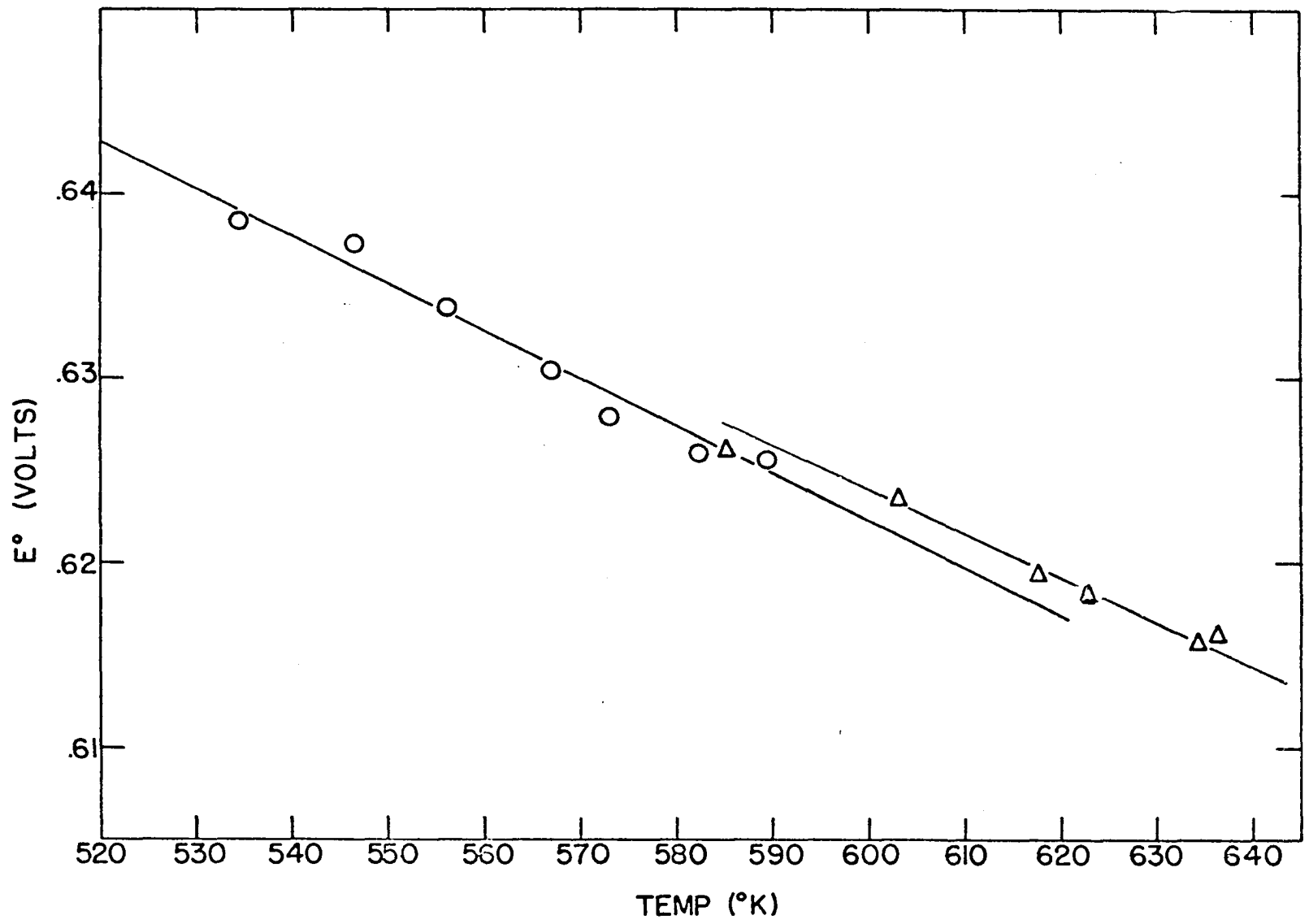
$$\Delta G^O_{273} = -29.5 \pm .1 \text{ kcal.}$$

$$\Delta H^O_{273} = -35.9 \pm .3 \text{ kcal.}$$

$$\Delta S^O_{273} = -11.8 \pm .4 \text{ e.u.}$$

Figure 6. Plot of E^O vs. absolute temperature to determine ΔH of electrode reaction in

O ——— equimolar sodium-potassium nitrate

Δ ——— pure sodium nitrate.

Solvent effect on E^O

In some kinetic studies of reactions in fused sodium-potassium nitrate solvents, a solvent cation effect has been reported. Duke and Shute (9) observed that the rate of decomposition of the bromate anion in fused sodium-potassium nitrate, which took place according to the reaction

$$BrO_3^- + Br^- = Br^- + O_2 \ ,$$
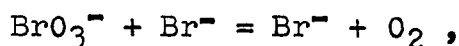
increased when the ratio of Na^+ to K^+ was increased. Schlegel (25) reported that for the reaction sequence in fused nitrates

$$Cr_2O_7^= + BrO_3^- = BrO_2^+ + 2 \ CrO_4^=$$

$$BrO_2^+ \longrightarrow \quad products$$
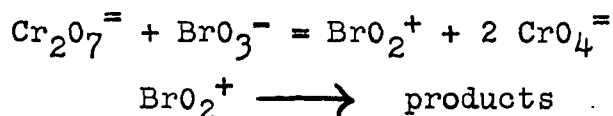
the equilibrium constant for the first reaction and the rate constant for the second reaction both increased when the Na^+ to K^+ ratio of the solvent was increased. In view of these reports it seemed necessary to investigate the dependence of the e.m.f. of the oxygen electrode on the Na^+ to K^+ ratio.

