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# Acid-base equilibria in fused alkali nitrates

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# ACID-BASE EQUILIBRIA IN FUSED ALKALI NITRATES

by

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Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1959

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# DEDICATION

To my parents

# I. INTRODUCTION

In recent years there has been great interest in the study of high temperature systems. Consequently, an increasing need for physico-chemical information on fused salt systems has arisen. In addition to its technological significance, it is of theoretical importance in the understanding of the liquid state. Furthermore, the knowledge of the structure of molten salts would aid in the understanding of concentrated solutions of electrolytes.

There are no good direct methods of investigating the structure of fused salts. Some interesting attempts have been made by means of X-ray diffraction studies (1, 2) and, recently, by spectrophotometric methods (3), but little direct information has been obtained. Thus it becomes necessary to resort to a study of the various properties of fused salts such as conductivities, viscosities, surface tensions, and activities. The activity of a component is actually a useful empirical number, which is of theoretical interest since it can be traced to forces of interaction between ions in the fused mixture and to their arrangement in space. A convenient method of studying activities is the study of acid-base equilibria.

The subject of acids and bases is one of the most interesting in chemistry. As a result, numerous concepts and definitions of acids and bases have been developed (4).

Among these the most widely known are the protonic concept of Brønsted (5) and Lowry (6) and the electronic concept developed by G. N. Lewis (7). According to the Brønsted concept, acids and bases are characterized and interrelated by the equation

$$\text{Acid} = \text{Base} + H^{+}.$$

An obvious limitation of this definition is that acids and bases are limited to hydrogen containing compounds. The Lewis electronic concept is more general than the protonic comcept. Indeed, the Brønsted theory is a special case of the Lewis theory. In terms of the Lewis theory, an acid is an atom, molecule or ion which can accept an electron pair.

Oxides have long been connected with acid-base character. For example, CaO and MgO are known as basic oxides and $SiO_2$ and $CO_2$ as acidic oxides. An acid-base reaction is the formation of a salt, for example,

$$SiO_2 + CaO = CaO{\cdot}SiO_2.$$

In 1939 Lux (8) announced a more precise acid-base definition which is suitable for oxides. According to his definition

$$\text{Base} = \text{Acid} + O^{--}.$$

For example,

$$CaO = Ca^{++} + O^{--}$$

and

$$SO_4^{--} = SO_3 + O^{--}.$$

This definition is analogous to that of Brønsted and, like the latter, can be reduced to one part of the more general theory of Lewis. The Lux concept is obviously limited; it excludes the possibility of regarding analogous reactions of sulfides and flourides as acid-base reactions. The usefulness of this theory in fused salts can be understood in view of the fact that many solvent systems in use are oxides or oxy-anions. Flood and Forland (9) have pointed out that acid strengths may be compared in oxide systems by comparing the magnitudes of the equilibrium constants defined as

$$K = a_{acid}\ a_{O^{-2}}/a_{base}.$$

It is the purpose of this thesis to study some acid-base reactions and establish a "scale of acidity" in alkali nitrate solvents.

## II. LITERATURE REVIEW

Equilibrium studies have been made of a number of acid-base systems in fused salts. Flood and his co-workers (10) studied the equilibrium

$$CaCO_3 = CaO(s) + CO_2(gas)$$

in various alkali carbonate melts by noting the decrease in weight as the temperature was raised. From their results they calculated activity coefficients and showed that the carbonate mixtures behaved as "regular solutions", which means that the entropy of mixing is the same as that for ideal mixtures.

Flood and Forland (11) studied the thermal decomposition of several pure pyrosulfates. The equilibrium reaction is

$$S_2O_7^{--} = SO_4^{--} + SO_3(gas).$$

They obtained values for

$$K = \frac{N_{SO_4^{--}} P_{SO_3}}{N_{S_2O_7^{--}}},$$

where N is the mole fraction, by determining the ratio $N_{SO_4^{--}}/N_{S_2O_7^{--}}$ in melts in equilibrium with $SO_3$ at a known pressure. The stability of the pyrosulfates increased in the order Ag, Li, Na-Tl, and K, which indicated that the stability of the oxygen bridge is highly influenced by the polarizing power of the cation. In general, the stability of the pyrosulfate ion decreases with decreasing radius and increasing polarizing power of the cations present. A similar reaction, the thermal decomposition of dichromate was investigated by Flood and Muan (12). The equilibrium is written

$$Cr_2O_7^{--} = CrO_4^{--} + \tfrac{1}{2}Cr_2O_3 + 3/4\ O_2.$$

The stability of the dichromates was found to increase in the order Tl, Na, and K.

Duke and Iverson (13) studied the reaction

$$2Cr_2O_7^{--} + 4NO_3^{-} = 4NO_2 + O_2 + 4CrO_4^{--}$$

in fused $KNO_3$-$NaNO_3$ eutectic. They showed that the mechanism consisted of two steps: the equilibrium

$$Cr_2O_7^{--} + NO_3^{-} = CrO_4^{--} + NO_2^{+}$$

followed by the slow step

$$NO_2^{+} + NO_3^{-} = \text{decomposition products.}$$

This equilibrium differs from those discussed earlier in that the equilibrium constant is very small. Therefore, the equilibrium was investigated kinetically by studying a reaction of the acidic product, the nitronium ion. From their results they were able to find values for the product of the equilibrium constant and the rate constant but were unable to separate the two quantities.

Aside from the above work, very little information on rate studies in fused salts is available. Freeman (14) studied the kinetics of thermal decomposition of $NaNO_3$ and the reverse reaction between $NaNO_2$ and oxygen by noting volume changes. On the basis of his results and calculations, he postulated the mechanism

$$NaNO_3 = NaNO_2 + O$$

$$O + NaNO_3 = NaNO_2 + O_2.$$

Freeman also studied the decomposition of $KNO_3$ by similar methods (15) and showed that the mechanism was the same as that for $NaNO_3$. An investigation of the decomposition of the perchlorates of Mg, Ca, Ba, and Al was conducted by Zinov'ev and Chadinova (16). They reported that the decomposition reaction consisted of a series of rather interesting reactions:

$$2Mg(ClO_4)_2 = Cl_2O_7 + (MgClO_4)_2 O \qquad 410^\circ$$

$$Cl_2O_7 = Cl_2 + 3.5O_2 \qquad 410^\circ\text{-}463^\circ$$

$$(MgClO_4)_2O = ClMg{\cdot}O{\cdot}MgClO_4 + 2O_2 \qquad 499^\circ\text{-}510^\circ$$

$$ClMg{\cdot}O{\cdot}MgClO_4 = (MgCl)_2O + 2O_2 \qquad 547^\circ.$$

Among the perchlorates, $KClO_4$ has been the object of considerable attention (17, 18, 19). The decomposition products are $ClO_3^-$, $O_2$, and $Cl^-$. Several mechanisms have been proposed and the most recent of these is (19):

$$KClO_4 = KClO_3 + O$$

$$KClO_3 = KCl + 3/2\ O_2$$

$$KClO_3 = 3/4\ KClO_4 + \tfrac{1}{4}KCl$$

where the first reaction is rate determining. Pechkovskii (20) studied the rate of decomposition of $MgSO_4$, that is,

$$MgSO_4 = MgO + SO_3$$

$$SO_3 = SO_2 + \tfrac{1}{2}O_2 .$$

Most of the rate studies in fused salts have been investigations of the decomposition of pure salts. One of the objectives of this thesis is to study some decomposition reactions in nitrate solvents.

