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Complex ions in fused salts

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IN FUSED SALTS.

Iowa State University of Science and Technology
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COMPLEX IONS IN FUSED SALTS

by

Harmon Mark Garfinkel

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

DEDICATION

To our parents

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I. INTRODUCTION

The great interest in fused electrolytes has stemmed from the increasing technological importance of high-temperature processes. Moreover it is hoped that the study of molten salts may lead to a better understanding of concentrated aqueous electrolytic solutions, since fused salts are very concentrated electrolytes, which because of the absence of the complicating effect of polar molecules such as water, are simpler in certain respects than the aqueous systems. The behavior of complex ions in aqueous systems has been a very fruitful field of study. Therefore it was felt that the same approach could be used to describe the specific interactions between unlike species in molten salts.

One may define a complex ion in molten salts in a variety of ways, for example, structurally, or in terms of models which agree with thermodynamic or kinetic behavior. Van Artsdalen (70) has suggested that a complex ion should have a lifetime long compared with molecular vibrational or collisional frequency, i.e., their existence should not be so short-lived as to prevent their detection or inference from some reasonable physical or chemical property.

Recently Gruen and McBeth (35, 36) and Gruen (34) have applied absorption spectroscopy in the visible and ultra-violet regions to solutions of colored halides dissolved in

molten nitrates. They found evidence for the existence of complex ions of the type $CoCl_n^{-n+2}$ and $NiCl_n^{-n+2}$ and have made calculations for the stepwise formation constants for the chloro-cobalt (II) complexes. Bues (10) has described Raman studies on the systems $ZnCl_2$-KCl and $CdCl_2$-KCl which led him to postulate the existence of the species $ZnCl_3^-$ and $CdCl_3^-$. There has been some question as to the exact nature of the complex species and Bredig and Van Artsdalen (9) have suggested that the species were more likely $ZnCl_4^{-2}$ and $CdCl_4^{-2}$.

Van Artsdalen (71) by means of cryometric measurements has shown that complex ion formation exists at high dilution in the case of lead (II) chloride, copper (II) chloride, cadmium chloride and bromide, and zinc chloride dissolved in molten sodium nitrate. Reactions were proposed and constants calculated for the species containing zero, two, and four chlorines per metal ion. Jander and Brodersen (49) using mercuric bromide as the solvent and potassium bromide as solute have suggested complexes of the type $KHgBr_3$ to explain the observed depression factors.

Cantor et al. (12) have measured the vapor pressure of ZrF_4 from molten RbF-ZrF_4 mixtures in order to obtain information on the change in ZrF_4 activity with composition. They interpreted the pronounced negative deviations from Raoult's law as a result of interactions between univalent and tetravalent cations and a common anion in a molten electrolyte. It

should be noted that there was no evidence for association in ZrF_4 vapor.

Duke and Iverson (19) have determined the complex formation constants for cadmium and lead chloro- and bromo-complexes in fused $NaNO_3$-KNO_3 eutectic as solvent. The method involved measuring the increase in solubility of the slightly soluble metal chromate as halide ion was added. Duke and Lawrence (20) used a similar technique to determine the formation constants of the chloro-lead and chloro-cadmium complexes in fused lithium perchlorate.

Formation constants of complex ions have also been determined from reaction kinetics, since formation of complex ions may control the concentration of a particular species and thereby control the rate at which that ion reacts chemically. Duke and Lawrence (21) have calculated stability constants for species of the type $ZnBr_n^{2-n}$ by studying the kinetics of the metal-bromide-bromate reaction in fused $NaNO_3$-KNO_3 eutectic solvent.

Potentiometric studies have been a standard method for establishing the existence and constitution of complex ions in aqueous solutions and this approach has been used rather extensively in molten halides. Hildebrand and Salstrom (42) used an e.m.f. method to study fused mixtures of silver bromide with each of four alkali bromides and found that these mixtures adhered remarkably well to the criteria for regular solutions. Delimarskii (16) has described a glass-tin-sodium electrode

for use in molten halides. Taking the sodium electrode potential as zero, he established a scale of electrode potentials in molten halides. Moreover it was found that the electrode potentials of the heavy metals become more negative on passing from the chlorides to the bromides and iodides.

Bockris et al. (6) have described a silver-silver chloride electrode (in LiCl-KCl eutectic) generally applicable to molten chloride systems up to 550°C and they determined the solubility product of AgCl in LiCl-KCl eutectic at 509°C. Flengas and Ingram (23, 24, 25) in addition, have reported a reversible silver-silver chloride reference electrode for use in KCl-NaCl melts at temperatures above 600°C. They have calculated complexing constants for a chloro-cadmium, chloro-cobalt (II), chloro-lead, chloro-nickel, and chloro-zinc complex in melts containing equimolar amounts of NaCl and KCl. The complex formed by lead chloride and nickel chloride was very weak, and the complex formed by zinc chloride was found to be fairly stable.

Senderoff[*] has found that a chlorine electrode with a porous graphite active surface, is a very reliable electrode, where it is compatible with the system under study. Senderoff and Brenner (65) have discussed an Ag, AgCl (LiCl-KCl) reference half-cell which they used to investigate the system

Figure 13. Deviation of the observed e.m.f. from the Nernst
            value for cells of type F without added MCl

K_3MoCl_6 in LiCl-KCl eutectic. They found that the molybdenum was present in solution as the stable complex ion $(MoCl_6)^{-3}$. Laitinen et al. (54) also have described the preparation of a chlorine electrode for use in molten salts. Furthermore Laitinen and Liu (55) have prepared a platinum-tetrachloroplatinate (II) reference electrode for use in molten chlorides; taking the electrode potential of the platinum electrode as zero, they were able to determine an e.m.f. series in molten LiCl-KCl eutectic. Thus it is seen that a great deal of attention has been given to molten chloride solvents mainly because of their stability and low oxidizing power.

However the situation has been somewhat different for molten nitrates since they are less stable than the chlorides and, in addition, are powerful oxidizing agents. Flengas and Rideal (26) have carried out potentiometric titrations of silver salts in solutions of molten $NaNO_3$-KNO_3. Since the silver salts were very insoluble in the molten alkali nitrate mixtures, precipitation titrations gave very good end points, and by titrating at a series of temperatures they were able to determine the solubility products as a function of temperature and from this information they calculated heats, free energies, and entropies of solution. When $AgNO_3$ was titrated with NaCN, insoluble AgCN was formed and it gave a typical end point, but the precipitate redissolved on the addition of excess cyanide, giving a second end point corresponding to the formation of the

soluble complex ion $Ag(CN)_2^-$. They reported the formation constant as 7.45×10^{10} ($molal^{-2}$) at $250^\circ C$, a surprisingly large number. The electrodes consisted of spectrographically pure silver wire 1.0 mm in diameter spot-welded to platinum wire and sealed into the end of Pyrex glass tubing. These electrodes were very stable and reversible at low concentrations of silver nitrate and the applicability of the Nernst equation to these electrodes was demonstrated to $\pm$ 0.5 mv.

By means of silver-silver nitrate, silver-silver chloride(s), and silver-silver bromide(s) electrodes it was thought that it might be feasible to apply potentiometric measurements to the study of complex ions in molten alkali nitrates.

Laity (56) has shown by a thermodynamic analysis that for solutions having the transport properties of the silver nitrate-sodium nitrate systems the terms for the liquid junction potential vanish from the expression for the e.m.f. He showed by means of e.m.f. measurements that at high concentrations of silver nitrate (greater than 0.08 mole fraction) these solutions deviate appreciably from ideality, but adhere remarkably well to the requirements for a regular solution.

Van Artsdalen (72) has shown by cryometric measurements that NaCl behaved ideally in $NaNO_3$ up to about 0.06 mole fraction of NaCl and similarly Kordes et al. (52) have shown that the $KCl-KNO_3$ system behaved ideally. Moreover Van Artsdalen (70) has shown that lead and cadmium nitrate behaved ideally in molten sodium nitrate. Therefore it was felt that it might be interesting to follow the e.m.f. of a

concentration cell with either silver, lead, or cadmium ions as a function of the halide ion and if any appreciable complexing occurred one would observe deviations from Nernst behavior that could be ascribed to complex ion formation.

Moreover because of the long-standing controversy between the adherents of the physical and "chemical" approaches to solution behavior it was felt that these measurements might afford a basis for comparison between the two approaches and might allow one even to decide which of the two approaches best describes the situation.

II. EXPERIMENTAL INVESTIGATION

A. Materials and Apparatus

A.C.S. reagent grade chemicals were used in all the experiments. Initially the sodium and potassium nitrate were recrystallized from redistilled water. However it was found that there was no noticeable effect when the above step was omitted. The Cl^{36} isotope was obtained from Oak Ridge National Laboratory as an aqueous solution of hydrochloric acid. The sodium chloride containing Cl^{36} was prepared by dissolving the salt in water, adding HCl^{36}, and evaporating the solution to dryness at $110^{\circ}C$.

The preparation of the electrodes was relatively straightforward. The silver-silver nitrate electrodes were prepared by spot welding a short length of #22 gauge silver wire, Handy and Harmon, (99.99$^+$% pure) to a three foot length of #22 gauge platinum wire. This, in turn, was annealed by heating to redness in a Meeker burner. The length of silver wire on the electrode to act as indicator was wound into a loose helix of approximately eight turns, and that of the reference was left a short piece one cm in length (Figure 1). The silver-silver bromide electrodes were prepared in a similar fashion except that the two straight lengths of silver wire were dipped into molten silver bromide and the electrodes were stored in a dark

Figure 1. Silver-silver nitrate reference and indicator electrode

INDICATOR
ELECTRODE

REFERENCE
ELECTRODE

PLATINUM - PYREX
SEAL

PLATINUM - SILVER
WELD
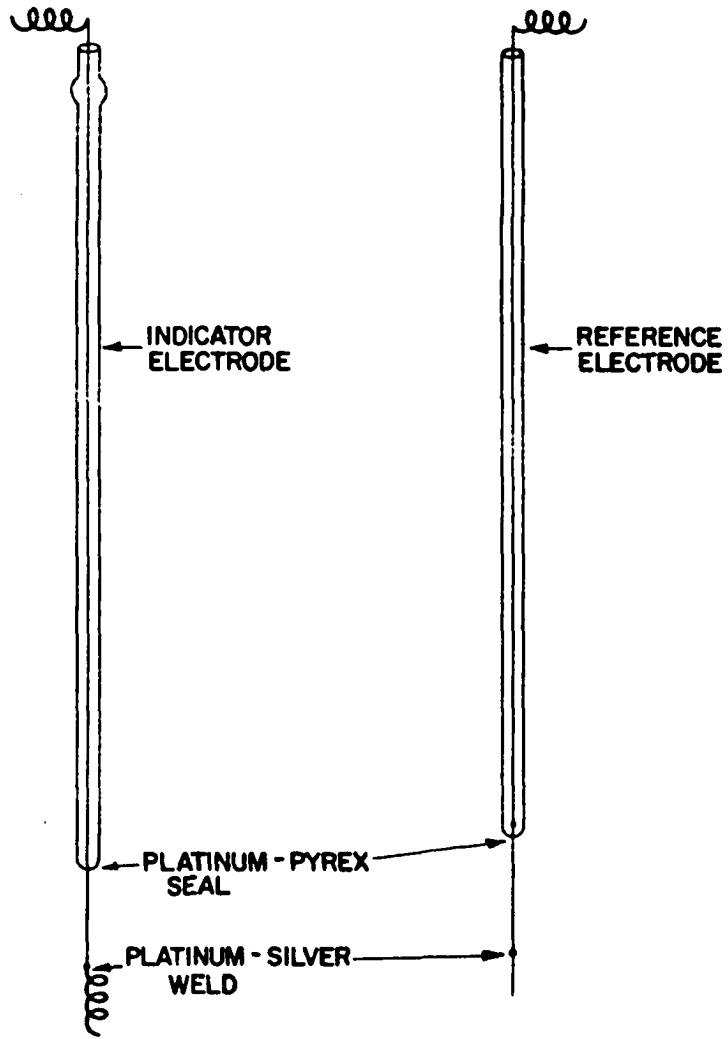
Figure 2.   Reference and reaction half-cells for the
            e.m.f. measurements

place until the time to be used. All these electrodes were sealed into 3 mm tubing to position the electrodes.

Silver-silver nitrate electrodes also were prepared by alternately coating a platinum helix with silver oxide and heating in a Marshall furnace at $450°C$ until silver metal completely covered the platinum wire. The electrodes prepared in this manner were not quite as satisfactory as those prepared in the above way because the former had to be renewed after each run while the latter, once prepared, could be used indefinitely. Silver-silver bromide electrodes prepared in a similar manner after the procedure of Hamer and Acree (40) also were satisfactory but could not be used too many times because cracks would develop at the high temperatures employed resulting in fluctuations in the e.m.f.

The reference half-cell was constructed from a 10 mm Pyrex sealing tube shaped into a small bubble to which was sealed a 13 inch tube about 5-6 mm I.D. A fine Pyrex fritted disc partially fused to reduce diffusion was used as the membrane. The reaction half-cell (Figure 2) consisted of a 60/50 ground glass joint sealed to a 300 ml flask. The head of the cell was fitted with four wells for the Pyrex stirrer, the reference half-cell, the indicator electrode, and the thermocouple. The "addition tube" was used to facilitate the mixing of reactants.