A determination of the standard e.m.f. of the electrode system was made, the solvent this time being pure sodium nitrate. The same reference electrode as previously used, was employed. Since pure sodium nitrate melts at 307 deg. C. it was necessary to increase the temperature. The measurements were made at 323 deg. C. The results are illustrated graphically in Figure 7 and the data are listed in Table 5. The temperature dependence of the standard e.m.f. in the pure sodium nitrate solvent was determined. The results are shown

in Figure 6 and the data are listed in Table 6. ΔG^O, ΔH^O,

and ΔS^O for the cell reaction at 323 deg. C. in pure sodium

nitrate were calculated to be:

$$\Delta G^O_{323} = - 28.89 \pm .01 \text{ kcal.}$$

$$\Delta H^O_{323} = - 35.46 \pm .42 \text{ kcal.}$$

$$\Delta S^O_{323} = - 11.0 \pm .7 \text{ e.u.}$$

Table 5. Variation of E with $(0^=)$ in pure $NaNO_3$ at 323 deg. C. P_{O_2} = 1 atm.

$(0^=)$ x 10^7 m.	E volts
2.920	.2398
4.175	.2490
6.775	.2612
9.375	.2698
11.98	.2762
14.58	.2812
17.30	.2860
19.90	.2890
22.52	.2927

Theoretical slope = .0591   Observed slope = .0591 $\pm$ .0002[a]
E^O_{323} = .6264 $\pm$ .0002 volts [a]

[a]Obtained from least squares analysis

The close agreement between the ΔH^O and ΔS^O values at

the two different temperatures indicated that the solvent

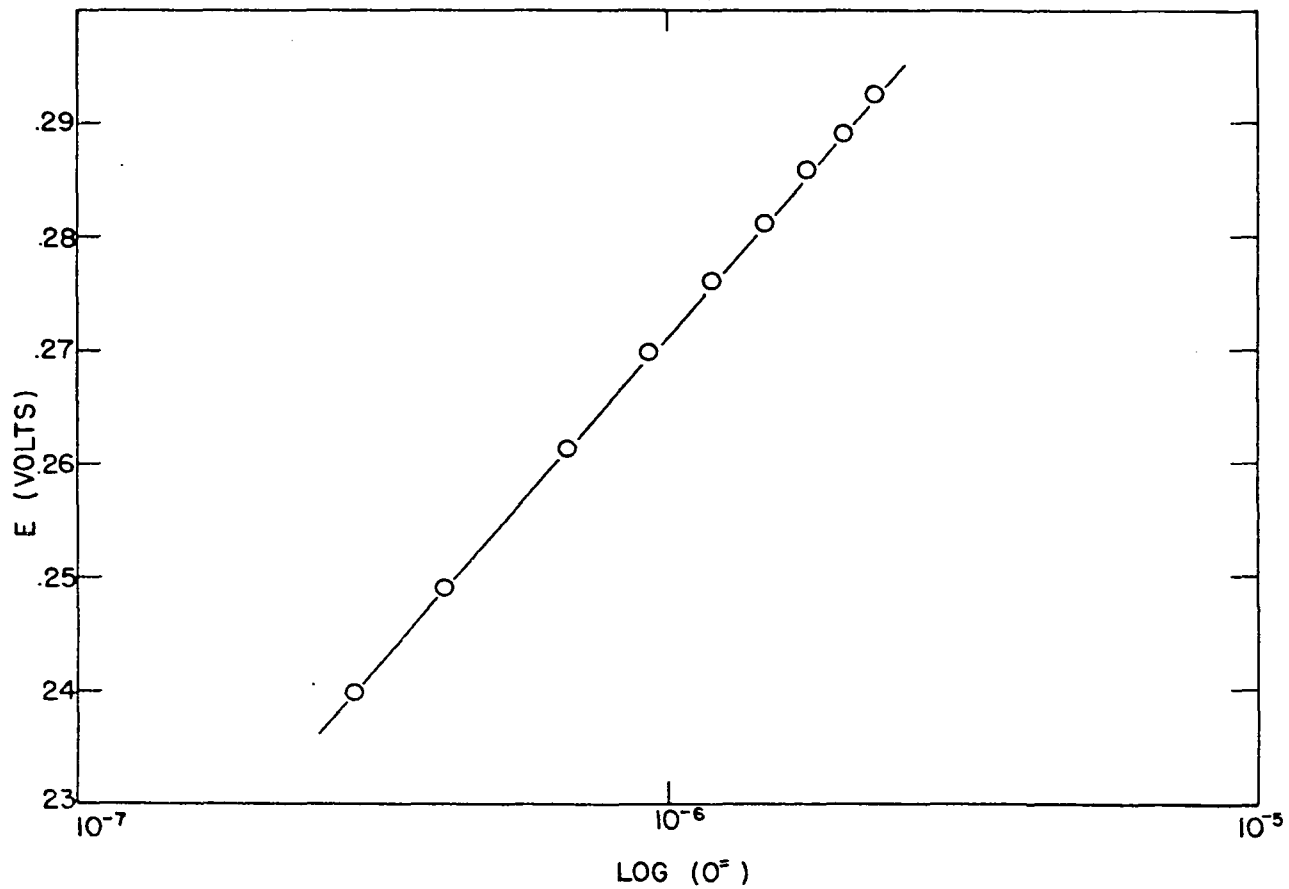cation ratio had little, if any, effect on the standard e.m.f.

Figure 7. Plot of E vs. log (O$^=$) to determine E^O for cell in pure sodium nitrate at 323° C.

An extrapolation of the standard e.m.f. in the pure sodium
nitrate solvent at 323 deg., .6264 volts, was made down to
the temperature 273 deg. C. with the temperature coefficient
given in Table 6. The standard e.m.f. obtained for this
hypothetical solvent was .6383 volts, in good agreement with
the value .6390 volts determined directly in the equimolar
sodium-potassium solvent at 273 deg. C.