## III. THE PYROSULFATE-NITRATE REACTION

### A. Experimental

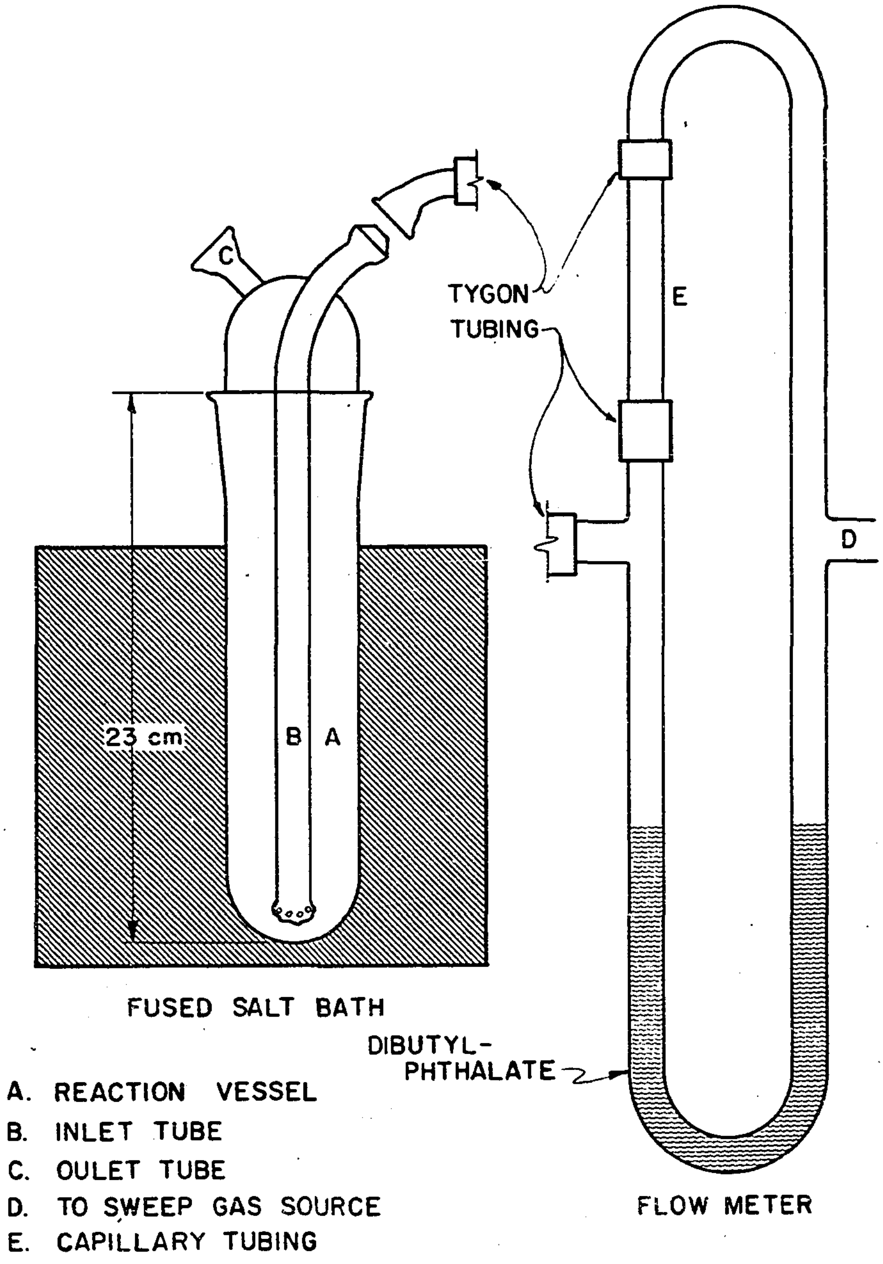
### 1. Materials and apparatus

A. C. S. reagent grade chemicals were used. All the rate determinations were carried out in an apparatus similar to that described by Duke and Iverson (13). The apparatus is shown in Figure 1. A test tube shaped reaction vessel was immersed in a constant temperature bath consisting of a molten eutectic mixture of $LiNO_3$, $NaNO_3$, and $KNO_3$. The fused salt bath was contained in an insulated enameled iron vessel 11 inches in diameter and 8 inches in depth. The temperature was maintained to within one degree of the required temperature with a chromel-alumel thermocouple connected to a Celectray controller (Weston Electrical Instrument Company).

The reaction vessel was made from a 32 mm O. D. Pyrex tube which was 10 inches long. A 34/45 standard taper joint was attached at the top. On the cap of the vessel were a gas outlet tube and a gas inlet tube which extended to within ½ inch of the bottom of the reaction vessel.

At first a coiled glass tube was immersed in the bath in order to preheat the nitrogen sweep gas. This was discontinued since it was found that there was no measurable difference between the bath temperature and that of the

Figure 1. Reaction vessel and flow meter


C
TYGON
TUBING
E
D
23 cm
B
A
FUSED SALT BATH
DIBUTYL-
PHTHALATE
FLOW METER
A. REACTION VESSEL
B. INLET TUBE
C. OULET TUBE
D. TO SWEEP GAS SOURCE
E. CAPILLARY TUBING

reaction melt with or without preheated gas.

The flow rate of the sweep gas was measured by means of a manometer, which was calibrated with a Precision Wet Test Gas Meter.

## 2. Procedure

All chemicals were dried for 2-3 hours at 110°C.

The rate of reaction was first studied by following the evolution of nitrogen dioxide. This was accomplished by adsorbing the gas onto Ascarite. However, at the nitrogen flow rate used during the runs, it was apparent that all of the evolved gas was not being adsorbed. The reaction was then followed by analyzing the acidity of the aqueous solutions of the samples which were drawn from the reaction mixture. The analysis made use of the reaction

$$KIO_3 + 5KI + 6H^+ = 6I^\circ + 6K^+ + 3H_2O$$

and the thiosulfate-iodine reaction (21).