A mixture of molten alkali nitrates was used as the constant temperature bath since it has a high thermal

60/50 → GROUND GLASS

300 ML REACTION COMPARTMENT

REFERENCE HALF-CELL

PYREX FRITTED DISC

ADDITION TUBE

STIRRER WELL

REFERENCE HALF-CELL WELL →

INDICATOR ELECTRODE WELL

GROUND GLASS

THERMOCOUPLE WELL
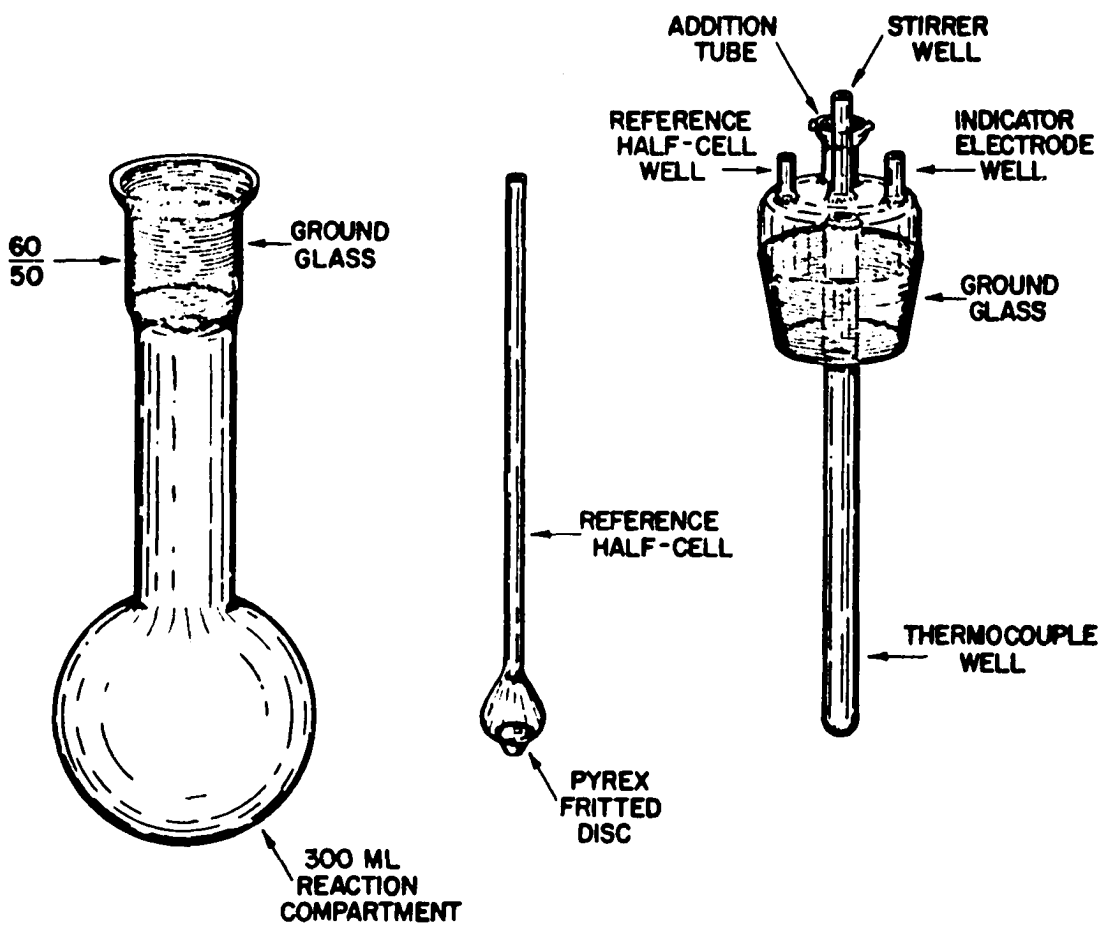
conductivity and relatively low melting point. A eutectic
mixture of $NaNO_3$-KNO_3 (about 1:1 mole) which melts at
approximately $220^\circ C$ was found to be superior to the ternary
Li:Na:K eutectic because it is less corrosive to glass although
it melts about 100° higher. The bath was heated primarily by
a 1500 watt ring heater. A small 2-300 watt heater, made by
winding nichrome wire around an alundum core and then coating
with Sauereisen, was kept in the bath protected by a Pyrex
tube. The latter heater in conjunction with an on-off con-
troller was used to control the temperature to $\pm$ $0.5^\circ C$. The
container of the bath had successive layers of asbestos paper,
aluminum foil, glass wool, and asbestos cloth wrapped around it
to a thickness of about one inch. To reduce radiation from the
surface of the bath a one-half inch thick transite cover was
used; holes were cut in the cover for the cell, stainless
steel stirrer, heater, and chromel-alumel thermocouple used to
activate the temperature controller. The bath was placed on
the ring heater and the setup was insulated on the bottom with
fire brick 2.5 inches thick.

All potential measurements were made with a Leeds and
Northrup type K potentiometer. A Leeds and Northrup type 2340
galvanometer was used as the null instrument. In some cases,
to increase the sensitivity, a Kintel vacuum tube voltmeter was
used as null instrument. All temperature measurements in the
cell were made with a chromel-alumel thermocouple calibrated

periodically by taking cooling curves of three or four standards such as pure tin, cadmium, bismuth, and lead. An ice bath was used as the cold junction.

A sixteen inch Marshall Tube Furnace, Marshall Products Co., with a Brown Indicating Controller, Model 156R16-PS-141, Minneapolis-Honeywell, Brown Instruments Division, was used for the radiotracer experiments. The temperature was measured with a chromel-alumel thermocouple, connected to the meter circuit of the controller. The power supply used to obtain direct current for electrolysis was a full-wave selenium rectifier circuit with a pi-section filter circuit, capable of delivering up to 300 ma D.C. at 35 volts. The D-C milliameter was used in conjunction with a silver coulometer to determine the current. The electrolysis was timed with a "Time-it", Precision Scientific Co.

Counting of radioactive samples was done with a Tracerlab TGClCT standard end window Geiger-Muller tube mounted in Housing Model AL14A, Technical Associates, and a Model 100 Berkeley Decimal Scaling Unit.

The cell used for radiotracer experiments is shown in Figure 3. The cells were made of Pyrex glass with a 10 mm diameter, 1.5 mm thick membrane of fritted Pyrex glass "ultrafine" porosity, Corning Glass Works. The porosity of the membrane was reduced by alternately treating the disc with ethyl silicate and HCl and then dehydrating the silica gel by

Figure 3. Cell for the determination of transport numbers

GLASS
MEMBRANE

←SIDEARM
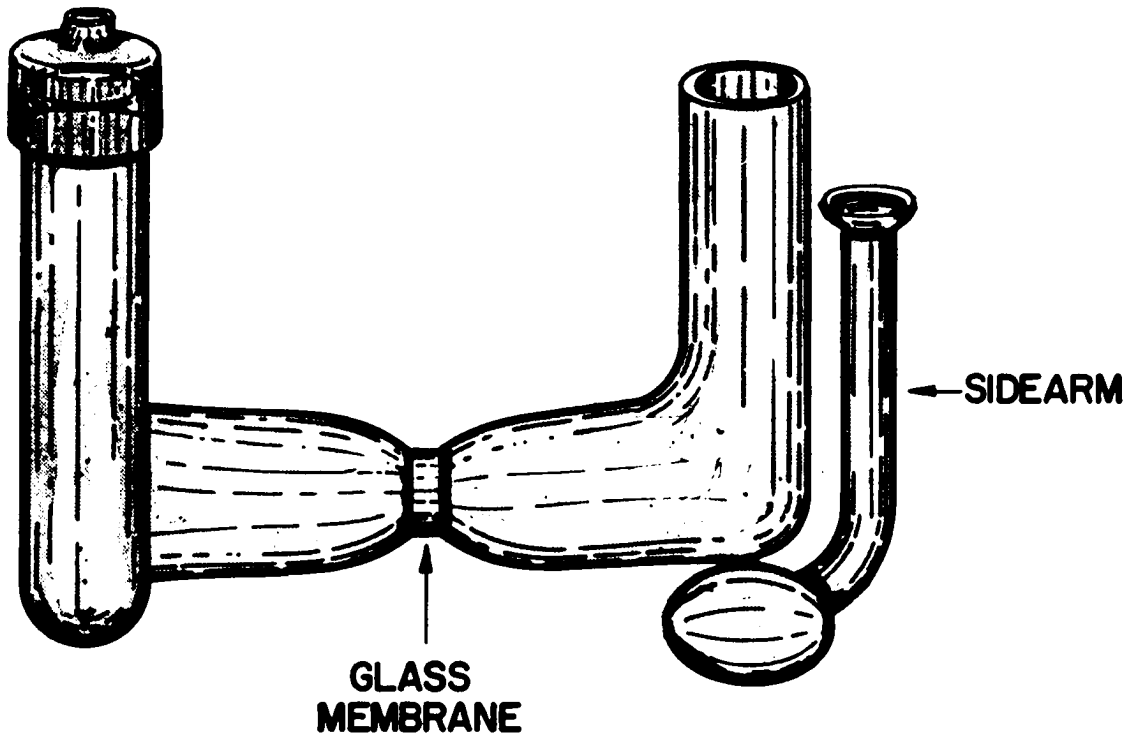
baking at 580°C. This treatment was repeated until more than two hours was required for one milliliter of water to flow through the membrane under suction. Heavy silver wire 3 mm thick was used for the electrodes. A dilute mixture of $NaNO_3 \cdot AgNO_3$ was used in the sidearm so that no AgCl would precipitate in the catholyte compartment. The bulb was separated from the compartment by a fine capillary.

B. Procedure

Before use all the reagents were dried in a vacuum dessicator containing $MgClO_4$ as dessicant. The $Cd(NO_3)_2 \cdot 4H_2O$ was dried by pumping on the sample for several days and then cautiously heating under vacuum; care was taken not to melt the sample because then there was considerable oxide formation. It was found that $Pb(NO_3)_2$ could be dried quite satisfactorily in the vacuum dessicator.

The experimental procedure did not vary too much in the different investigations. The solutions to be used as reference were made up in quantities of about 25 gms and stored in the vacuum dessicator. In the runs involving the silver halides, a weighed amount of $NaNO_3$ and KNO_3 was added to the cell which was positioned in the nitrate bath. The total weight of the solvent was 5-600 gms. At first helium from the Bureau of Mines, which was shown by Brady (8) to contain less

than 1.5 ppm of oxygen, was bubbled through the melt for several hours. $AgNO_3$ obtained by selecting clear crystals from "Baker Analyzed" reagent material was then added to the melt. However it was found that omission of the sparging step did not affect the results and this led to the conclusion that there was no appreciable silver oxide formation. Lyalikov [61] using KNO_3 as the supporting electrolyte in the polarographic study of fused salts found very stable waves for Ag^+, Cd^{++}, and Pb^{++} which remained practically unchanged during polarographic analysis. Then the reference cell was inserted into the head, the liquid levels were adjusted and the electrodes, the thermocouple, and motor driven Pyrex stirrer were set into place. After thermal equilibrium was reached the potential was measured for comparison with the Nernst value. Thereupon the potential was followed as a function of the concentration of the halide ion.

The procedure for the divalent metal bromides was similar except that silver-silver bromide electrodes were used and after thermal equilibrium was reached the potential was followed as a function of the concentration of M^{++}.

In all cases the concentrations of the reacting species were kept less than 0.01 ion fraction and in the case of the silver halides the concentrations were such that the product of the molalities of silver and halide ion did not exceed the solubility product. In order to verify that the salts of the

divalent metals were dry at the end of the run an aliquot of the solution was titrated with EDTA using napthyl azoxine after the method of Fritz et al. (30). In all cases the concentration of the metal checked very well with the value determined by adding weighed amounts of the dried metal nitrate.

In the radiotracer experiments the right-hand (catholyte) compartment of the cell was filled with Cl^*-nitrate mixture. The anolyte was filled with a $NaCl-NaNO_3$ mixture of the same concentration as the catholyte and the sidearm was filled with the silver nitrate-sodium nitrate mixture. A silver electrode was inserted into the sidearm and into the catholyte mixture, whereupon the latter was capped and the cell was placed in a tube furnace at the temperature of the run. As soon as thermal equilibrium was reached, a measured D.C. current was passed for a known time. The cell was then withdrawn, frozen, and split at the membrane to separate anolyte and catholyte; care was taken not to contaminate any of the anolyte salt with that of the catholyte. The two halves of the cell were dissolved in aqueous ammonia. The Cl^* was precipitated from ammoniacal solution with excess silver nitrate and counted as silver chloride. In order to obtain a smooth precipitate, it was necessary to keep the solution ammoniacal during the precipitation. A self-absorption curve was obtained, giving counting rate as a function of sample weight. All samples were corrected to a standard weight by means of this curve. The

weight of the anolyte salt was obtained by precipitating the total chloride. The concentration of the mixture was controlled by carefully weighing and mixing the solid salts prior to the run.