<div align="center">Nitrate Ion Dissociation Constant</div>

Discussion

If the nitrate ion dissociates according to reaction
(3), then, in a nitrate solvent, the equilibrium constant
can be written

$$(14) \qquad K_1 = (NO_2^+)\,(O^=) \ .$$

If the concentration of oxide ion is eliminated from equation
(14) and the Nernst expression for the oxygen electrode,
equation (11), the equation

$$(15) \qquad E = E^o - \frac{RT}{2F} \ln \frac{(P_{O_2})^{\frac{1}{2}}(NO_2^+)}{K_1}$$

is obtained. Therefore, it should be possible to determine
K_1 with a measurement of E and nitryl ion concentration at a
known pressure of oxygen. In the presence of the pyrosulfate
anion, equilibrium (5) is established and the nitryl ion
concentration can be represented as a function of the
equilibrium constant of reaction (5), K_2,

$$(16) \qquad (NO_2^+) = \frac{K_2(S_2O_7^=)}{(SO_4^=)^2} \ .$$

Table 6. Variation of E^o with temperature in pure $NaNO_3$
$(O^=) = 1.87 \times 10^{-6}$.

Temp. ^oK	E volts	E^o volts
634.5	.3597	.6157
636.5	.3609	.6160
625.5	.3546	.6183
603.0	.3420	.6235
535.2	.3316	.6262
617.7	.3500	.6193

Slope = (- 2.39 ± .15) x 10^{-4} volts/deg.[a]

[a] Obtained from least squares analysis.

Since the nitryl ion and the pyrosulfate ion are both acidic, define T_a, the total acidity, as the sum of their concentrations,

$$(17) \qquad T_a = (S_2O_7^=) + NO_2^+) \ .$$

The nitryl ion concentration can be eliminated from equations (16) and (17) to give the expression

$$(18) \qquad T_a = (S_2O_7^=)(1 + \frac{K_2}{(SO_4^=)^2}) \ .$$

If the pyrosulfate ion concentration is eliminated from (18) and (16), the nitryl ion concentration can be expressed

$$(19) \qquad (NO_2^+) = \cfrac{T_a}{1 + \cfrac{(SO_4^=)^2}{K_2}} \, .$$

When this expression for the nitryl ion concentration is substituted into equation (15), the equation

$$(20) \qquad E = E^O - \frac{RT}{2F} \ln \frac{(P_{O_2})^{\frac{1}{2}} T_a}{K_1(1 + \frac{(SO_4^=)^2}{K_2})}$$

results. Therefore, K_1 can be determined from a measurement of E and T_a at a known oxygen pressure, since the sulfate ion concentration can be made sufficiently large so that the additional sulfate produced from the pyrosulfate decomposition will be small in comparison.

Pyrosulfate-sulfate equilibrium constant

Duke and Yamamoto (10) have determined the constant K_2 for reaction (5) by following the kinetics of the pyrosulfate decomposition in nitrate solvents for which the rate expression (8) was developed. Because of the relatively large probable errors in the data given by Duke and Yamamoto, it seemed advisable to redetermine K_2 with the oxygen electrode.

It might be expected that this physical method of determination would be more accurate than the chemical method used by these workers.

Equation (8) indicates that the rate of the decomposition is pseudo-first order in total acidity. Therefore, a plot of log T_a against time should give a straight line. Since the oxide ion concentration is inversely proportional to the total acidity, the potential of the oxygen electrode should be a linear function of log T_a. Therefore, a plot of potential against time should be a straight line, with a slope equal to $RTk'/2F$, where k' is the pseudo-first order rate constant.

Pseudo-first order rate constants were determined at 250, 275 and 300 deg. C. for known sulfate concentrations. The data obtained are listed in Tables 7, 8, and 9 along with the reciprocal of k'. The values of the reciprocal of k' at each temperature were plotted against the square of the sulfate ion concentration. This procedure is illustrated in Figures 8, 9, and 10. The ordinate intercept on these graphs is the specific rate constant for the pyrosulfate decomposition. The equilibrium constant K_2 is obtained by dividing the ordinate intercept, $\frac{1}{k}$, by the slope, $\frac{1}{kK_2}$.

The values of K_2 and k obtained for the three temperatures are listed in Table 10.

In the determination of the rate and equilibrium constant for the pyrosulfate decomposition at 300 deg. C., two different flow rates were used. As indicated in Table 10, the specific rate constant is dependent on the rate of gas flow but the equilibrium constant isn't. This observation agrees with that of Duke and Yamamoto (10).

Table 7. Pseudo rate constants and reciprocals at various $SO_4^=$ ion concentrations at 250 deg. C. Flow rate of sweep gas is .152 1/min.

$(SO_4^=)$ m.	$(SO_4^=)^2$x 10^3 m.^{2}	k' x 10^{-2} min.$^{-1}$	$\frac{1}{k'}$ min.
.124	15.4	1.00	100.0
.0612	3.74	2.05	48.7
.0422	1.78	2.61	38.3
.142	20.2	.819	122.0
.0728	5.31	1.79	55.8
.116	13.4	1.12	89.5
.0884	7.82	1.415	70.5

Table 8. Pseudo rate constants and reciprocals at various $SO_4^=$ ion concentrations at 275 deg. C. Flow rate of sweep gas is .270 1./min.