The procedure was as follows: 100 grams of the solvent, $KNO_3$- $NaNO_3$ eutectic, were weighed out and melted in the reaction vessel. The desired amount of $Na_2SO_4$ was added and dry nitrogen gas was bubbled through the melt for 1-2 hours. Solid $K_2S_2O_7$ was then added to the melt. Samples were drawn out at periodic intervals by means of the preheated dropper. After cooling, the samples were weighed and dissolved in water. To the aqueous solution, excess KI and $KIO_3$ were added and the solution was then titrated with 0.01 N $Na_2S_2O_3$ using a starch indicator. The water used in the analysis was first boiled and then stored in a flask protected by a drying tube containing Ascarite. Furthermore, the samples were dissolved just prior to the titration. These precautions were taken in order to minimize the error due to the solubility of $CO_2$ from the air.

a. Solubility studies The solubility of $Na_2SO_4$ in the eutectic solvent was studied in the following manner: molten solvent in a large test tube was saturated with $Na_2SO_4$ at a temperature 25 degrees higher than the desired temperature. The melt was stirred by bubbling nitrogen for at least one hour. After cooling to the desired temperature and allowing the excess $Na_2SO_4$ to settle, samples of 4-8 grams were removed with a preheated dropper. Since undissolved sodium sulfate settled to the bottom of the tube, no filtration was necessary. After cooling, the samples were weighed and gravimetrically analyzed for sulfate.

## B. Results and Discussion

Preliminary investigations of the decomposition of $K_2S_2O_7$ in $KNO_3$-$NaNO_3$ eutectic showed that the reaction proceeds rapidly at 235°C with evolution of nitrogen dioxide. Addition of $Na_2SO_4$ retarded the reaction, which indicated that an equilibrium is involved. It was also found that the rate increased when the nitrogen flow rate was raised. The order with respect to $S_2O_7^{--}$ was one and was independant of the nitrogen flow rate.

The above observations coincide with the results observed by Duke and Iverson (13) for the decomposition of dichromate ion in the same solvent. It is, therefore, reasonable to expect the mechanism for the pyrosulfate reaction to be analogous to that of the dichromate reaction. The mechanism can be written as the equilibrium

$$S_2O_7^{--} + NO_3^- = NO_2^+ + 2SO_4^{--} \qquad (1)$$

followed by the slow step

$$NO_2^+ + NO_3^- = \text{decomposition products.} \qquad (2)$$

It is interesting to note that Gillespie and Graham (22) studied the effect of nitric acid on the freezing point of oleum and proposed the reactions

$$HNO_3 + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4$$

$$HNO_3 + HS_2O_7^- = NO_2^+ + 2HSO_4^- \ .$$

The rate studies were carried out at 235°C and 275°C. The nitrogen flow rate was 0.21 liters per minute for all the runs. This is the flow rate used in the dichromate study and was utilized in this work so that the two reactions could be compared. The pseudo-first order rate constants, obtained from log $(H^+)$ versus time plots, are shown in Tables 1 and 2. The low values for 0.20 m $SO_4^{--}$ at 235° and 0.30 m $SO_4^{--}$ at 275° are probably due to supersaturation of the melt with $SO_4^{--}$.

It was first thought that the acidity of the aqueous solutions of the samples was due entirely to the hydrolysis of $S_2O_7^{--}$. Hence the concentration of $S_2O_7^{--}$, in terms of moles per 1000 grams of solvent, was calculated from the acidity and weight of the sample. In view of equations 1 and 2, the rate law was expressed as

$$\frac{d(S_2O_7^{--})}{dt} = -k(NO_2^+). \qquad (3)$$

Substituting the equilibrium constant

$$K = \frac{(SO_4^{--})^2(NO_2^+)}{(S_2O_7^{--})} \qquad (4)$$

into equation 3, one gets

Table 1. The variation of the pseudo first rate constants with sulfate ion at 235° C.

| Initial ($SO_4^{--}$) m | k' minutes$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | 0.01m $S_2O_7^{--}$ | 0.02m $S_2O_7^{--}$ | | 0.03m $S_2O_7^{--}$ | | "Average"[a] |
| | | Run I | Run II | Run I | Run II | x10$^2$ |
| 0 | - | 0.0853 | 0.100 | - | - | 8.9 ± 0.5 |
| 0.05 | - | 0.0344 | 0.0419 | - | - | 3.7 ± 0.4 |
| 0.08 | - | - | - | 0.0315 | - | 3.2 |
| 0.10 | - | 0.0265 | - | 0.0224 | 0.0320 | 2.8 ± 0.4 |
| 0.125 | - | 0.023 | 0.021 | - | - | 2.2 ± 0.1 |
| 0.15 | - | 0.0197 | 0.0204 | 0.0213 | - | 2.1 ± 0.1 |
| 0.175 | - | 0.019 | 0.018 | - | - | 1.8 ± 0.03 |
| 0.20 | 0.0164 | 0.0134 | 0.0154 | 0.0106 | 0.0161 | 1.5 ± 0.2 |
| 0.21 | 0.0150 | - | - | - | - | 1.5 |
| 0.22 | 0.0159 | - | - | - | - | 1.6 |
| 0.25 | - | - | 0.0150 | 0.0173 | 0.0161 | 1.6 ± 0.1 |

[a] The average k' was obtained by plotting all the data for a particular sulfate concentration on the same graph and drawing the best straight line through all the points.

$$\frac{d(S_2O_7^{--})}{dt} = -kK\frac{(S_2O_7^{--})}{(SO_4^{--})^2} \; . \qquad (5)$$

One can readily see that if the change in the sulfate ion concentration is small during a reaction, the pseudo first order rate constant can be written as

$$k' = \frac{kK}{(SO_4^{--})^2} \; . \qquad (6)$$

Table 2. The variation of the pseudo first order rate constant with sulfate ion concentration at 275°C. (0.02m $S_2O_7^{--}$)

| $(SO_4^{--})$ m | k'<br>Run I | <br>Run II |
|---|---|---|
| 0.07 | 0.091 | 0.083 |
| 0.10 | 0.077 | 0.075 |
| 0.15 | 0.054 | 0.052 |
| 0.20 | 0.048 | 0.050 |
| 0.225 | 0.042 | 0.042 |
| 0.25 | 0.034 | 0.042 |
| 0.30 | 0.030 | 0.035 |
| 0.34 | 0.034 | - |

However when kK was calculated, it increased as the initial sulfate ion concentration increased, indicating that this expression for k' is incorrect. The following calculation involving equation 3 was then made. A plot of $(S_2O_7^{--})$ versus time was made and normals to the smoothed curve were drawn. Values for $d(S_2O_7^{--})/dt$ were obtained from the perpendiculars to the normals. The values for kK were calculated for $(SO_4^{--})^2$, $(SO_4^{--})^1$, and $(SO_4^{--})^0$. The results (see Table 3) seemed to indicate that the order with respect to sulfate is zero, which in fact was not the case.