III. EXPERIMENTAL RESULTS AND CALCULATIONS

A. Complexes of Silver

1. Halide complexes

Consider the cell A

$$Ag^O \left| \begin{array}{l} AgNO_3 \ (m'_{Ag^+}) \\ NaNO_3-KNO_3 \ (eutectic) \end{array} \right\| \left| \begin{array}{l} AgNO_3 \ (m_{Ag^+}) \\ NaNO_3-KNO_3 \ (eutectic) \end{array} \right| Ag^O \qquad (A)$$

in which the solute concentration is so low that essentially all the bridge current is carried by solvent ions. Then the e.m.f. is given by

$$E = \frac{2.30 \ RT}{F} \log \frac{a_{AgNO_3}}{a'_{AgNO_3}} \qquad (1)$$

where a represents the activity and the prime refers to the left-hand (reference) cell. If the ratio of the practical activity coefficients which are defined by

$$\gamma_{AgNO_3} = \frac{a_{AgNO_3}}{m_{Ag^+} \cdot m_{NO_3^-}} \qquad (2)$$

is constant as should be the case in very dilute solutions, then equation 1 becomes the Nernst equation for a concentration cell

Figure 4. Check of the Nernst slope for cell A at 334°C

$$E_n = \frac{2.30\ RT}{F} \log \frac{m_{Ag^+}}{m'_{Ag^+}} \tag{3}$$

where m represents the molality and E_n is the Nernst potential.

Cells of type A in which the m_{Ag^+} was varied by addition of silver nitrate to the solvent were found to be quite stable and reproducible. E.m.f. values changed less than 0.6 mv on standing overnight at temperatures below 400°C. Figure 4 shows points representing typical data obtained from such cells at 334°C. The theoretical slope was 0.120 and that determined analytically from the data in Table 1 was 0.120. The data at 366°C gave the theoretical slope equal to 0.126 and the experimental slope was 0.124. Since the concentration of the mixed solvent was the same on both sides and because of the good agreement of the experimental value to that of the theoretical value of the slope, there was justification in the neglect of the liquid junction potential. Furthermore this indicated that the activity coefficient of silver nitrate was constant within experimental error at molalities between 4.34×10^{-2} and 3.50×10^{-4} which agreed with the conclusion of Flengas and Rideal (26). In view of the extremely dilute solutions employed, adoption of the standard state such that the activity coefficient was unity at infinite dilution led to the conclusion that γ_{AgNO_3} was unity over the concentration range studied.
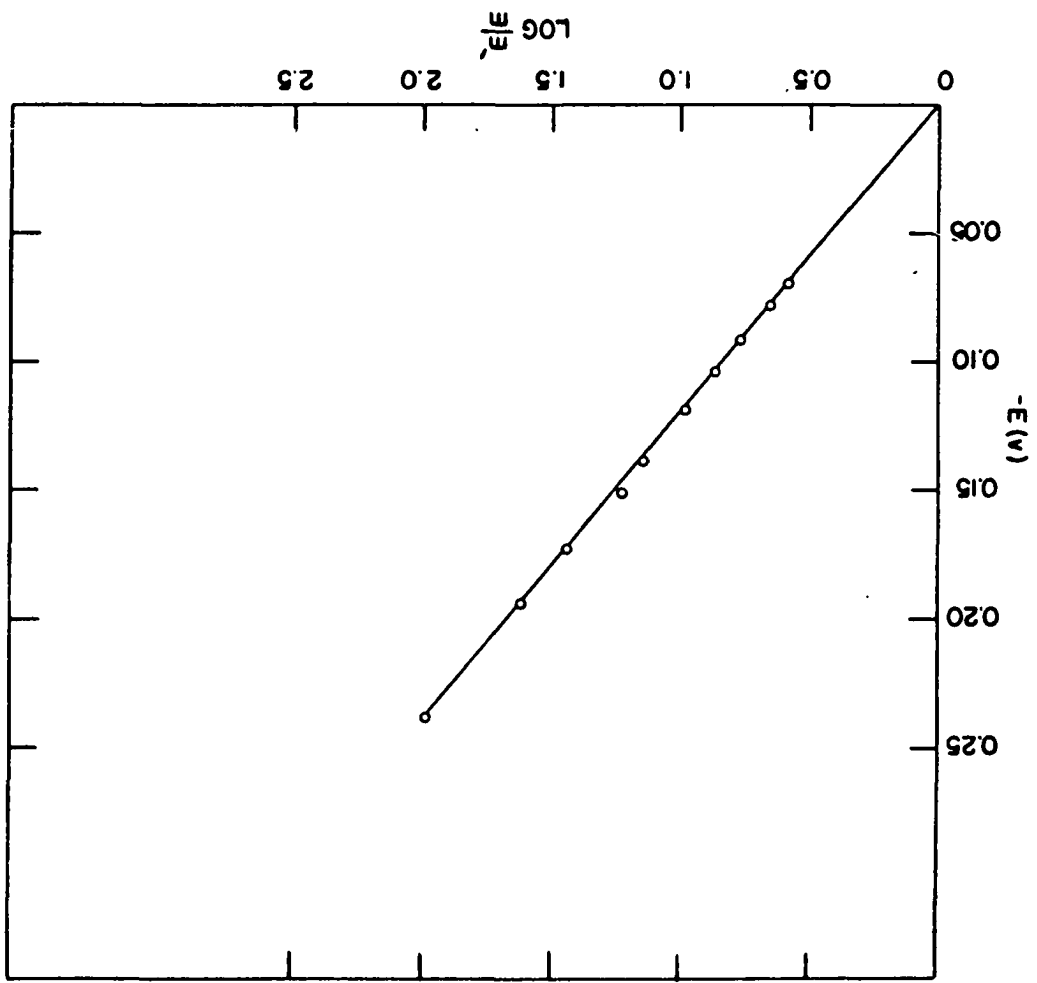
Table 1. Data for the verification of the Nernst limiting law for cells of type A

$t(°C)$	$m'_{Ag^+} \times 10^2$	m_{Ag^+}	$-E(v)$	$\log \dfrac{m'_{Ag^+}}{m_{Ag^+}}$
366	4.34	0.350	0.258	2.09
		1.09	0.198	1.60
		1.93	0.167	1.35
		3.25	0.139	1.12
		4.15	0.126	1.02
		5.44	0.111	0.902
334	3.77	0.378	0.238	2.00
		0.902	0.194	1.62
		1.38	0.173	1.44
		2.13	0.151	1.23
		2.70	0.139	1.15
		3.94	0.119	0.981
		5.24	0.103	0.857
		6.47	0.0914	0.766
		8.39	0.0777	0.652
		9.76	0.0698	0.587

The e.m.f.'s have been measured for cells of the type

$$\text{Ag}^{\text{o}} \left| \begin{array}{l} \text{AgNO}_3 \ (\text{m'}_{\text{Ag}}+) \\ \text{Na-KNO}_3 \ (\text{eutectic}) \end{array} \right\| \begin{array}{l} \text{AgNO}_3 \ (\text{m}_{\text{Ag}}+) \\ \text{KX} \ (\text{m}_{\text{X}-}) \\ \text{Na-KNO}_3 \ (\text{eutectic}) \end{array} \left| \text{Ag}^{\text{o}} \right. \qquad (B)$$

as a function of the concentration of KX which was increased by incremental additions. Here X^- was either Cl^- or Br^-. Since the solutions used in this study always contained less than 0.01 ion fraction of chloride ions, the liquid junction potential due to transference should be small.

However in order to obtain a quantitative estimate of the contribution of the liquid junction to the Nernst potential of cell B, the transport number of chloride was determined in mixtures of $NaCl^{36} \cdot NaNO_3$ as a function of the mole fraction of sodium chloride. These measurements were performed by the radiotracer technique. The values of t_{Cl^-} as a function of N_{Cl^-} (ion fraction of chloride) is given in Table 2. The rather poor precision as shown by the data in Table 2 is usual when an attempt is made to determine the fraction of the current carried by the chloride ion whenever its transport number is so small. At any rate t_{Cl^-} has been found to follow the approximate relationship

$$t_{Cl^-} = (t_{NO_3^-})(N_{Cl^-}) \qquad (4)$$

where $t_{NO_3^-}$ is 0.29. This is the value for the pure salt,

$NaNO_3$, determined by Duke and Owens (22).

Table 2. Transport number, t_{Cl^-}, of chloride in $NaCl \cdot NaNO_3$ mixtures as a function of N_{Cl^-}

N_{Cl^-}	Number of runs	$(t_{Cl^-})_{exp}$	$(t_{Cl})_{calc}$
0.05	4	0.024 ± 0.009	0.015
0.06	4	0.016 ± 0.001	0.016
0.20	5	0.041 ± 0.030	0.060

Thus it is seen that at the concentrations employed t_{Cl^-} would be extremely small and for all practical purposes the liquid junction potential with chloride added could be neglected.

Moreover as KX was added to the right-hand compartment, and $m_{Ag^+} \cdot m_{X^-}$ was such that no AgX precipitated, deviations from equation 3 were noted that could not be accounted for simply by dilution. These deviations were ascribed to complex ion formation.

Consider the stepwise reactions

$$Ag^+ + X^- \rightleftharpoons AgX \qquad (5)$$

and

$$AgX + X^- \rightleftharpoons AgX_2^- \tag{6}$$

Now upon the addition of the alkali halide, since the silver ion is assumed to be complexed according to the above scheme, the potential of the cell B is given by

$$E = \frac{2.30 \ RT}{F} \log \frac{m''_{Ag^+}}{m'_{Ag^+}} \tag{7}$$

where m''_{Ag^+} is the concentration of the silver ion after addition of KX. Then one can write

$$-\Delta E = +E_n - E = \frac{2.30 \ RT}{F} \log \frac{m_{Ag^+}}{m''_{Ag^+}} \tag{8}$$

It is apparent that the total silver ion can be expressed as a sum.

$$T_{Ag^+} = (Ag^+) + (AgX) + (AgX_2^-) = m_{Ag^+} \tag{9}$$

If $T_{Ag^+} \ll T_{X^-}$ then the species Ag_2Cl^+ can be neglected and

$$K_1 = \frac{(AgX)}{(Ag^+) \cdot T_{X^-}} \tag{10}$$

and

$$K_2 = \frac{(AgX_2^-)}{(AgX) \cdot T_{X^-}} \tag{11}$$

Upon substitution for (AgX) and (AgX$_2^-$) into equation 6 one obtains

$$\frac{m_{Ag^+}}{m''_{Ag^+}} = 1 + K_1 T_{X^-} + K_1 K_2 T_{X^-}^2 \qquad (12)$$

where T_{X^-} is the total molality of the chloride. If one now substitutes for the left-hand side of equation 12, then

$$10^{-\frac{\Delta EF}{2.3\, RT}} = \beta = 1 + K_1 T_{X^-} + K_1 K_2 T_{X^-}^2 \qquad (13)$$

and

$$\frac{\beta - 1}{T_{X^-}} = \theta = K_1 + K_1 K_2 T_{X^-} \qquad (14)$$

Some typical data for these systems in $NaNO_3$-KNO_3 with bromide and chloride are shown in Table 3. It is appropriate to note that since the solubility product of AgBr is much smaller than that for AgCl smaller increments of KBr were added and this resulted in a greater relative uncertainty in T_{Br^-} than in T_{Cl^-}.

If β is plotted against T_{X^-} then

$$\lim_{T_{X^-} \to 0} d\beta / dT_{X^-} = K_1 \qquad (15)$$

Table 3. Electromotive force as a function of the halide ion concentration

A. Chloride

| $t = 333°C$ | | | $t = 342°C$ | | | $t = 367°C$ | | |
| $m_{Ag^+} = 0.838 \times 10^{-3}$ | | | $m_{Ag^+} = 0.782 \times 10^{-3}$ | | | $m_{Ag^+} = 0.579 \times 10^{-3}$ | | |
$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ
0.248	0.0045	36.3	0.780	0.0121	33.3	0.994	0.0155	32.6
0.533	.0095	37.5	1.16	.0179	34.5	1.31	0.0199	33.2
0.846	.0148	38.8	1.32	.0201	34.8	1.74	0.0257	34.1
1.17	.0202	40.4	1.49	.0226	35.6	2.04	0.0297	35.0
1.55	.0262	42.1	1.70	.0255	36.5	2.54	0.0360	36.3
1.98	.0330	44.7	1.85	.0275	36.8	3.06	0.0424	37.8
2.50	.0408	47.5	2.12	.0309	37.3	3.63	0.0489	39.3
2.77	.0444	48.5	2.34	.0337	38.0	3.92	0.0522	40.2
3.15	.0495	50.3	2.61	.0370	38.7	4.23	0.0555	41.0
3.45	.0532	51.5	2.88	.0406	40.0	4.50	0.0582	41.6
3.92	.0589	53.5	3.08	.0430	40.6	4.80	0.0613	42.5
4.27	.0631	55.2	3.40	.0463	41.2	5.15	0.0648	43.5
4.80	.0691	57.6	3.76	.0507	42.8	5.50	0.0682	44.4
5.15	.0729	59.2	4.02	.0532	43.0	5.88	0.0718	45.6
5.64	.0781	61.6	4.46	.0580	44.6	6.25	0.0754	46.8
6.16	.0833	64.0	4.91	.0625	45.8	6.64	0.0787	47.7
6.64	.0879	66.3	5.33	.0664	46.9	7.06	0.0824	48.9
7.08	.0920	68.4	5.74	.0702	48.1	7.36	0.0848	49.6
7.47	.0955	70.3	-	-	-	7.85	0.0885	50.6
7.88	.0991	72.3	-	-	-	-	-	-

Table 3. (Continued)