$(SO_4^=)$ m.	$(SO_4^=)^2$x 10^3 m.^{2}	k' x 10^{-2} min.$^{-1}$	$\frac{1}{k'}$ min.
.0579	3.35	6.32	15.8
.1185	14.05	4.63	21.6
.158	24.9	3.43	29.1

Table 9. Pseudo rate constants and reciprocals at various $SO_4^=$ ion concentrations at 300 deg. C.

Flow rate 1/min.	$(SO_4^=)$ m.	$(SO_4^=)^2 \times 10^3 m^2$	$k' \times 10^{-2} min^{-1}$	$\frac{1}{k'}$ min.
.238	.0595	3.56	1.49	6.7
.238	.150	22.5	1.14	8.8
.238	.179	32.4	.99	10.1
.238	.0348	1.21	1.61	6.21
.085	.1498	22.4	1.04	9.60
.085	.0877	7.7	1.28	7.80
.085	.051	2.61	1.48	6.76
.085	.0585	3.41	1.40	7.10
.085	.170	29.0	.94	10.65

Table 10. Specific rate and equilibrium constants for the pyrosulfate decomposition in an equimolar (Na,K) NO_3 solvent.[a]

$T^{\circ}C.$	$k \times 10^3 min^{-1}$	$K \times 10^3$ Ref. (10)	$K \times 10^3$ This study
250	31 ± 6	26	$7.25 \pm .74$
275	74 ± 3		$21.82 \pm .22$
290	86 ± 3 [b]		$37.80 \pm .38$ [b]
300	162 ± 1 [c]	38	$50.83 \pm .02$ [c]
	149 ± 1 [d]		$50.38 \pm .13$ [d]

[a] All results calculated from least squares analysis.
[b] Obtained from NO_2 gas electrode.
[c] Flow rate .238 l/min.
[d] Flow rate .085 l/min.

From the temperature dependence of the equilibrium constant the heat of reaction for the pyrosulfate decomposition was obtained. If the thermodynamic relation

$$\Delta G^O = -RT\ln K$$

is substituted into equation (13), and if the resulting equation is integrated under the assumption that ΔH^O is constant over the temperature range under consideration, the equation

$$(21) \qquad \ln K = -\frac{\Delta H^O}{RT} + I$$

is obtained, where I is an integration constant.

The common logarithm of the equilibrium constant was plotted against the reciprocal of the absolute temperature. This plot is illustrated in Figure 11. The slope of the resulting line, which was $\Delta H^O/4.6$, led to the value $45.2 \pm .7$ kcal./mole for ΔH^O.

A comparison of the equilibrium constants for the pyrosulfate decomposition obtained by Duke and Yamamoto (10) with those obtained in this study, indicates agreement only within an order of magnitude. It is considered that the equilibrium constants determined in this work are based on more accurate experimental data. The specific rate constants cannot be compared because of the different flow rates of the sweep gas.