Table 3. Calculation of kK in equation 5 for $(SO_4^{--})^n$, where n is 0, 1, and 2; 0.03 m $K_2S_2O_7$, 0.10 m $Na_2SO_4$, 235°C., $N_2$ flow rate 0.21 liters per minute

| | $-\frac{d(S_2O_7^{--})}{dt} \times 10^4$ | $(S_2O_7^{--}) \times 10^3$ | $k'_2 \times 10^4$ | $k'_1 \times 10^3$ | $k'_0$ |
|---|---|---|---|---|---|
| 1. | 5.5 | 20.6 | 3.8 | 3.2 | 2.67 |
| 2. | 4.2 | 18.4 | 3.45 | 2.8 | 2.28 |
| 3. | 3.6 | 16.4 | 3.53 | 2.8 | 2.19 |
| 4. | 3.3 | 14.7 | 3.8 | 2.9 | 2.24 |
| 5. | 2.9 | 11.8 | 4.6 | 3.4 | 2.46 |
| 6. | 2.4 | 9.3 | 5.1 | 3.6 | 2.58 |
| 7. | 1.8 | 7.4 | 5.1 | 3.5 | 2.44 |

The possibility of the presence of an appreciable concentration of nitronium ion in the melt was then taken into consideration. The acidity would be due to the reactions

$$S_2O_7^{--} + H_2O = 2H^+ + 2SO_4^{--},$$

and

$$NO_2^+ + H_2O = 2H^+ + NO_3^-.$$

The rate law can be expressed in terms of the total acidity

$$T_A = (S_2O_7^{--}) + (NO_2^+), \qquad (7)$$

that is,

$$-\frac{dT_A}{dt} = k(NO_2^+). \qquad (8)$$

Equations 4, 5, and 7 can be combined to give

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

where the pseudo first order rate constant is

$$k' = \frac{kK}{K + (SO_4^{--})^2}. \qquad (10)$$

The most interesting feature of equation 10 becomes apparent when one considers its reciprocal

$$\frac{1}{k'} = \frac{1}{k} + \frac{(SO_4^{--})^2}{kK}. \qquad (11)$$

If $1/k'$ is plotted against $(SO_4^{--})^2$, the intercept would be $1/k$ and the slope $1/kK$. Hence one can calculate K by dividing the intercept with the slope.

A graph of equation 11 where 1/k' is plotted against the square of the initial sulfate ion concentration is shown in Figure 2. The straight lines show that there is good agreement between the theoretical and observed results. The rate constants and the equilibrium constants were calculated and are given in Table 4.

Table 4. Rate and equilibrium constants and temperature effects on reactions of pyrosulfate and dichromate with fused nitrate

| k | T | $K_{S_2O_7^{--}}$ | T | $K_{Cr_2O_7^{--}}$[a] |
|---|---|---|---|---|
| .038 | 235° | 0.026 | 250° | $8.5 \times 10^{-14}$ |
| .096 | 275° | 0.038 | 300° | $3.8 \times 10^{-12}$ |
| $E_a = 12 \pm 3$ kcal | | $\Delta H = 5$ kcal | | $\Delta H = 50 \pm 5$ kcal |

[a] From extrapolation of data in references (13 and 23).

Using these results and equation 8, the sulfate ion concentrations were calculated for some of the runs. Values for $\frac{dT_A}{dt}$ were obtained from $T_A$ versus time curves. A typical example of the results is shown in Table 5.

Figure 2. Plot of reciprocal rate data versus $(SO_4^{--})^2$ to determine k and K

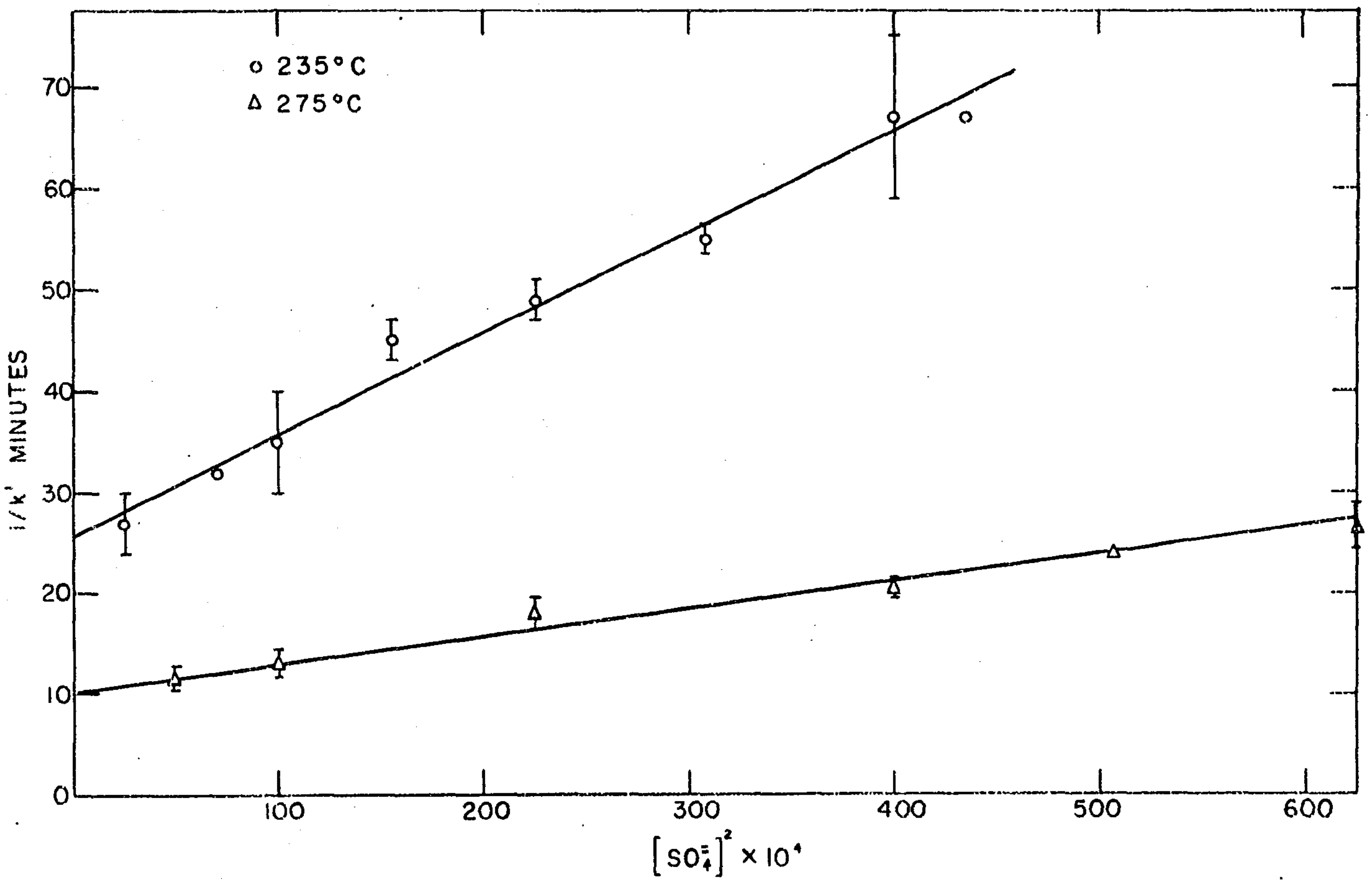

○ 235°C
Δ 275°C
70
60
50
40
30
20
10
0
100
200
300
400
500
600
i/k' MINUTES
$[SO_4^{=}]^2 \times 10^4$