A. Chloride

$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ
0.267	0.0039	27.3	0.0601	0.0009	25.0
0.571	.0083	28.2	0.275	0.0038	26.2
1.02	.0148	29.9	0.434	0.0060	26.5
1.41	.0201	30.9	0.603	0.0083	26.5
1.76	.0249	32.1	0.906	0.0124	27.6
2.22	.0309	33.5	1.20	0.0161	27.9
2.75	.0373	34.8	1.49	0.0196	28.2
3.18	.0423	35.9	1.75	0.0228	28.9
3.52	.0462	36.8	2.11	0.0269	29.4
4.16	.0532	38.6	2.44	0.0306	29.9
4.67	.0585	39.9	2.93	0.0358	30.7
5.00	.0619	40.9	3.32	0.0396	31.0
5.32	.0649	41.6	-	-	-
5.78	.0694	43.0	-	-	-
6.34	.0743	44.3	-	-	-
6.92	.0794	45.8	-	-	-
7.52	.0842	47.2	-	-	-
8.24	.0900	49.1	-	-	-
9.03	.0960	51.2	-	-	-
9.75	.1012	53.1	-	-	-
10.2	.1044	54.3	-	-	-
11.1	.1099	56.1	-	-	-

t = 374°C $\quad$ $m_{Ag^+} = 0.845 \times 10^{-3}$

t = 380°C $\quad$ $m_{Ag^+} = 0.325 \times 10^{-3}$

Table 3. (Continued)

A. Chloride

| | $t = 401^{\circ}C$ | | | $t = 439^{\circ}C$ | |
| | $m_{Ag^+} = 0.132 \times 10^{-2}$ | | | $m_{Ag^+} = 0.147 \times 10^{-2}$ | |
$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E(v)$	θ
0.528	0.0067	23.1	0.487	0.0055	19.3
1.15	0.0147	25.0	1.00	0.0114	20.5
1.77	0.0221	26.1	1.60	0.0177	21.0
2.43	0.0295	27.2	2.19	0.0237	21.6
3.02	0.0359	28.2	2.82	0.0299	22.3
3.64	0.0423	29.3	3.32	0.0345	22.8
4.18	0.0477	30.4	3.89	0.0398	23.5
4.58	0.0514	31.0	4.46	0.0448	24.2
5.15	0.0566	31.9	5.24	0.0514	25.1
5.70	0.0615	32.9	5.83	0.0562	25.8

Table 3. (Continued)

B. Bromide

T_{Br^-} x 10^3	$-\Delta E(v)$	θ	T_{Br^-} x 10^3	$-\Delta E(v)$	θ	T_{Br^-} x 10^3	$-\Delta E(v)$	θ
t = 366°C m_{Ag^+} = 0.331 x 10^{-3}			t = 375°C m_{Ag^+} = 0.737 x 10^{-3}			t = 376°C m'_{Ag^+} = 1.04 x 10^{-3}		
0.418	0.0027	120	1.26	0.0066	100	1.05	0.0054	96.2
1.46	0.0083	111	2.06	0.0107	103	2.16	0.0109	99.1
2.21	0.0123	113	2.90	0.0148	105	2.90	0.0146	103
3.45	0.0181	113	3.78	0.0190	108	3.93	0.0195	106
4.43	0.0225	113	4.54	0.0225	110	4.94	0.0241	109
5.57	0.0276	116	5.42	0.0264	112	5.62	0.0272	111
6.77	0.0324	118	6.18	0.0298	115	6.14	0.0294	112
7.95	0.0374	122	7.02	0.0333	117	6.65	0.0315	114
9.15	0.0419	125	-	-	-	-	-	-
t = 380°C m_{Ag^+} = 0.326 x 10^{-3}			t = 380°C m_{Ag^+} = 0.770 x 10^{-3}			t = 414°C m_{Ag^+} = 0.562 x 10^{-3}		
1.95	0.0095	94.9	1.77	0.0089	97.2	0.170	0.0070	74.1
2.74	0.0132	96.7	2.49	0.0124	99.2	0.335	0.0136	77.3
3.64	0.0171	98.4	3.16	0.0154	99.7	0.485	0.0191	78.6
4.46	0.0206	99.8	3.90	0.0185	100	0.619	0.0239	80.5
5.62	0.0252	100	4.61	0.0217	103	0.784	0.0295	82.5

Table 3. (Continued)

				B. Bromide				
t = 380°C			t = 380°C			t = 414°C		
m_{Ag^+} = 0.326 x 10^{-3}			m_{Ag^+} = 0.770 x 10^{-3}			m_{Ag^+} = 0.562 x 10^{-3}		
T_{Br^-} x 10^3	-ΔE(v)	θ	T_{Br^-} x 10^3	-ΔE(v)	θ	T_{Br^-} x 10^3	-ΔE(v)	θ
6.39	0.0286	104	5.26	0.0244	104	0.935	0.0346	85.2
7.32	0.0321	106	5.89	0.0270	105	1.10	0.0399	87.7
8.21	0.0354	107	6.62	0.0299	106	1.26	0.0441	88.1
9.21	0.0389	109	7.16	0.0321	108	1.40	0.0481	89.9
10.1	0.0421	111	7.76	0.0343	109	1.54	0.0527	93.6

Figure 5. Determination of K_1 by method of limiting slopes at 367°C

and Θ plotted versus T_{X^-} should yield a straight line with K_1 equal to the intercept and $K_1 K_2$ equal to the slope. Some typical plots are shown in Figures 5, 6, and 7, where a least squares treatment was used to get the best straight line. These constants could also be extracted by graphically differentiating the plot of β versus T_{X^-} with a tangentimeter which is essentially a device consisting of a plane mirror fixed at right angles to a straight edge. When the edge of the mirror rests on the curve, the reflection appears to be a continuation of the curve. Only when the mirror is at right angles to the curve do the curve and the image form a continuous smooth line; at any other angle there is a break or kink where the curve and image join. When the mirror is set perpendicular to the curve at a given point, the attached straight edge is parallel to the tangent of the curve at the point, and so determines the slope of the curve. The differentiation of β can be carried out at a series of halide ion concentrations. A plot of the slope, $d\beta/dT_{X^-}$ versus T_{X^-} should give a straight line with intercept K_1 and slope $2 K_1 K_2$. When this was attempted it was found that the points scattered somewhat more than in the method previously described. Therefore all calculations were made by the first approach.

The data of Hill et al. (44) on the system $AgNO_3-NaCl-NaNO_3$ and Blander et al. (4) on the system $AgNO_3-KCl-NaNO_3$ were treated in a similar manner. These authors have made

Figure 6. Plot to show linearity of the derived equation 14
for the silver nitrate system when KCl is added
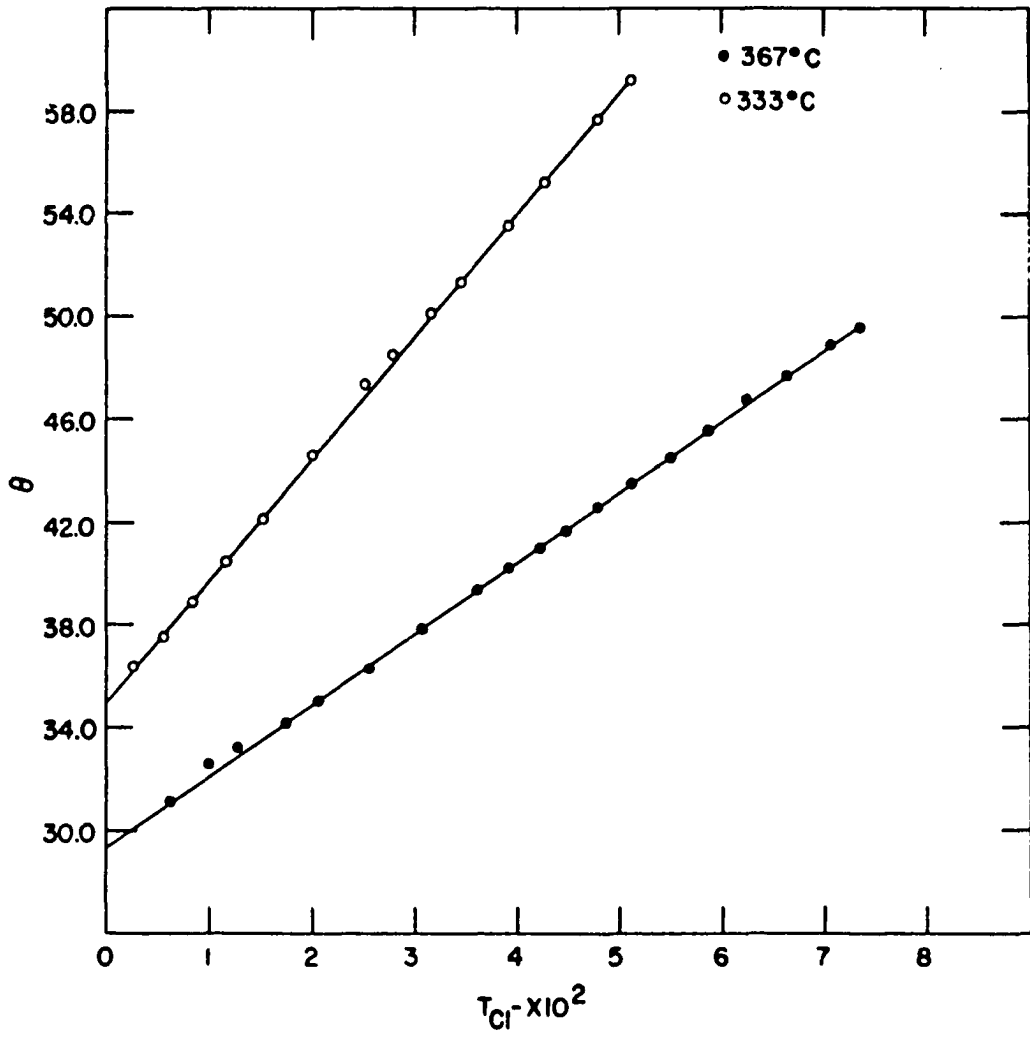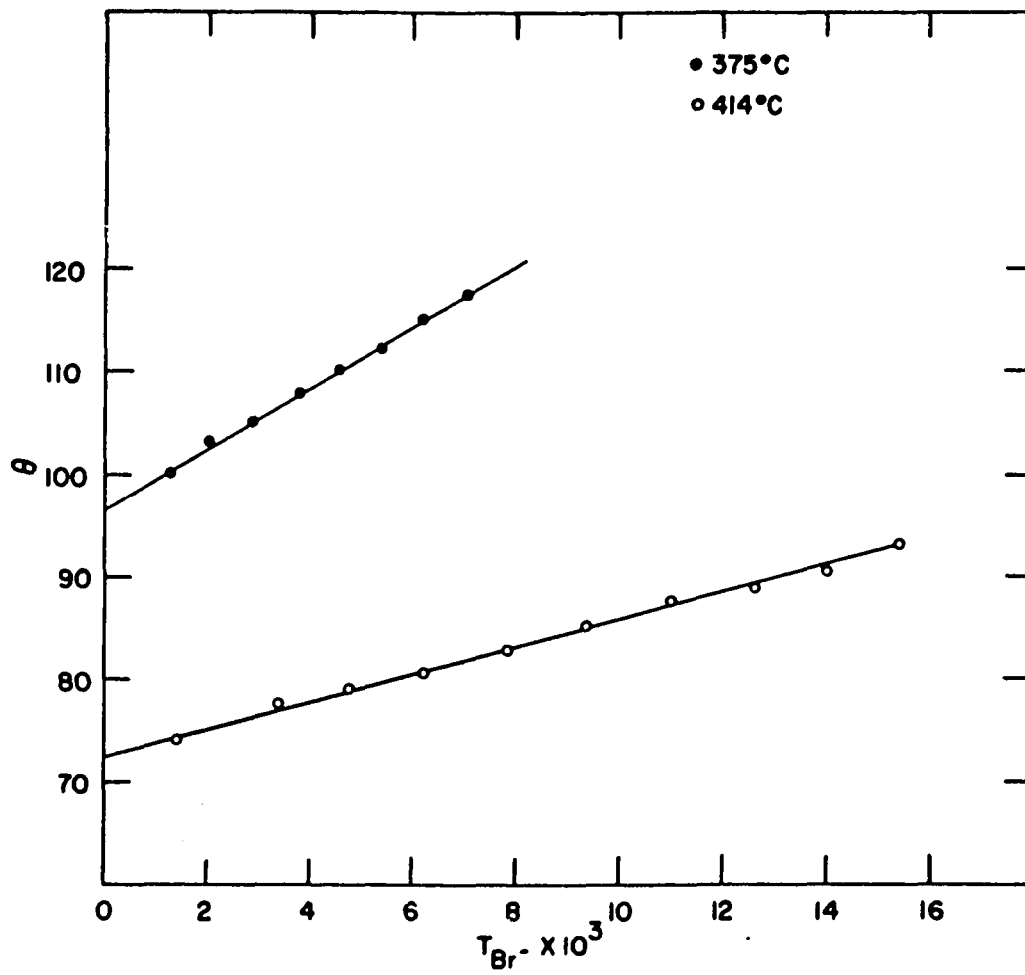
)
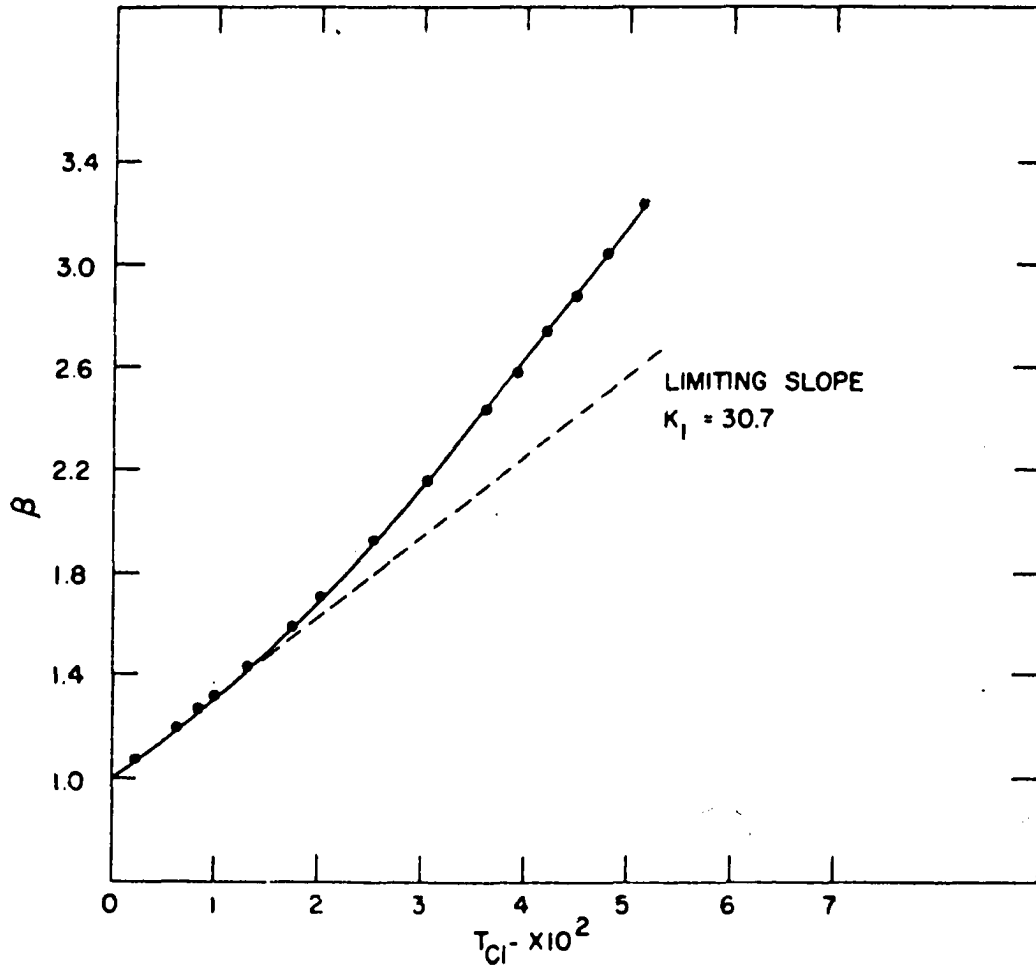
Figure 7.   Plot to show linearity of the derived equation 14
            for the silver nitrate system when KBr is added