Determination of total acid

The concentration of total acid, T_a, present at any time was determined by an iodometric titration. A sample
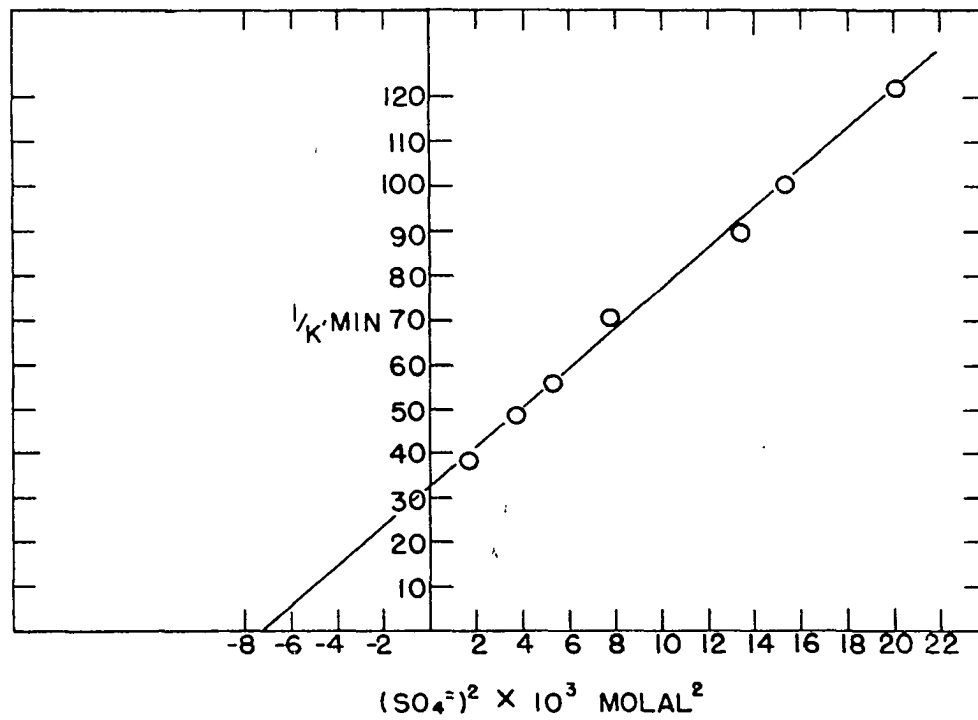
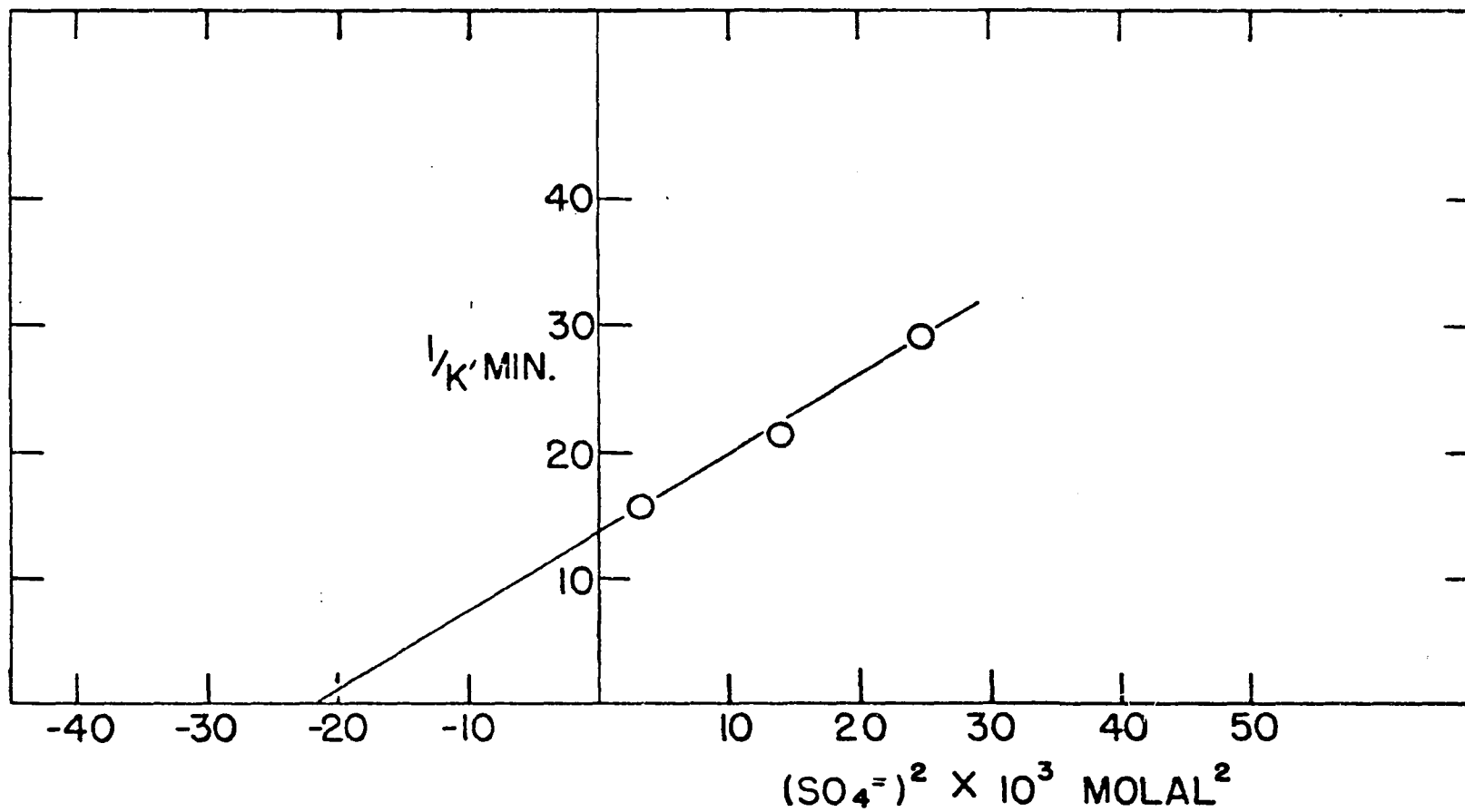Figure 8. Plot of reciprocal rate data vs. $(SO_4^=)^2$ to determine k and K at 250° C.

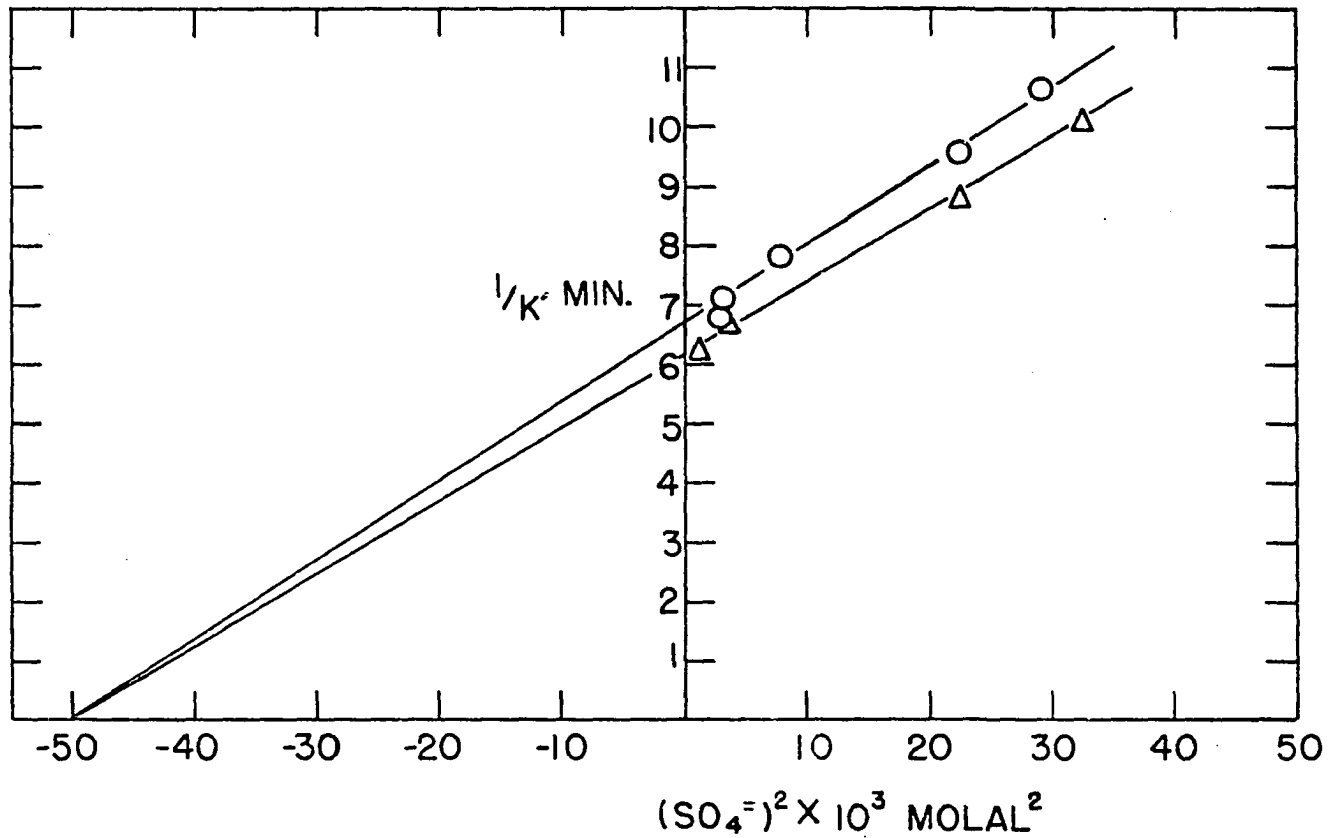Figure 9. Plot of reciprocal rate data vs. $(SO_4^=)^2$ to determine k and K at 275° C.