Table 5. Calculation of sulfate ion concentration from equation 8 and K = 0.038. Initial ($SO_4^{--}$) = 0.175m, Initial ($S_2O_7^{--}$) = 0.02m, 275°C., $N_2$ flow rate 0.21 liters per minute

| Time (minutes) | $T_A \times 10^2$ (m) | $-\frac{dT_A}{dt} \times 10^4$ | ($SO_4^{--}$) (m) |
|---|---|---|---|
| 5 | 5.8 | 9.4 | 0.19 |
| 10 | 5.3 | 8.9 | 0.19 |
| 15 | 4.9 | 7.7 | 0.20 |
| 20 | 4.4 | 7.5 | 0.19 |
| 25 | 4.0 | 6.9 | 0.18 |
| 60 | 2.6 | 4.4 | 0.19 |

It should be noted that the sulfate ion concentration increases during the reaction. Consequently, the values for K obtained from the graph may be slightly smaller than the true values. The heat of reaction for the decomposition of one mole of $S_2O_7^{--}$ was calculated by means of the equation

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R} \qquad (12)$$

and the energy of activation, $E_a$, was obtained from the Arrhenius equation

$$k = Ae^{E_a/RT}, \qquad (13)$$

where k is the rate constant. The heat of reaction was 5 kcal and the energy of activation 12 ± 3 kcal.

In the discussions thus far molalities have been used in place of activities. This can be partially justified since the solutions were relatively dilute. At this point, however, it seems appropriate to review some works pertaining to activity coefficients in fused salts. To date, knowledge is quite limited on this subject. Twenty seven years ago Hildebrand and his co-workers published a series of papers on e.m.f. studies of fused mixtures of AgBr in the alkali bromides. The results were summarized in the final paper (24). They showed that these mixtures behaved as "regular solutions". In Hildebrand's words (25), "A 'regular solution' is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged." Consider a binary mixture consisting of components A and B. The free energy change involved in transferring one mole of A in an ideal solution to one mole of A in a "regular solution" is

$$\bar{F}_A^R - \bar{F}_A^i = RT \ln \frac{a_A}{N_A} , \qquad (14)$$

where $a_A$ is the activity of A in the solution referred to pure liquid A as the standard state and $N_A$ is the mole fraction of A. From the definition of "regular solutions", $\Delta S$ is zero. Therefore, $\bar{F}_A^R - \bar{F}_A^i = \Delta\bar{H}_A$. Hildebrand also showed that $\Delta\bar{H}_A = bN_B{}^2$, where b is a constant independent of composition and temperature. Equation 14 can then be written

$$RT \ln \gamma_A = bN_B{}^2 \tag{15}$$

where $\gamma_A$ is the activity coefficient of component A and $N_B$ is the mole fraction of B. Hildebrand and Salstrom calculated the activity coefficients for AgBr where pure AgBr is taken as the standard state. Nearly all the information on activity coefficients in molten salts pertains to binary mixtures. The investigators first show that the mixtures are regular solutions and then use equation 15 to calculate $\gamma$. Flood's work on mixtures of $CaCO_3$ in the alkali carbonates (10) has been discussed earlier. Laity (26) studied $AgNO_3$-$NaNO_3$ mixtures by means of e.m.f. measurements. He measured the potential of a concentration cell with transference, and simply showed that there is a significant difference between the actual and ideal potentials. Blander and his co-workers (27) have recently made e.m.f. studies of dilute solutions of $AgNO_3$ in $NaNO_3$ and in $KNO_3$. They found that the activity coefficients of $AgNO_3$ were much lower in $KNO_3$ than in $NaNO_3$. However, in most studies of reactions in fused salts, the investigators have assumed the activity of a component is equal to the concentration, because of a lack of adequate information on this subject.

1. The dichromate-nitrate reaction (13)

Since the dichromate and the pyrosulfate reactions have the same slow step and were studied under similar conditions, the rate constants obtained in this study can be used to calculate the equilibrium constant for the former. The results (see Table 4) show that $Cr_2O_7^{--}$ is a much weaker acid than $S_2O_7^{--}$. The heat of reaction for the decomposition of one mole of $Cr_2O_7^{--}$ in the $KNO_3$-$NaNO_3$ eutectic is 50 ± 5 kcal. As discussed earlier, Flood and his co-workers (11, 12) studied the reactions

$$K_2S_2O_7\ (l) = K_2SO_4\ (l) + SO_3\ (g) \qquad (16a)$$

and

$$K_2Cr_2O_7\ (l) = K_2CrO_4\ (l) + \tfrac{1}{2}Cr_2O_3\ (s) + 3/4\ O_2\ (g) \qquad (16b)$$

where l, s, and g are liquid, solid, and gas respectively. They found that the heats of reaction were 40 kcal per mole for reaction 16a and 20 kcal per mole for reaction 16b at 610°-750°C. The latter value must be viewed with some reservations since the workers failed to establish conclusively that an equilibrium existed. In order to compare the heats of reaction obtained in this work for the decomposition of pyrosulfate and dichromate in the eutectic melt, with those obtained by Flood and his co-workers, the heats of reaction for

$$SO_3\ (g) + 2KNO_3\ (l) = K_2SO_4\ (l) + N_2O_5\ (g) \qquad (17a)$$

and

$$\tfrac{1}{2}Cr_2O_3\ (s) + 3/4\ O_2\ (g) + 2KNO_3\ (l) = K_2CrO_4\ (l) + N_2O_5\ (g) \qquad (17b)$$

were added to the heats of reaction for reactions 16a and 16b. Rough estimates of the heats for reaction 17a and reaction 17b were obtained from the heats of formation (28) of the gases and the solid salts, and they were, respectively, -10 kcal and 45 kcal. The corrected heats are 30 kcal per mole for the sum of reaction 16a and reaction 17a and 65 kcal per mole for the sum of reaction 16b and reaction 17b. These values can now be compared with those shown in Table 4.

Actually, it was found that $Cr_2O_7^{--}$ is stable in alkali nitrate melts and the reaction proceeded at a measurable rate only when heavy metal ions, which precipitate the chromate ion, were added. The actual reaction studied was

$$2Pb^{++} + Cr_2O_7^{--} + NO_3^{-} = NO_2^{+} + 2PbCrO_4.$$

The heat of reaction for the above is 5 kcal per mole of $Cr_2O_7^{--}$. This value was calculated from the heat of reaction of the equilibrium and the heat of solution for $PbCrO_4$. The latter is 25 kcal per mole and was calculated from the solubility studies of $PbCrO_4$ in the eutectic melt

(23).