measurements similar to those described in this paper in order to test a new theory based on a quasi-lattice model of a molten salt system; this will be discussed later in comparison to the "chemical" approach. Moreover the authors found that at $500^{\circ}C$, which is approximately $80-100^{\circ}$ above the temperature at which decomposition becomes appreciable, the e.m.f. drifted about 1.0 mv in one hour; this is apparently a result of the loss of $AgNO_3$ since nitrite added to the system in excess of the silver nitrate concentration had no effect on the Nernst potential. This drift in the potential was noticed in the $NaNO_3-KNO_3$ eutectic solvent (0.53:0.47 mole fraction respectively) even at $460^{\circ}C$ although the drift was somewhat slower. The values of the constants K_1 and K_2, previously defined, which were calculated from the above data are tabulated in Table 4. All the constants reported are in units of $molal^{-1}$. K_{1B} is the constant calculated from the quasi-lattice model corresponding to K_1 previously defined. It is inserted in this table for comparison.

Using the familiar equation

$$\left(\frac{\partial \ln K_1}{\partial T}\right)_P = \frac{d \ln K_1}{dT} = \frac{\Delta H_1^{\circ}}{RT^2} \tag{16}$$

one can calculate the enthalpy change, ΔH°, for the reactions described by equations 10 and 11 in the solvents KNO_3, $NaNO_3-KNO_3$, and $NaNO_3$. Here the subscript i refers to the individual
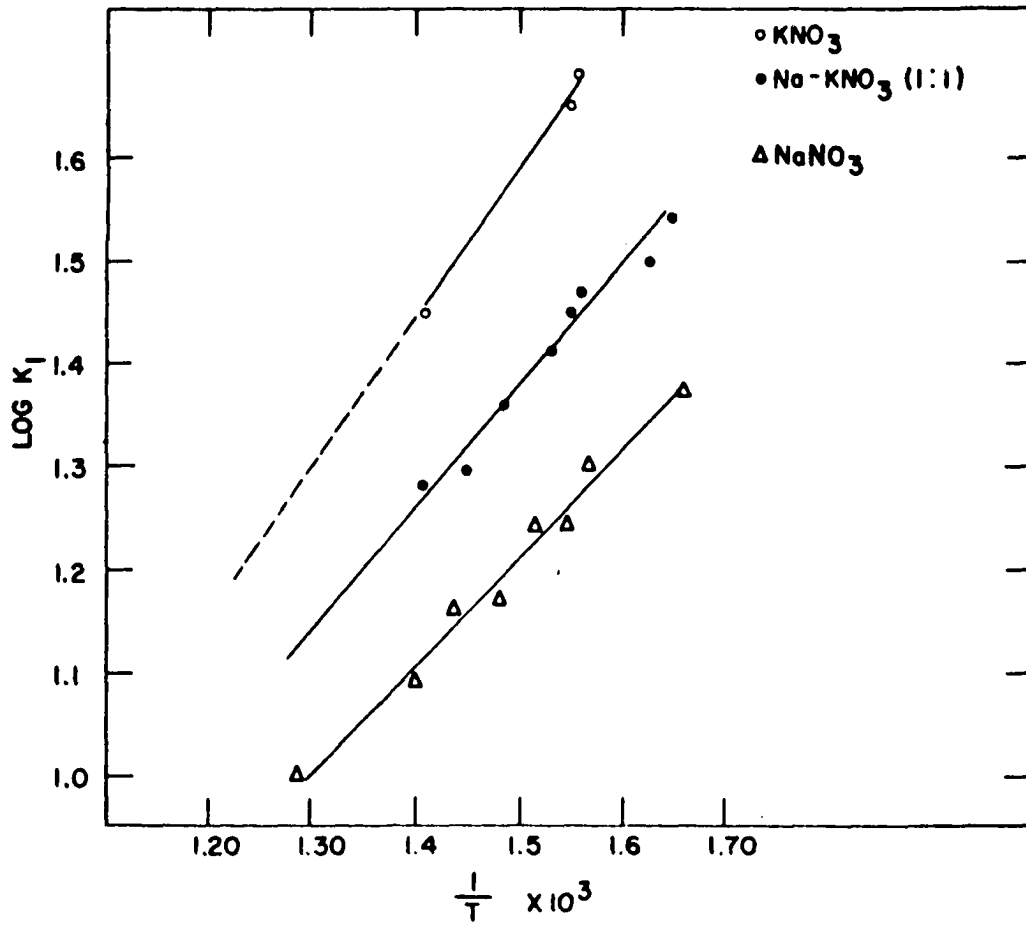
Table 4. Stability constants (molal^{-1})

Solvent	System	t°C	K_1 x 10^{-1}	K_{1B} x 10^{-1}	K_2 x 10^{-1}
KNO_3[a]	Ag^+,Cl^-	370	4.75	-	1.82
		436	2.85	-	1.25
$Na-KNO_3$	Ag^+,Cl^-	333	3.47	-	1.39
		342	3.10	-	0.969
		367	2.96	-	0.916
		374	2.80	-	0.893
		380	2.56	-	0.653
		401	2.26	-	0.810
		439	1.91	-	0.602
$Na-KNO_3$	Ag^+,Br^-	366	9.95	-	2.56
		375	9.64	-	3.09
		376	9.33	-	3.33
		380	9.32	-	1.86
		380	9.35	-	2.05
		414	7.23	-	1.84
$NaNO_3$[b]	Ag^+,Cl^-	331	2.35	2.34	1.02
		364	2.00	1.92	0.635
		385	1.72	1.74	0.574
		402	1.50	1.49	0.535
		423	1.44	1.36	0.282
		438	1.23	1.24	0.413
		500	0.984	0.932	0.220

[a]Constants calculated from the data of Blander et al. (4).

[b]Constants calculated from the data of Hill et al. (44).

reactions. These values are listed in Table 5. The values in parentheses were determined from two values. ΔE_B is the energy of interaction calculated from the quasi-lattice theory; it is included for comparison. Figure 8 shows the temperature dependence of log K_1 for the chloride system in the mixed solvent, pure $NaNO_3$, and KNO_3. It is seen that the heat of

Figure 8.   Temperature dependence of K_1 in various solvents
for the system Ag^+, Cl^-

reaction in the "chemical" approach agrees quite well with that of the interaction energy, ΔE, of the quasi-lattice model in the system with $NaNO_3$ as solvent. The data in the literature was rather sparse and did not afford comparison in the other solvents.

Table 5. Heats of reaction

Reaction	Solvent	$-\Delta H$ (kcal/mole)	$-\Delta E_B$ (kcal/mole)
$Ag^+ + Cl^- = AgCl$	KNO_3 [a]	(7.09)	5.65
$AgCl + Cl^- = AgCl_2^-$		(5.21)	
$Ag^+ + Cl^- - AgCl_2$	$NaNO_3$-KNO_3	5.01	
$AgCl + Cl^- = AgCl_2^-$		10.8	
$Ag^+ + Br^- = AgBr$	$NaNO_3$-KNO_3	5.94	
$AgBr + Br^- = AgBr_2^-$		13.9	
$Ag^+ + Cl^- = AgCl$	$NaNO_3$ [b]	4.60	4.62
$Ag^+Cl + Cl^- = AgCl_2^-$		8.30	

[a]Heats calculated from the data of Blander et al. (4).
[b]Heats calculated from the data of Hill et al. (44).

Hill and Wetmore (46) have postulated the species Ag_2Cl^+ to explain their transport data in the system $AgCl$-$AgNO_3$. In order to determine if Ag_2Cl^+ is important, at least with respect to current carrying species, a solution of $AgCl^*$,

0.27 N_{Cl^-}, in $AgNO_3$, was made up. The $AgCl^*$-$AgNO_3$ solution was to be the catholyte and the non-radioactive mixture was added to the anode compartment. Silver electrodes were inserted, the cell was capped and a measured current was passed through the cell for a known amount of time. Now it was assumed that if any radioactivity passed over to the catholyte salt it must have been a result of electroendosmosis, diffusion, or migration of the cationic species Ag_2Cl^+. Several such runs were performed and upon counting samples taken from the catholyte it was found that the activity was just about that of the background showing that there is no species Ag_2Cl^+ carrying current in the system investigated. From the data of cell B, where X^- is chloride, a crude estimate of K_3 defined as

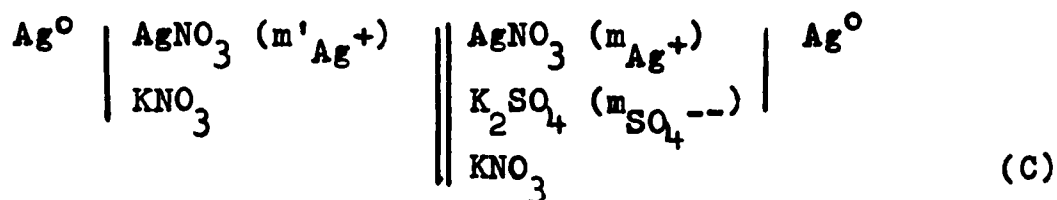$$K_3 = \frac{(Ag_2Cl^+)}{(AgCl)(Ag^+)} \tag{17}$$

was made and found to be of the order of one. However it must be remembered that this is only an estimate since the experiment was performed with chloride in excess of silver in order to suppress the species Ag_2Cl^+. By means of chlorine electrodes one could determine K_3 rather precisely running the experiment with low chloride and high silver concentrations.

2. **Other complexes**

A procedure similar to that described above was tried with NaF and K_2CrO_4. However it was found that no appreciable

complexing occurred even upon the addition of large amounts of the complexing reagent. This is also true for KNO_2.

Watt and Blander (73) have made measurements on the cell

$$Ag^O \left| \begin{array}{c} AgNO_3 \ (m'_{Ag^+}) \\ KNO_3 \end{array} \right| \left| \begin{array}{c} AgNO_3 \ (m_{Ag^+}) \\ K_2SO_4 \ (m_{SO_4^{--}}) \\ KNO_3 \end{array} \right| Ag^O \qquad (C)$$

to test the limitations of the quasi-lattice model which, according to the authors, strictly applies to mixtures of cations and anions, respectively, of the same size and charge. These data were treated by means of the "chemical" approach and an equilibrium constant was calculated for the species $AgSO_4^-$.

As previously described any deviations from ideality, $-\Delta E$, in this system were ascribed to complex ion formation. Now the change in e.m.f. upon the addition of K_2SO_4 is given by

$$\Delta E = \frac{RT}{F} \ln \frac{N_{Ag^+} \cdot N_{NO_3^-}}{N'_{Ag^+} \cdot N'_{NO_3^-}} \qquad (18)$$

where N_i is the ion fraction of the component indicated. Since the Nernst law was shown to hold to better than 0.5 mv for dilute solutions of $AgNO_3$ in pure KNO_3 the ratio of the rational activity coefficients which are defined by

$$\gamma_{AgNO_3} = \frac{a_{AgNO_3}}{N_{Ag^+} \cdot N_{NO_3^-}} \qquad (19)$$

was assumed to be unity.