Figure 10. Plot of reciprocal rate data vs. $(SO_4^=)^2$ to determine k and K at 300° C.

was withdrawn from the reaction vessel in a preheated

pipette. After being weighed, the sample was dissolved in

water. The pyrosulfate and nitryl ions present reacted with

water to produce H^+ according to the reactions

$$S_2O_7^= + H_2O = 2\ SO_4^= + 2\ H+$$

$$NO_2^+ + H_2O = NO_3^- + 2\ H^+ .$$
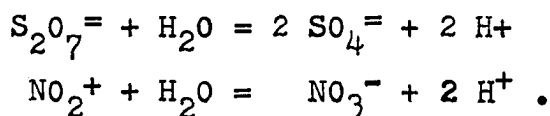
Hence $T_a = (S_2O_7^=) + (NO_2^+) = 2\ (H^+)$. Excess potassium

iodide and potassium iodate were added to the solution.

These reacted with the H^+ to give free iodine

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_2 + 3\ H_2O.$$
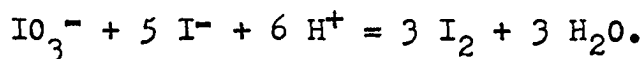
The iodine was then titrated with sodium thiosulfate, the

end point being determined with a starch indicator.

To determine the e.m.f. corresponding to a known total

acid concentration at 250 deg. C., several samples were

withdrawn from a pyrosulfate decomposition reaction in which

the initial sulfate ion concentration was 8.84×10^{-2} molal.

The results obtained are listed in Table 11. Similar data

were obtained at 300 deg. C. with an initial sulfate ion

concentration of .170 molal, and are listed in Table 12.

Calculation of NO_3^- dissociation constant

Equation (20) was used to calculate the dissociation

constant for the nitrate ion. The standard e.m.f. of the

oxygen - silver electrode system is .6420 volts at 250

deg. C. and .6290 volts at 300 deg. C. The equilibrium

constant for the pyrosulfate - sulfate equilibrium, K_2 ,

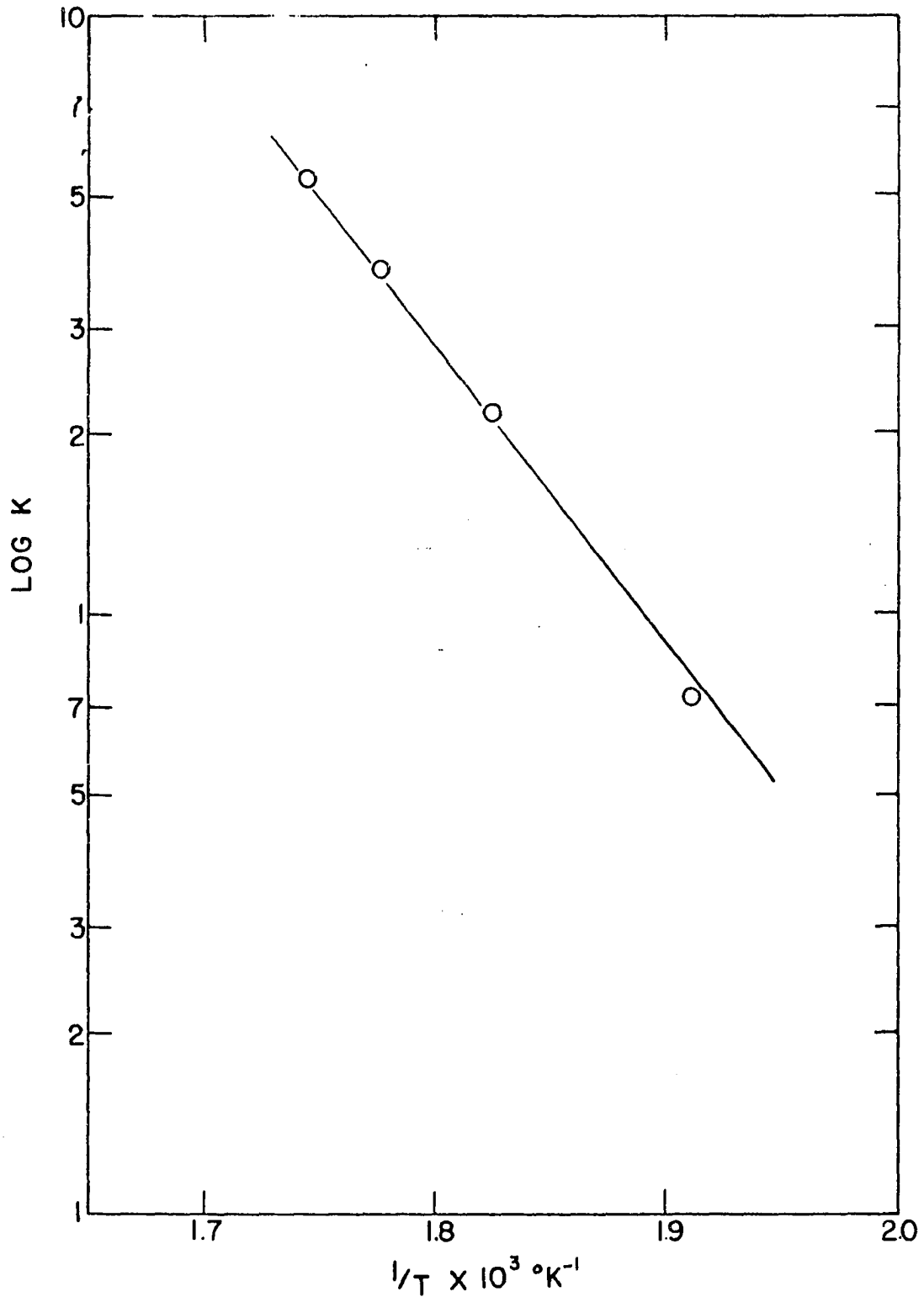is 7.25×10^{-3} at 250 deg. C. and 50.45×10^{-3} at 300 deg. C.