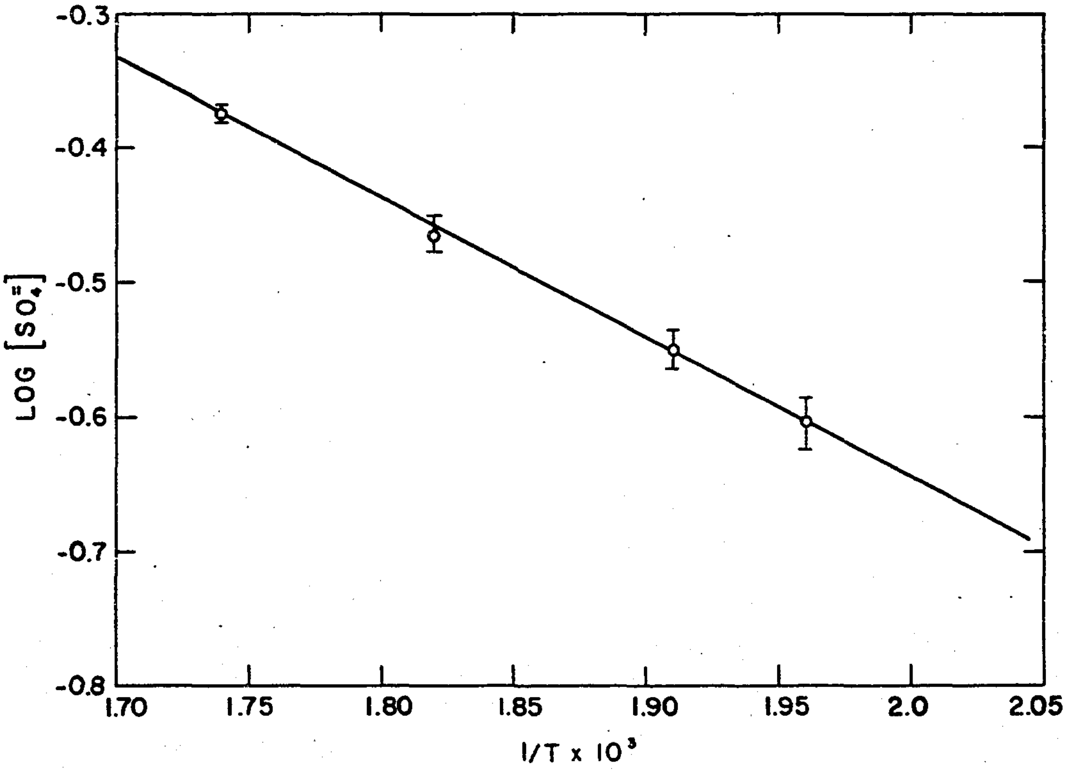
### 2. The solubility of $NaSO_4$ in 50% $NaNO_3$-$KNO_3$

The solubility studies were carried out at 235°, 250°, 275°, and 300°C. The results are shown in Table 6. Figure 3 is a plot of the solubility versus 1/T from which the value 4.7 kcal per mole was obtained for the heat of solution.

Table 6. Solubility of $Na_2SO_4$ in 50% $NaNO_3$-$KNO_3$

| T °C. | $\frac{\text{moles } Na_2SO_4}{\text{1000g solvent}} \times 10^2$ |
|---|---|
| 235° | 25 ± 1 |
| 250° | 28.2 ± 0.7 |
| 275° | 34.2 ± 0.8 |
| 300° | 42.1 ± 0.5 |

Figure 3. Temperature dependency of the solubility of $Na_2SO_4$ in $KNO_3$-$NaNO_3$ eutectic melt; log molality versus $1/T \times 10^3 \ {}^{\circ}K^{-1}$


-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
LOG $[SO_4^=]$
1.70
1.75
1.80
1.85
1.90
1.95
2.0
2.05
$1/T \times 10^3$

# IV. THE METAL NITRATE DECOMPOSITION REACTIONS

## A. Experimental

### 1. Materials and apparatus

A. C. S. reagent grade chemicals were used. Some attempts were made to obtain an anhydrous metal nitrate solution. The method which seemed most promising made use of the reaction

$$M + 3NH_4NO_3 = M(NO_3)_2 + N_2 + 2NH_3 + 3H_2O,$$

where M can be Zn, Cd, Mg, Co, Ni, Cu, or Bi (29). In the procedure, some $NH_4NO_3$ is dissolved in the eutectic melt and the metal is added. A vigorous reaction takes place as the metal dissolves. It was found that only very dilute solutions of the metal nitrates could be obtained by this method. Consequently, the metal nitrates were simply dried under vacuum for 2-3 days prior to its use.

The apparatus described on page 9 was used.

### 2. Procedure

Approximately 100 grams of the solvent were weighed out and fused. Dry nitrogen was bubbled for 1-3 hours; in the case of pure $LiNO_3$, nitrogen was bubbled for 4-5 hours. Solid metal nitrate was then added to the solvent. Although the nitrates were vacuum dried, water flashed out of the melt and condensed on the upper regions of the reaction vessel. This water evaporated in about 5 minutes. The first sample was drawn out about 15 minutes after the solid was added to the melt. The solid metal oxides were filtered as the samples were removed, by means of a wad of glass wool placed at the tip of the dropper. The sample was weighed and then dissolved in water and analyzed for the metal ion by titrating with versene using naphthol azoxine as the indicator (30).

It should be noted that the filtration of the metal oxides was not complete, but this error was found to be negligible. This was shown by filtering the aqueous solutions of some samples through a medium porosity, sintered glass crucible prior to the titration. The differences in the metal ion concentration found by the two methods were less than one percent. In the case of pure $LiNO_3$, it was impossible to draw the melt through the glass wool. Therefore, samples containing the oxides were removed with a preheated dropper. After cooling, the samples were weighed and dissolved in water. The insoluble oxides were then removed by filtration. In this procedure the greatest source of error is the weight of the sample which includes the metal oxide. The magnitude of this error is small as shown in Table 7.

The initial metal ion concentration was that of the first sample.

Table 7. Percent CuO and ZnO in $LiNO_3$ samples

| Total wt. | Wt. CuO or ZnO | % oxide |
|---|---|---|
| 1.414 g | 0.014 | 1.0 |
| 2.289 | 0.054 | 2.3 |
| 1.573 | 0.026 | 1.6 |
| 1.418 | 0.030 | 2.1 |

## B. Results and Discussion

### 1. The rate studies in the eutectic solvent

In principle, the results of the pyrosulfate study enable one to establish a scale of acidity based on the absolute nitronium ion concentration. The general acid-base equilibrium is

$$\text{Acid} + NO_3^- = \text{Base} + NO_2^+ . \tag{12}$$

The equilibrium constant

$$K = \frac{(\text{Base})\ (NO_2^+)}{(\text{Acid})} \tag{13}$$

is then a measure of the strength of the acid.