Since the change in potential upon the addition of potassium sulfate was so small, the effect of dilution had to be taken into account. Since $N'_{NO_3^-} = 1$, then

$$N_{NO_3^-} = 1 - N_{SO_4^{--}} \qquad (20)$$

and

$$\bar{N}_{Ag^+} \cong \frac{N'_{Ag^+}}{1 + 2N_{SO_4^{--}}} \qquad (21)$$

where $\bar{N}_{Ag^+}$ is the ion fraction of silver after dilution by K_2SO_4.

Upon substitution of equations 20 and 21 into 18 one obtains

$$-\Delta E = \frac{RT}{F} \ln \frac{\bar{N}_{Ag^+}(1 + 2N_{SO_4^{--}})}{N_{Ag^+}(1 - N_{SO_4^{--}})} \qquad (22)$$

For small sulfate one may make the approximations

$$\ln (1 + 2N_{SO_4^{--}}) \cong 2N_{SO_4^{--}} \qquad (23)$$

and

$$-\ln (1 - N_{SO_4^{--}}) \cong N_{SO_4^{--}} \tag{24}$$

Since in pure KNO_3, where n_j is the number of moles of the solvent

$$N_i = \frac{n_i}{n_i + n_j} \tag{25}$$

and

$$m_i = \frac{n_i}{n_j M_j/1000} = \frac{9.9 n_i}{n_j} \tag{26}$$

then one can write

$$m_i \cong 9.9 \ N_i \tag{27}$$

and equation 22 can be rewritten as

$$10^{-(\frac{\Delta EF}{2.3RT} + 0.131 \ T_{SO_4^{--}})} = \beta = \log \frac{\bar{m}_{Ag^+}}{m_{Ag^+}} \tag{28}$$

Now since $T_{SO_4^{--}} >> T_{Ag^+}$, then

$$K = \frac{(AgSO_4^-)}{(Ag^+) T_{SO_4^{--}}} \tag{29}$$

and,

$$T_{Ag^+} = Ag^+ + AgSO_4^- = \bar{m}_{Ag^+} \qquad (30)$$

If equations 29 and 30 are substituted in equation 28 one obtains the final result, viz.,

$$\beta = 1 + K_1 T_{SO_4^{--}} \qquad (31)$$

The constant K was determined using the data from the literature. K was found to be rather insensitive to temperature. This was most probably a result of the range of values of the potential change i.e., the larger the potential change, the greater the precision of the data and conversely. The values of K at various temperatures are listed in Table 6 where K_B is the value calculated from the lattice model. The value of K was determined by plotting β versus $T_{SO_4^{--}}$; the slope is K. The values of K at various temperatures are shown in Table 6. Figure 9 shows the plot described above where all the points at various temperatures have been included to demonstrate the insensitivity of K to changes in temperature.

Figure 9. Plot to show linearity of equation 31 in the silver
          nitrate-potassium sulfate system, and the apparent
   insensitivity of K to change in temperature

Table 6. Variation of K with temperature

t($^\circ$C)	K(molal^{-1})	$m_{Ag}^{+} \times 10^2$	K_B(molal^{-1})
363	1.3	1.00	1.2
408	1.2	2.85	1.2
449	1.3	2.89	1.3

B. Complexes of Lead and Cadmium

The first step in investigating other metal-halide complexes was to decide what the most interesting systems were and to determine whether the systems were amenable to an investigation similar to that of the silver systems. Because of the similarity of the solvent properties of the fused nitrates with water, it was thought that the chloride complexes of lead and cadmium would be of interest. Not only were their metal nitrates stable in fused alkali nitrates and they formed ideal solutions in dilute concentration but also there were values in the literature for stability constants determined by other methods to afford comparison.

Now a reversible chlorine electrode had been reported for fused chloride systems as previously noted. Similarly a reference electrode of the type Ag, AgCl(KCl, LiCl), already described, has been reported for use in chloride melts.
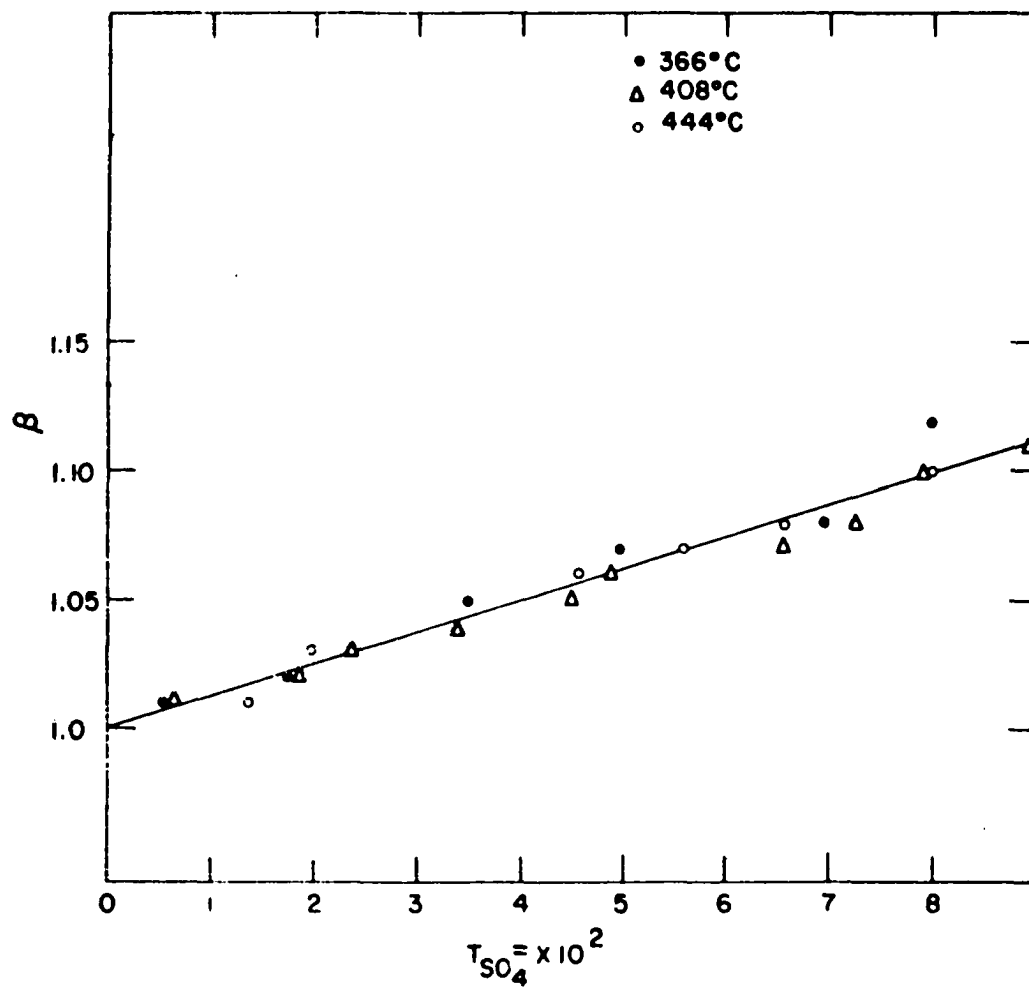
However none had been reported for use in molten nitrate melts.
Therefore an attempt was made to prepare a reference electrode
of the type Ag/AgCl(s). The solubility product of silver
chloride had been reported as $(4.89 \pm 0.20) \times 10^{-6}$ $(molal)^2$
in fused Na-KNO$_3$ at 248°C. Thus it was decided that an
electrode of this kind might be feasible at low temperatures
(225-250°C) and relatively high chloride concentration, i.e.,
0.01 molal.

However all sorts of difficulties arose with these
electrodes. Fluctuations occurred in the electrodes; two
apparently identical electrodes in the same solution gave a
different e.m.f. even after very long periods of equilibration;
changes occurred in the e.m.f. when the electrodes were gently
shaken; changes in the concentration of the solution did not
result in changes with the e.m.f. which agreed with those
predicted by the Nernst equation; and the potential did not
return to the equilibrium value after polarization.
Irrespective of the method of preparation these electrodes did
not respond reversibly.

In the main this may be explained by the data of Panish
et al. (63). They obtained activity, free energy, heat, and
entropy data for solid solutions of AgCl and NaCl from about
300-400°C by studying galvanic cells of the type

$$\text{Ag}^\circ \mid \begin{array}{c} \text{AgCl, NaCl} \\ \text{solid soln} \end{array} \mid \text{Cl}_2$$
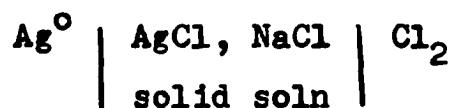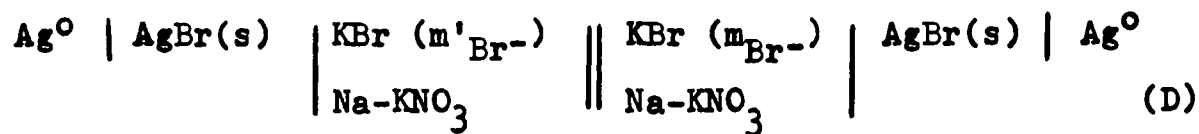
It was found, that the e.m.f. change of the above cell with silver chloride concentration was not monotonic. The curves for AgCl activity in the solid state as a function of composition at 300 and 400°C were particularly interesting in that they indicated an immiscibility gap in which super-saturation could be obtained readily. At any rate there were pronounced positive deviations in this system at high NaCl concentrations and slight negative deviations at high AgCl concentrations. Thus as the NaCl concentration varied in the melt so would the activity of the solid AgCl and thus its activity term would not cancel in the expression for the e.m.f. of the concentration cell. Another way of saying the same thing is that the solubility product of AgCl at different NaCl concentrations would be different.

Forland (28) regarded results such as these as a reflection of the relative deformability of the AgCl and NaCl lattices, the AgCl lattice being more deformable than the NaCl lattice. At high NaCl concentrations the positive deviations resulted from the distortions resulting from the introduction of AgCl in the rigid NaCl lattice. This is accompanied by an increase in energy. However at high AgCl concentrations the deformable AgCl lattice accommodates the presence of NaCl without an increase in energy.

Since the Ag, AgCl(s) electrodes proved to be irreversible, it was thought that Ag, AgBr(s) electrodes might be more

Figure 10. Test of the validity of the Nernst limiting law
for cells of type D at 261°C

successful. Cells of the type

$$Ag^{o} \mid AgBr(s) \; \left| \begin{matrix} KBr \; (m'_{Br-}) \\ Na-KNO_3 \end{matrix} \right| \left| \begin{matrix} KBr \; (m_{Br-}) \\ Na-KNO_3 \end{matrix} \right| \; AgBr(s) \mid Ag^{o} \quad (D)$$

were set up and as before the e.m.f. was followed as a function of the bromide ion concentration in the eutectic solvent. Just as with the silver electrodes the Nernst limiting law was followed indicating that

$$\frac{\gamma'_{Br^-}}{\gamma_{Br^-}} = 1 \qquad (32)$$

in the concentration range 1.24×10^{-3} to 9.32×10^{-2} molal; furthermore it justified neglect of the liquid junction potential so that the e.m.f. of cell D is given by

$$E = \frac{2.30 \; RT}{F} \log \frac{m'_{Br^-}}{m_{Br}} \qquad (33)$$

As before the left-hand (primed) side is the reference half-cell. Some typical data is shown in Table 7 where $m'_{Br-} = 9.32 \times 10^{-2}$ and the temperature is $261^{o}C$.