Figure 11. Plot of log K vs. the reciprocal of the
absolute temperature to determine ΔH of
reaction for the pyrosulfate dissociation.

Table 11. Variation of e.m.f. with T_a at 250° C. Initial
$(SO_4^=) = 8.84x10^{-2}$m. P_{O_2} = .104 atm.

Sample	Time	T_a x 10^3 m.	E volts .
1	60 min.	4.13	-.5094
2	75 min.	3.60	-.5052
3	90 min.	3.47	-.4994
4	105 min.	3.14	-.4970
5	4 hrs.	1.25	-.4696
6	5 hrs.	.791	-.4558
7	6 hrs.	.681	-.4462

Table 12. Variation of e.m.f. with T_a at 300° C. The
initial $(SO_4^=)$ = .170 molal. P_{O_2} = .354 atm.

Sample	Time	T_a x 10^3 m.	E volts
1	6 min.	11.30	-.5222
2	10 min.	10.52	-.5100
3	16 min.	8.63	-.4943
4	25 min.	6.94	-.4785
5	30 min.	6.04	-.4710
6	38 min.	5.28	-.4631

If these values are substituted into equation (20) and if
the resulting equation is solved for the nitrate ion
dissociation constant, K_1, the following relations are
obtained:

$$(22) \quad \log K_1(250) = \frac{E - .6839}{.0518} + \log T_a$$

$$(23) \quad \log K_1(300) = \frac{E - .6529}{.0568} + \log T_a \; .$$

The values for K_1 obtained from the data in Tables 11 and 12 are listed in Table 13.

Table 13. Variation of K_1 with time.

Temp. °C.	Time	$-\log K_1$	K_1
250	60 min.	25.421	3.79×10^{-26}
	75 min.	25.400	3.98 "
	90 min.	25.307	4.93 "
	105 min.	25.300	5.01 "
	4 hrs.	25.171	6.74 "
	5 hrs.	25.103	7.89 "
	6 hrs.	24.983	10.40 "
300	6 min.	22.635	2.317×10^{-23}
	10 min.	22.451	3.540 "
	16 min.	22.261	5.483 "
	25 min.	22.078	8.356 "
	30 min.	22.005	9.886 "
	38 min.	21.924	11.91 "

At both temperatures the value of K_1 increased with time. This can be explained if account is taken of the increase of the sulfate ion concentration with time due to

the decomposition of the pyrosulfate. The derivation of
equation (20) assumed that this concentration was constant.
If the values of K_1 at each temperature are plotted against
time, a straight line is approximated. Therefore, an
extrapolation to zero time should give the true dissociation
constant of the nitrate ion. A least squares extrapolation
gave the following values for the true dissociation constant:

$$K_1(250) = (2.74 \pm .27) \times 10^{-26}$$

$$K_1(300) = (5.66 \pm .1) \times 10^{-24} .$$

If the assumption is made that the enthalpy of dissociation
is constant in the temperature range 250-300 deg. C.,
substitution into the familiar Clausius-Clapeyron equation

$$\text{Log} \frac{K_1(300)}{K_1(250)} = \frac{\Delta H(T_2-T_1)}{2.3RT_2T_1}$$

gives the enthalpy of dissociation the value 63.8 kcal/mole.

Carbonate Ion Dissociation Constant

Dissolved in an equimolar sodium-potassium nitrate
solvent, sodium carbonate exhibits strong basic properties.
Acids such as pyrosulfate and dichromate are quickly
neutralized. The basic nature of the carbonate ion can be
attributed to a dissociation

$$(24) \qquad CO_3^{=} = CO_2 + O^{=}$$
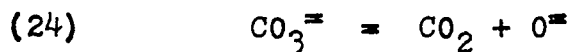
in which oxide ion is produced. The determination of the
dissociation constant for reaction (24) should be straight
forward if the oxygen electrode previously described is

used. The concentration of the oxide ion can be obtained from the e.m.f. This value can be substituted into the dissociation constant expression and, if the CO_2 pressure is maintained at a constant value, the value of the dissociation constant can be calculated if the initial carbonate ion concentration is known.