Exploratory studies were conducted with several Lewis acids. The results were as follows:

(1) $P_2O_7^{-4}$ - $Na_4P_2O_7$ was insoluble in the eutectic solvent at 275°C.

(2) $As_2O_3$ - This compound did not show any visible reaction, but sublimed at 275°C.

(3) $B_2O_3$ - There was no visible reaction at 275°C.

(4) $Pb^{++}$ - A saturated solution of $Pb(NO_3)_2$ in the eutectic melt showed no visible reaction at 275° and 350°C. After 24 hours a small amount of lead oxide was noted.

(5) Cu - $Cu(NO_3)_2$ decomposed with the formation of $NO_2$ and CuO at 275°.

(6) Zn - $Zn(NO_3)_2$ decomposed with the evolution of $NO_2$ and the formation of a white solid, ZnO.

On the basis of these observations, $Cu^{++}$ and $Zn^{++}$ were selected to be studied. Lawrence[1] observed that $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Cd(NO_3)_2$ decomposed in a similar manner.

The decomposition of $Cu(NO_3)_2$ was studied at 300°, 325°, and 350°C. and the $Zn(NO_3)_2$ reaction was studied at 350° and 378°C. A first order dependence in metal ion concentration was observed. The pseudo first order rate constants obtained from log $(M^{++})$ versus time plots are tabulated in Table 8.

The mechanism can be written as follows:

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[1] Lawrence, Walter W., Ames, Iowa. Qualitative observations on metal nitrate decompositions. Private communication. 1959.

$$M^{++} + NO_3^- = MO\ (s) + NO_2^+$$

$$NO_2^+ + NO_3^- = \text{decomposition products}$$

where the latter is the rate determining step. The rate law is expressed as

$$-\frac{d(M^{++})}{dt} = k\ (NO_2^+) \tag{14}$$

$$= \underline{kK}\ (M^{++})$$

where

$$K = \frac{(NO_2^+)}{(M^{++})} \quad .$$

It has been assumed that the oxides are insoluble. This rate law is consistent with the observed first order dependence in metal ion. Some work by Neumann and Sonntag (32) on the decomposition pressures of $Cu(NO_3)_2$ showed that $N_2O_5$ is involved. They studied the system

$$Cu(NO_3)_2\ (\text{solid}) = CuO\ (\text{solid}) + 2NO_2\ (\text{gas}) + \tfrac{1}{2}O_2\ (\text{gas})$$

and indicated that $4CuO \cdot 3N_2O_5$ is formed as an intermediate. The pseudo first order rate constants are equal to kK. Since the reactions were run under conditions similar to the pyrosulfate reaction, the data for the latter can be extrapolated to find k for these temperatures and the equilibrium constants can be calculated. These values are also shown in Table 8.

Table 8. Pseudo first order rate constants and equilibrium constants for metal ion-nitrate reaction. Nitrogen flow rate 0.21 liters per minute

| $Cu(NO_3)_2$ | | | | $Zn(NO_3)_2$ | | | |
|---|---|---|---|---|---|---|---|
| T | $k(min^{-1})^a$ | K x $10^3$ | n | T | $k(min^{-1})^a$ | K x $10^4$ | n |
| 300° | 0.15 | 1.6 ± 0.1 | 3 | 350° | 0.4 | 2.9 | 2 |
| 325° | 0.25 | 4.7 ± 0.3 | 2 | 378° | 0.6 | 17 | 2 |
| 350° | 0.4 | 13 | 1 | - | - | - | - |

[a] Obtained from extrapolation of data in Table 4.

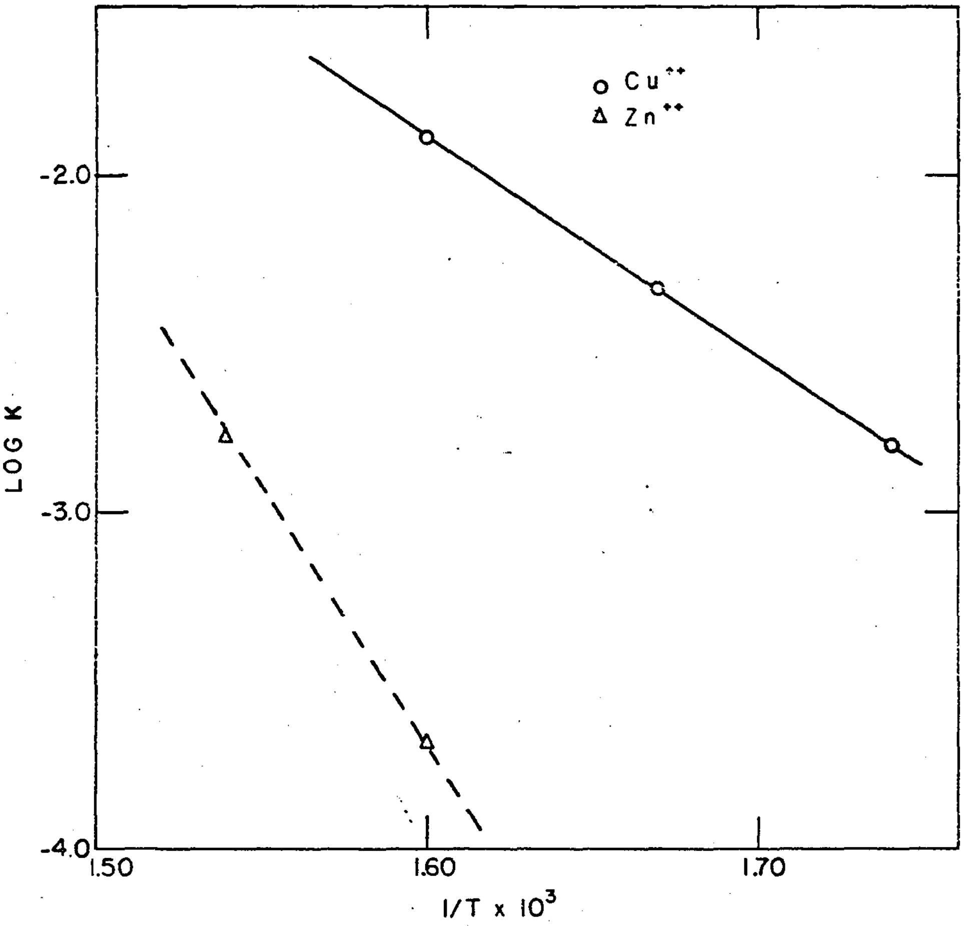
The relative strengths of the acids, which have been studied, are, in the order of increasing acid strength $Cr_2O_7^{--}$, $Zn^{++}$, $Cu^{++}$, and $S_2O_7^{--}$. This is in agreement with results found in aqueous solutions.