The theoretical slope was 0.106 and that calculated analytically from the data in Table 7 was 0.102. A plot of the data is shown in Figure 10. At very low m_{Br}, i.e., when m_{Br} is of the order of $\sqrt{Ksp}$ for AgBr a slight deviation is
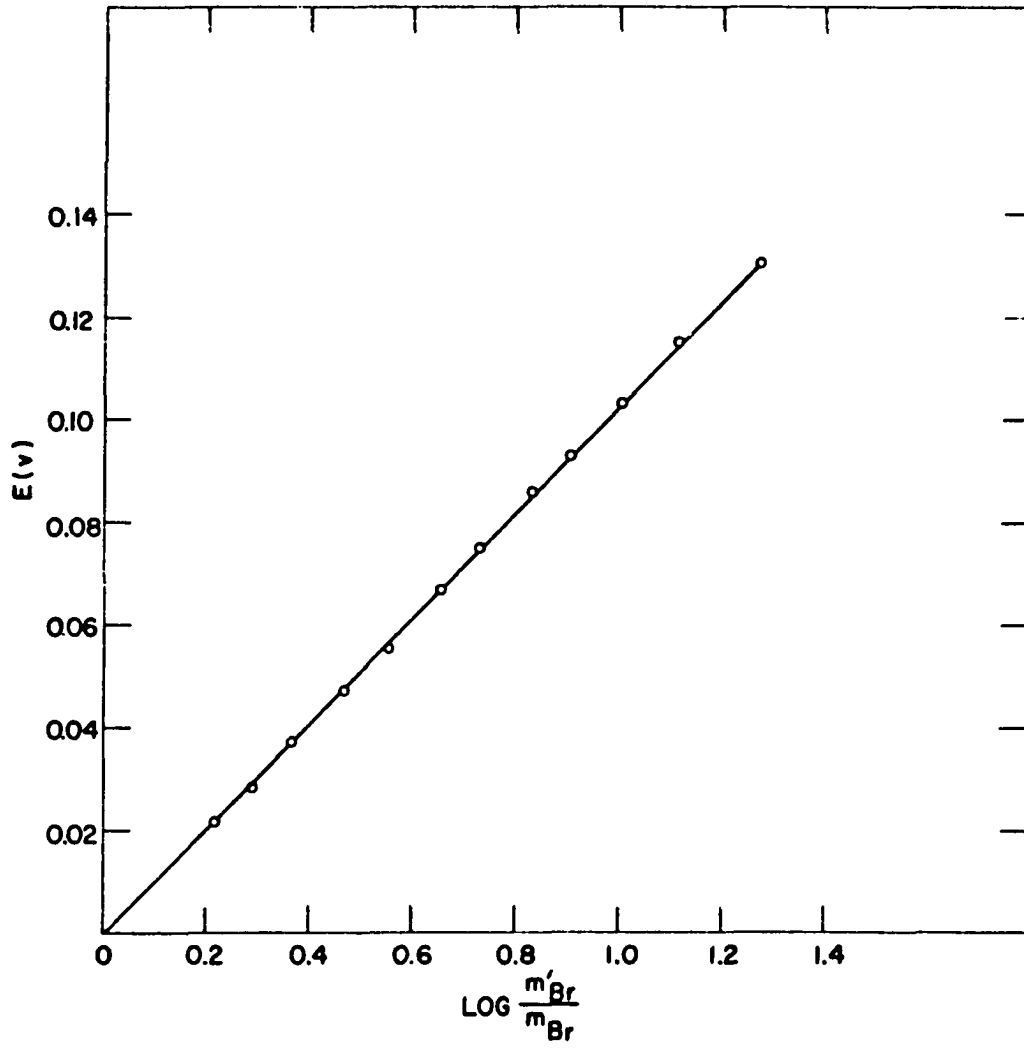
Table 7. Data to determine validity of Nernst limiting law
for cell D at 261°C

$m_{Br^-} \times 10^2$	E(v)	$\log \dfrac{m'_{Br^-}}{m_{Br^-}}$
0.124	0.183	1.88
0.281	0.153	1.52
0.495	0.130	1.28
0.704	0.115	1.12
0.916	0.103	1.01
1.14	0.0932	0.913
1.37	0.0860	0.833
1.72	0.0749	0.734
2.06	0.0668	0.656
2.57	0.0567	0.559
3.18	0.0471	0.467
3.94	0.0371	0.374
4.79	0.0280	0.289
5.57	0.0210	0.224

noted because of the additional bromide in solution due to the
dissolution of the electrode. In addition this was tried at
299°C where the calculated slope was 0.113 and the experimental
slope was 0.110 and at 325°C where the theoretical slope was

0.118 and the experimental slope was 0.117.

Because of the oxidizing power of the nitrate solvent a stable Cd^0 or Pb^0 electrode could not be prepared although they are quite stable in halide melts. Therefore the experiments had to be designed such that some of the complex species would be eliminated, i.e., their relative concentrations would be so low as to be undetectable.

It is now advantageous to define the constant

$$K_n = \frac{(MBr_n^{2-n})}{(MBr_{n-1}^{3-n})(Br^-)} \tag{34}$$

where M is either lead or cadmium. If the T_M^{++} is much greater than T_{Br^-}, then, since

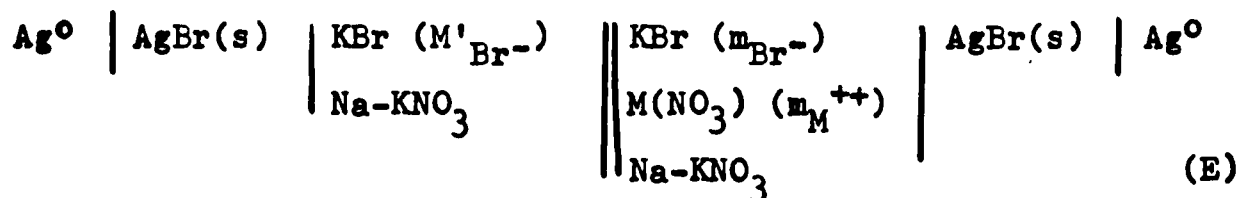$$T_{Br^-} = Br^- + \sum_{n=1}^{r} nMBr_n^{2-n} \tag{35}$$

one can write

$$\frac{T_{Br^-}}{Br^-} = 1 + K_1 T_M + 2K_1 K_2 T_M Br^- + \cdots \cdots \tag{36}$$

Cells of the type

Figure 11. Plot of β versus $T_{Pb^{++}}$ to show applicability of equation 38

$$\text{Ag}^0 \mid \text{AgBr(s)} \mid \begin{array}{l} \text{KBr } (\text{M}'_{\text{Br}^-}) \\ \text{Na-KNO}_3 \end{array} \mid\mid \begin{array}{l} \text{KBr } (\text{m}_{\text{Br}^-}) \\ \text{M(NO}_3) \ (\text{m}_\text{M}^{++}) \\ \text{Na-KNO}_3 \end{array} \mid \text{AgBr(s)} \mid \text{Ag}^0 \qquad \text{(E)}$$

were set up and the potential was followed as a function of the lead and cadmium concentration. Some typical data are given in Tables 8 and 9. As before one can write

$$\Delta E = \frac{2.30 \ RT}{F} \log \frac{m_{\text{Br}^-}}{m''_{\text{Br}^-}} = \frac{2.30 \ RT}{F} \log \frac{T_{\text{Br}^-}}{\text{Br}^-} \qquad (37)$$

Thus equation 36 transforms into

$$10^{\frac{\Delta EF}{2.30 \ RT}} = \beta = 1 + K_1 T_M + 2K_1 K_2 T_M \text{Br}^- + \ldots \qquad (38)$$

If only the species MBr^+ is important in the concentration range studied then a plot of β versus T_M^{++} should yield a straight line with intercept of unity and slope equal to K_1. Some typical plots are given in Figures 11 and 12. The correction due to dilution was applied in all cases although it was found to be small. Since the slope of the cadmium plot was equal to 100, the metal ion concentration was corrected and thus K_1 for cadmium was 1.08×10^2 at 256°C. The data at the other temperatures were treated similarly.

Other cells similar to E were set up; however in order to obtain the constants for any other species present in this

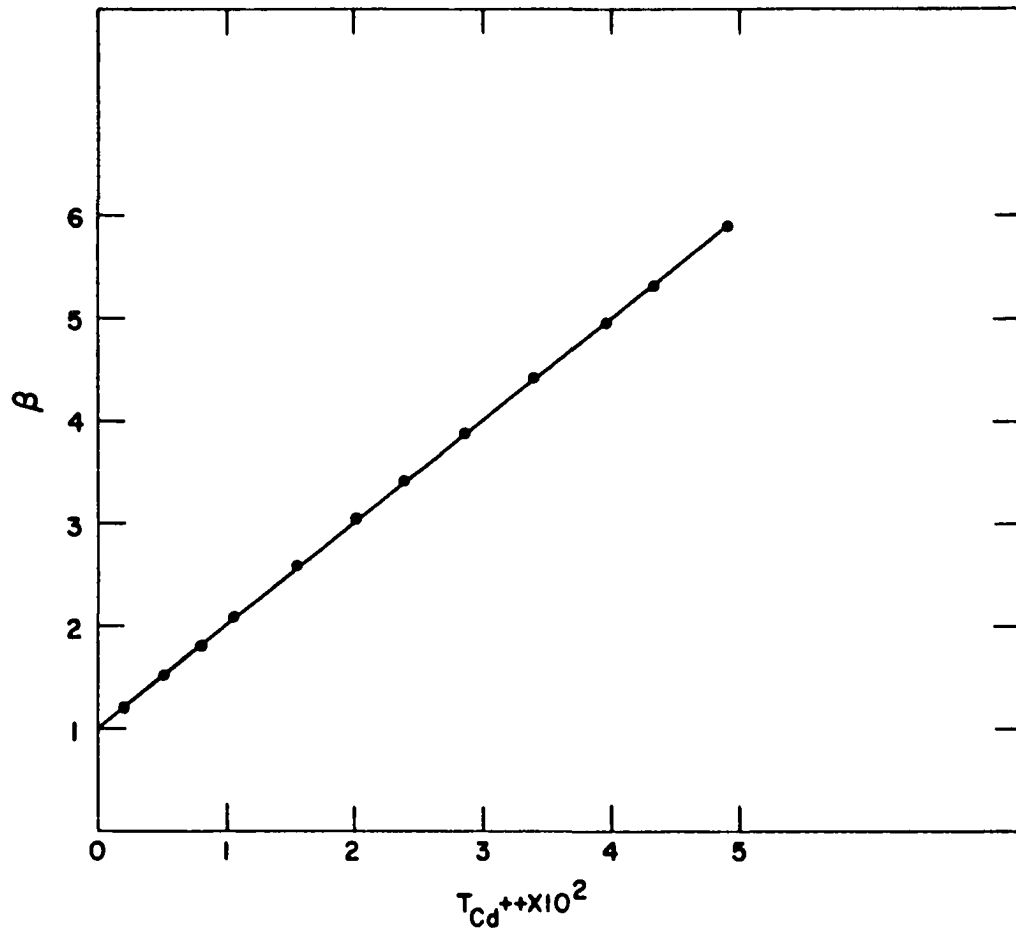Figure 12. Plot of β versus $T_{Cd^{++}}$ to show applicability of equation 38 at 256°C
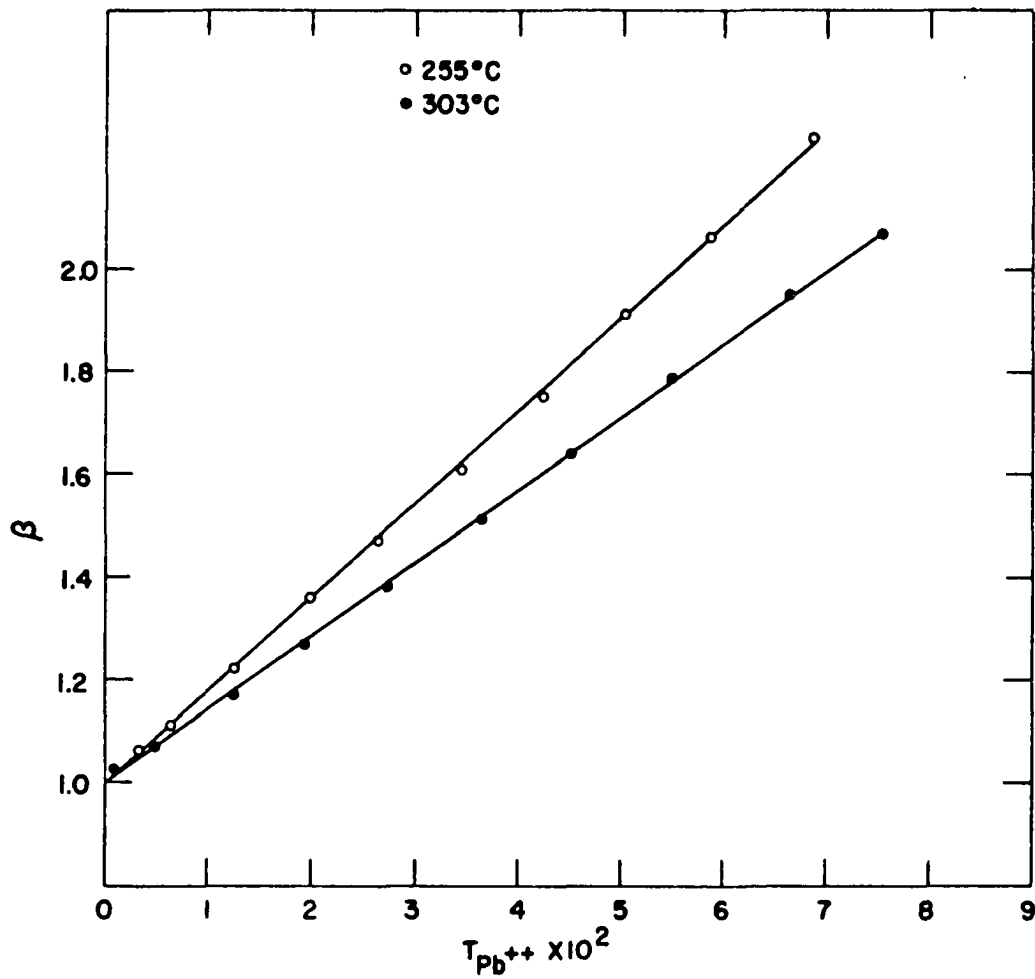
Table 8. Variation of e.m.f. of cell E as a function of the concentration of $Pb(NO_3)_2$

$T_{Pb^{++}} \times 10^2$	$\Delta E(v)$	β	$T_{Pb^{++}} \times 10^2$	$\Delta E(v)$	β
t = 255°C			t = 303°C		
0.372	0.0028	1.06	0.139	0.0009	1.02
0.643	0.0049	1.11	0.538	0.0033	1.07
1.27	0.0093	1.22	1.27	0.0078	1.17
2.00	0.0141	1.35	1.92	0.0119	1.27
2.64	0.0179	1.47	2.74	0.0165	1.38
3.46	0.0223	1.61	3.65	0.0211	1.51
4.22	0.0262	1.75	4.51	0.0251	1.64
5.04	0.0301	1.91	5.52	0.0295	1.79
5.86	0.0339	2.07	6.64	0.0337	1.95
6.86	0.0381	2.26	7.54	0.0371	2.07

t = 319°C

$T_{Pb^{++}} \times 10^2$	$\Delta E(v)$	β
0.741	0.0039	1.17
1.58	0.0054	1.23
2.08	0.0063	1.28
2.95	0.0078	1.35
4.14	0.0097	1.45
4.90	0.0110	1.53
5.86	0.0126	1.62
6.87	0.0149	1.77

mixture, the bromide ion had to be greater than the metal ion concentration. The best procedure would be to run the experiment with high bromide and low metal using electrodes reversible to the metal ion. However since this was not