To 400 grams of equimolar sodium-potassium nitrate solvent .3184 grams of sodium carbonate were added to give a carbonate ion concentration of 8.99×10^{-3} molal if it is assumed that 100% dissociation takes place. Voltage and pressure measurements gave the dissociation constants listed in Table 14.

Table 14. Carbonate ion dissociation constant at 300° C. Initial $(CO_3^=) = 8.99 \times 10^{-3}$ m.

| P_{CO_2} atm.	P_{O_2} atm.	E volts	K
.24	.72	.3157	6.91×10^{-5}
.41	.56	.3044	6.50×10^{-5}

These values for the dissociation constant for the carbonate ion appeared to be much too large. From thermodynamic information available (18, 29) the Gibbs free energy change for the reaction

$$(25) \qquad Na_2CO_3(solid) = Na_2O(solid) + CO_2 \text{ (gas)}$$
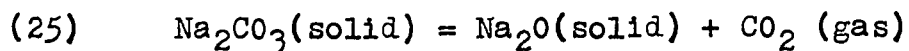
at 600 deg. K. was calculated to be about 55 kcal/mole which would give a dissociation constant on the order of 10^{-20}.

Although there was no information available concerning the solvation energies of the various ionic species in solution, it did not seem reasonable that the difference of 14 to 15 orders of magnitude in the dissociation constants of reactions (24) and (25) could be accounted for in this manner. It seemed possible that some other equilibrium was occuring which would reduce the activity of the oxide ion.

One very likely process which could occur would be the reaction of a nitrate ion with an oxide ion to form an orthonitrate ion

$$(26) \qquad NO_3^- + O^= = NO_4^{-3} .$$
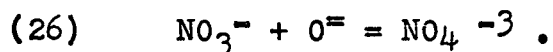
Although the existence of such an ion has not been unequivocally demonstrated, several researchers have offered evidence in support of such an ion. It was first mentioned in 1938 by Zintl and Morawietz (30) to explain the products of a reaction between sodium oxide and sodium nitrate. More recently Kohlmuller (19) prepared both sodium and potassium orthonitrates and offered thermogravimetric analyses in support of the existence of the orthonitrate ion.

The presence of nitrate as the solvent anion renders any chemical method for the determination of a change in the nitrate ion activity almost useless. To make such measurements a different solvent is needed, to which small amounts of nitrate ion could be added. Since anhydrous lithium perchlorate is liquid in the temperature range of interest, 250-350 deg. C., and since it has an oxy-anion, it could

possibly serve as a solvent in which to study the equilibrium (26).

The following qualitative experiment was performed. A known quantity of lithium oxide was added to a known quantity of anhydrous lithium perchlorate which had been fused. The potential between a silver-glass electrode, similar in nature to the reference electrode previously described in this study, and an oxygen gas-platinum electrode was measured. Additional quantities of lithium oxide were added, the potential increasing after each addition. This indicated that the electrode system was at least responding to an increase in oxide ion concentration. Then, known amounts of lithium nitrate were added at different times. After each addition of lithium nitrate the potential of the electrodes was observed to decrease. This decrease in potential indicated that the activity of the oxide ion was being decreased. More quantitative measurements could not be made at this time because of the uncertainty as to the degree of dissociation of lithium oxide

$$Li_2O = LiO^- + Li^+$$

$$LiO^- = Li^+ + O^=$$
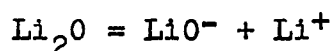
and because of the attack of the lithium salts on the pyrex reaction vessel. However, it is felt that these qualitative observations lend support to the formation of the orthonitrate ion. A spectroscopic analysis is needed to definitely prove the existence of the orthonitrate ion.

SUMMARY

A practical electrode system involving an oxygen
electrode and a silver-glass electrode was developed for use
in an equimolar sodium-potassium nitrate solvent. The
reversibility of this system was established and the standard
e.m.f. and the temperature dependence of the standard e.m.f.
were determined. From this information, the ΔG°, ΔH°, and
ΔS° for the cell reaction were calculated. The standard
e.m.f., the temperature dependence of the standard e.m.f.,
ΔG°, ΔH°, and ΔS° were also determined for this oxygen
electrode in a pure sodium nitrate solvent. Close agreement
of the ΔH° and ΔS° values indicated that the standard e.m.f.
of the electrode system was independent of the Na^{+} to K^{+}
ratio of the solvent. This electrode system made possible
the direct measurement of oxide ion concentration.

The equilibrium constant for the reaction

$$S_2O_7^{=} + NO_3^{-} = 2SO_4^{=} + NO_2^{+}$$
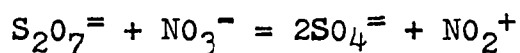
was reevaluated and more accurate values for several
temperatures were obtained than those previously published.
Also the ΔG°, ΔH°, and ΔS° for this reaction were determined.
With the aid of these equilibrium constants the dissociation
constant of the nitrate ion in nitrate solvents was deter-
mined at two temperatures. The ΔH° for the nitrate ion
dissociation was calculated.

The dissociation constant for the decomposition of the

carbonate ion in an equimolar sodium-potassium nitrate solvent was determined. The value obtained was much larger than would be expected from known thermodynamic information. The reaction of an oxide ion with a nitrate ion to give an orthonitrate ion

$$NO_3^- + O^= = NO_4^{-3}$$
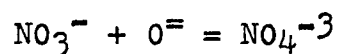
was proposed to explain the apparent lowering of the oxide ion activity. In support of this proposition, it was shown that the addition of nitrate ion to anhydrous lithium perchlorate containing a known quantity of lithium oxide lowered the activity of the oxide ion a small amount.

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