Figure 4 is a plot of 1/T versus log K for the two reactions. The heats of reaction were calculated from the slopes and are 30 kcal/mole and 67 kcal/mole, respectively, for $Cu(NO_3)_2$ and $Zn(NO_3)_2$.

### 2. The rate studies in pure alkali nitrates

The rate studies were conducted in pure $LiNO_3$, $NaNO_3$, and

Figure 4. Temperature dependency of the equilibrium constants for the $Cu^{++}$ - $NO_3^-$ and $Zn^{++}$ - $NO_3^-$ reactions; log equilibrium constant versus $1/T \times 10^3$ $^{o}K^{-1}$


○ Cu⁺⁺
Δ Zn⁺⁺
-2.0
-3.0
-4.0
LOG K
1.50
1.60
1.70
I/T x 10³

$KNO_3$ at 325° for $Cu(NO_3)_2$ and 350° for $Zn(NO_3)_2$. The pseudo first order rate constants are shown in Table 9.

Table 9. Variation of pseudo first order rate constant with solvent

| Solvent | $k' \times 10^3$ minutes$^{-1}$<br>$Cu^{++a}$ | <br>$Zn^{++b}$ |
|---|---|---|
| $LiNO_3$ | 170 ± 10 | 4.7 ± 0.1 |
| $NaNO_3$ | 13 ± 1 | 0.37 ± 0.02 |
| 50% $NaNO_3$-$KNO_3$ | 5.3 | 0.12 ± 0.01 |
| $KNO_3$ | 2.8 ± 0.2 | 0.091 ± 0.001 |

$^a$325°C.

$^b$350°C.

The most interesting aspect of these results is the marked increase in the rate as one goes to the nitrates of the smaller alkali metal ion. However the ratio of the pseudo first order rate constant for $Cu^{++}$ to that of $Zn^{++}$ was essentially the same (37 ± 4) in all the solvents. If the rate constant, k, is the same in all the solvents, then one can calculate the equilibrium constants. One is probably not justified in doing this, for if k does remain the same, then the rate is likely to decrease as the cation of the solvent is made smaller. This can be seen if one considers the solvation of the alkali metal ion. $Li^+$ would be more strongly solvated than $Na^+$, which in turn would be more strongly solvated than $K^+$. In other words, an equilibrium like

$$M^+ + xNO_3^- \ = \ M(NO_3)_x^{-(x-1)}$$

where M is Li, Na, or K, would lie farther to the right for the smaller metal ion. As a result, the activity of the nitrate is lowered, shifting the acid-base equilibrium (equation 12) to the left. Although this effect would be small, the variation in K would affect the rate in an opposite manner from that observed.

Perhaps a more reasonable explanation could be found if one considers the effect of the solvent on the stability of the nitronium ion. There is evidence that nitrate ions stabilize $NO_2^+$. Eyring and Daniels (32) found that the decomposition rate of $N_2O_5$ is much slower in 96% $HNO_3$ than in the gas phase or in inert solvents. They attributed this to the formation of stable complex ions of the form $(N_2O_5 \cdot nNO_3)^{-n}$, which can also be written $(NO_2 \cdot nNO_3)^{-(n-1)}$, in view of the fact that $N_2O_5$ is probably dissociated in the melt (13). It has been mentioned earlier that the formation of the solvated alkali metal ion complex would decrease the activity of the nitrate ion, which would, in effect, decrease the stability of the nitronium ion. More conclusive information would be obtained by studying the pyrosulfate reaction in the pure alkali nitrates. In this way one can find the values of k in these solvents.

## V. SUMMARY

The reaction

$$S_2O_7^{--} + NO_3^- = 2SO_4^- + NO_2^+$$

and the slow step which follows

$$NO_3^- + NO_2^+ = \text{decomposition products}$$

were studied kinetically in fused $KNO_3$-$NaNO_3$ eutectic. The equilibrium was found to lie far enough to the right, so that the equilibrium constant, K, could be determined. K as well as the rate constant, k, were determined at two temperatures. The heat of reaction at this temperature range was estimated.

The results of this investigation make it possible to establish a scale of acidity based upon the absolute nitronium ion concentration. The general acid-base equilibrium can be written

$$\text{Acid} + NO_3^- = \text{Base} + NO_2^+.$$

The acid strengths can be compared by comparing the magnitudes of the equilibrium constants defined by

$$K = \frac{(\text{Base})\ (NO_2^+)}{(\text{Acid})} .$$

The equilibrium constant for the reaction

$$Cr_2O_7^{--} + NO_3^- = 2CrO_4^{--} + NO_2^+$$

was calculated from the data obtained by Duke and Iverson (13) and the results of this study. The reaction

$$M^{++} + NO_3^- = MO\ (\text{solid}) + NO_2^+,$$

where M is Cu and Zn was also studied in the eutectic solvent. The equilibrium constants were determined at three temperatures for $Cu^{++}$ and at two temperatures for $Zn^{++}$.

The metal-nitrate reactions were also studied in pure alkali nitrates. It was found that the rates were greatly affected by the size of the cation of the solvent. The rates increased in the order $KNO_3$, $NaNO_3$, and $LiNO_3$. A tentative explanation for this behavior has been offered.

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The author is indebted to his wife, Irene, for her encouragement and understanding.

# VIII. APPENDIX

## A. The Nature of the Gaseous Decomposition Reaction

The rate determining step in the reactions, which have been investigated in this work, has been written

$$NO_2^+ + NO_3^- = \text{decomposition products.}$$

The principal decomposition products are $NO_2$ and oxygen. It has been found that the rate increases as the flow rate of the nitrogen sweep gas is raised. If oxygen is substituted for nitrogen as the sweep gas, the same rate is observed at the same flow rate as the nitrogen.

In view of these observations, one might speculate that the rate determining process consists of the following steps:

1. A reversible equilibrium

$$NO_2^+ + NO_3^- = N_2O_5 \ .$$

2. The diffusion of $N_2O_5$ through the melt to the gas bubbles or to the surface.

3. The decomposition of $N_2O_5$ in the gas phase,

$$N_2O_5 = 2NO_2 + O \ .$$

The decomposition of $N_2O_5$ in the gas phase at elevated temperatures is extremely fast; consequently, $N_2O_5$ would decompose immediately upon entering the gas bubble. The slow process is then the diffusion step. A larger flow rate would result in greater stirring of the reaction mixture, thereby increasing the rate of diffusion. The activation energy calculated for the rate determining step actually consists of a term involving the equilibrium constant for step 1 and the activation energy for the diffusion process. Since the same rate is observed for oxygen and nitrogen sweep gases, the decomposition reaction is irreversible for all practical purposes.