Table 9. Variation of the e.m.f. of cell E as a function of the concentration of $Cd(NO_3)_2$

$T_{Cd^{++}} \times 10^2$	$\Delta E(v)$	β	$T_{Cd^{++}} \times 10^2$	$\Delta E(v)$	β
	t = 256°C			t = 303°C	
0.177	0.0071	1.17	0.590	0.0875	6.35
0.519	0.0191	1.52	0.669	0.0929	7.10
0.795	0.0270	1.80	0.749	0.0979	7.89
1.07	0.0338	2.09	0.830	0.1023	8.64
1.55	0.0435	2.58	0.896	0.1055	9.23
2.02	0.0509	3.04	0.983	0.1096	10.1
2.41	0.0564	3.42	1.08	0.1136	10.9
2.86	0.0621	3.87	1.16	0.1169	11.7
3.40	0.0682	4.42	1.27	0.1203	12.5
3.95	0.0734	4.94	-	-	-
4.34	0.0768	5.32	-	-	-
4.93	0.0814	5.87	-	-	-

t = 298°C

$T_{Cd^{++}} \times 10^2$	$\Delta E(v)$	β
0.308	0.0102	1.23
0.808	0.0227	1.58
1.14	0.0297	1.83
1.64	0.0380	2.16
2.04	0.0438	2.43
2.41	0.0484	2.66

feasible, an attempt was made to estimate the higher constants by means of the procedure outlined here, by following the potential change upon the addition of $M(NO_3)_2$ at high bromide concentration. In this case, then, equation 38 is no longer

valid. Along with equation 35 one must write

$$T_{M^{++}} = M^{++} + \sum_{n=1}^{r} MBr_n^{2-n} \tag{39}$$

Solving for the concentration of each one of the MBr_n^{2-n} species by means of equations 39 and 34, one obtains, after making some simple substitutions, the equation

$$A + BK_1 + CK_1K_2 + DK_1K_2K_3 + \ldots \ldots = 0 \tag{40}$$

where

$$A = \frac{T_{Br^-} - (Br^-)}{T_{M^{++}}}$$

$$B = (A - 1)(Br^-)$$

$$C = (A - 2)(Br^-)^2$$

$$D = (A - 3)(Br^-)^3$$

This was tried at 306°C for lead and 256 and 274°C for cadmium. The values of K_1 determined previously were assumed and then an attempt was made to solve these equations simultaneously. With the lead system a consistent set of values could be obtained only if, for n greater than three, all K_n were assumed zero; that is the method is insensitive to such species as $PbCl_3^-$, $PbCl_4^{-2}$, etc. Once K_2 was determined, in

order to determine whether this constant was real, the concentration of free bromide was determined and compared with the value determined by equation 33. If only K_1 were used the calculated value of bromide was about 10 per cent too high. When the average value of K_2 was used in addition the calculated value of bromide was 2-3 per cent that determined by equation 33. These data are given in Table 10. In all calculations corrections for dilution were made. These data gave $K_2 = 6.17 \pm 0.60$.

Taking K_1 equal to $(1.08 \pm 0.04) \times 10^2$ for the cadmium system at 256°C the same approach was used as with the lead system. However in this instance both K_2 and K_3 were determined by the proper choice of concentration range. A value for K_4 could have been determined but it was thought that this would be extending this approach beyond its limitations. Table 11 shows the constancy of K_2 and the definite concentration dependence of K_3 which might indicate the need for the inclusion of K_4. This same treatment was utilized at 274°C. Table 12 compares the values of K_n determined by other methods with those determined here.

Iverson (48) determined the values of K_n given in Table 12 by determining the solubility product of $CdCrO_4$ in the fused eutectic solvent and then investigating the increase in solubility of the cadmium salt on the addition of alkali bromide. This increase in solubility was attributed to complex

Table 10.   Parameters in the determination of higher lead complexes at 306°C

$T_{Pb^{++}} \times 10^2$	$\Delta E(v)$	A	$-B \times 10^2$	$-C \times 10^3$	K_2	$(Br^-)_{obs}$	$(Br^-)_{calc}$
0.581	0.0032	0.651	2.05	4.81	5.49	0.060	0.061
0.986	0.0053	0.632	2.10	4.47	5.40	0.057	0.057
1.51	0.0081	0.613	2.09	4.06	5.63	0.054	0.054
2.12	0.0113	0.590	2.08	3.62	5.90	0.051	0.050
2.64	0.0140	0.572	2.06	3.30	6.15	0.048	0.049
3.27	0.0170	0.542	2.07	2.99	6.04	0.045	0.047
4.04	0.0210	0.521	2.01	2.63	6.52	0.042	0.043
4.62	0.0226	0.482	2.10	2.48	5.42	0.041	0.040
5.29	0.0256	0.464	2.04	2.24	5.71	0.038	0.039
6.12	0.0291	0.0442	1.99	1.99	5.89	0.036	0.037
7.58	0.0356	0.410	1.85	1.56	6.91	0.031	0.033
8.61	0.0397	0.387	1.77	1.33	7.52	0.029	0.030
9.46	0.0427	0.0369	1.72	1.21	7.61	0.027	0.027

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Table 11. Parameters in the determination of higher cadmium complexes

			A. At 255°C				
$T_{Cd^{++}} \times 10^2$	$\Delta E(v)$	A	$-B \times 10^2$	$-C \times 10^4$	$-D \times 10^5$	K_2	K_3
0.457	0.0084	1.99	-4.54	0.211	9.78	-	12.5
0.804	0.0150	1.90	-3.57	1.58	6.90	-	12.8
1.16	0.0215	1.78	-2.68	2.60	4.95	-	11.8
1.59	0.0295	1.64	-1.85	3.01	3.28	-	10.9
1.89	0.0346	1.53	-1.37	3.15	2.56	-	8.97
2.21	0.0400	1.44	-1.01	2.96	1.90	-	8.46
2.52	0.0449	1.36	-0.742	2.71	1.43	-	8.35
3.09	0.0531	1.21	-0.363	2.36	0.925	-	5.68
3.47	0.0581	1.13	-0.202	2.09	0.696	-	4.94
3.98	0.0643	1.04	-0.0472	1.76	0.484	-	4.38
4.50	0.0701	0.949	0.0607	1.49	0.346	54.9	-
5.05	0.0755	0.867	0.144	1.32	0.268	49.9	-
5.57	0.0803	0.808	0.182	1.07	0.187	52.9	-
6.27	0.0861	0.734	0.223	0.897	0.135	50.9	-
7.03	0.09167	0.667	0.247	0.734	0.0955	50.5	-
7.63	0.0958	0.623	0.256	0.638	0.0747	50.4	-
8.36	0.1003	0.574	0.262	0.542	0.0566	49.9	-
9.08	0.1045	0.534	0.262	0.465	0.0440	50.0	-
9.80	0.1083	0.498	0.260	0.401	0.0345	50.1	-
10.7	0.1130	0.461	0.252	0.337	0.0259	51.9	-
11.6	0.1170	0.428	0.246	0.290	0.0203	51.7	-
12.3	0.1200	0.405	0.240	0.261	0.0171	51.8	-

Table 11. (Continued)

| | | | B. At 274°C | | | | |
$T_{Cd^{++}} \times 10^2$	$\Delta E(v)$	A	$-B \times 10^2$	$-C \times 10^4$	$-D \times 10^5$	K_2	K_3
0.126	0.0033	1.27	-6.02	3.63	1.92	-	2.32
0.328	0.0087	1.19	-3.80	3.24	1.45	-	1.28
0.584	0.0152	1.13	-2.25	2.60	0.967	-	3.73
0.837	0.0213	1.04	-0.592	2.22	0.688	-	2.91
1.20	0.0295	0.925	0.953	1.73	0.423	50.1	-
1.61	0.0377	0.814	1.99	1.36	0.267	48.4	-
2.05	0.0454	0.717	2.58	1.06	0.172	46.8	-
2.54	0.0532	0.634	2.82	0.814	0.109	47.2	-
3.04	0.0599	0.563	2.93	0.647	0.0734	46.3	-
3.71	0.0679	0.488	2.88	0.479	0.0447	47.3	-
4.40	0.0751	0.430	2.75	0.367	0.0290	48.4	-
5.23	0.0823	0.373	2.61	0.282	0.0189	46.6	-

Table 12. Stability constants for metal-bromide complex ions
in fused $NaNO_3$-KNO_3 eutectic

Complex species	t°C	K_n	t°C	K_n[a]
$PbBr^+$	255	18.4 ± 0.5	250	18 ± 3
	303	14.2 ± 0.4	275	13 ± 3
	319	11.3 ± 0.3	300	11 ± 2
$PbBr_2$	306	6.2 ± 0.6	300	2 ± 1
$CdBr^+$	256	108 ± 4	250	20 ± 4
	274	95.0 ± 6.0	-	--
	298	75.0 ± 3.7	300	24 ± 5
$CdBr_2$	256	51.2 ± 4.0	250	5 ± 3
	274	47.6 ± 9.0	300	5 ± 3
$CdBr_3^-$	256	10.5 ± 3.0	-	--
	274	2.6 ± 1.0	-	--

[a]Values determined by Iverson (48).

ion formation and the constants, K_n, defined by equation 34
were calculated on this basis. The agreement in the case of
the lead complexes is surprisingly good. However there is a
marked difference in the cadmium complexes. It is felt that
the values determined here are more reasonable since Iverson
found that for cadmium both the chlorides and bromides had the
same stability constants. Duke and Lawrence (21) evaluated

K_n for zinc bromide complexes in the Na-KNO_3 eutectic solvent at 250°C from kinetic data and found K_1 = 250, K_2 = 40, and K_3 = 10.4; these K are in units of molality^{-1}. Therefore it would seem that the values for cadmium determined by Iverson were somewhat low although it must be mentioned that the determination of the K_n by the measurement of the e.m.f. should be much more precise than measurement by the solubility product method.
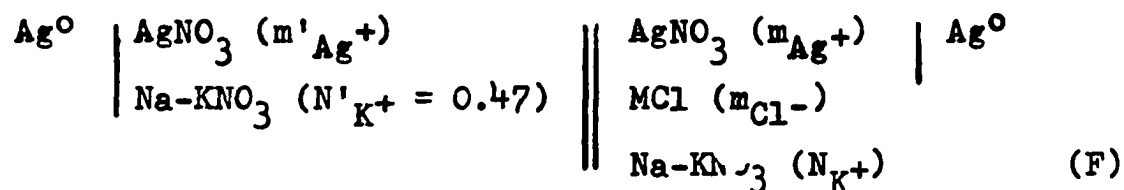
C. Solvent Effects

As is evident from the data of Table 4, there is a definite trend in the K's for the silver-chloride system as the size of the solvent cation changes. Blander and Braunstein (5) noticed this effect in their discussion of the quasi-lattice model with measurements in pure KNO_3 and some preliminary measurements in $NaNO_3$. The negative deviations from ideality increased upon going from $NaNO_3$ to KNO_3 as solvent. It should be pointed out that this effect has been noted in other solvent systems. Lantratov and Alabyshev (57, 58, 59) studied the systems $PbCl_2$-KCl, $PbCl_2$-NaCl, $PbCl_2$-LiCl, $PbCl_2$-$BaCl_2$, $PbCl_2$-$SrCl_2$, $PbCl_2$-$CaCl_2$, $CdCl_2$-NaCl, $CdCl_2$-KCl, $CdCl_2$-$BaCl_2$, $ZnCl_2$-NaCl, and $ZnCl_2$-KCl. They found that the negative deviations from ideality decreased with decrease in radius and increase in cationic

charge of the solvent cation.

It was thought that it might be interesting to determine the dependence of K_1 and K_2 on the solvent cation concentration in the silver-chloride system.

The measurements were similar to that described in section A and will not be discussed in detail. Cells of the type F

$$Ag^o \left| \begin{matrix} AgNO_3 \ (m'_{Ag^+}) \\ Na-KNO_3 \ (N'_{K^+} = 0.47) \end{matrix} \right| \left| \begin{matrix} AgNO_3 \ (m_{Ag^+}) \\ MCl \ (m_{Cl^-}) \\ Na-KNO_3 \ (N_{K^+}) \end{matrix} \right| Ag^o \qquad (F)$$

were set up. In these measurements a Kintel vacuum tube voltmeter was used as null instrument so that the amount of current drawn when determining the e.m.f. would be kept at a minimum. It was found that when MCl was absent (M is either sodium or potassium) the potential difference of the two half-cells deviated from that of the Nernst value in a very regular fashion. If the deviation is defined as

$$-\delta E = + E_{obs} - E_n \qquad (41)$$

where, as before, $-E_n$ is the Nernst potential of cells of type A, then as the N_{K^+} increased δE became more negative; this is shown in Figure 13. Before the reference (left-hand) electrode could be used a determination of the effect of this
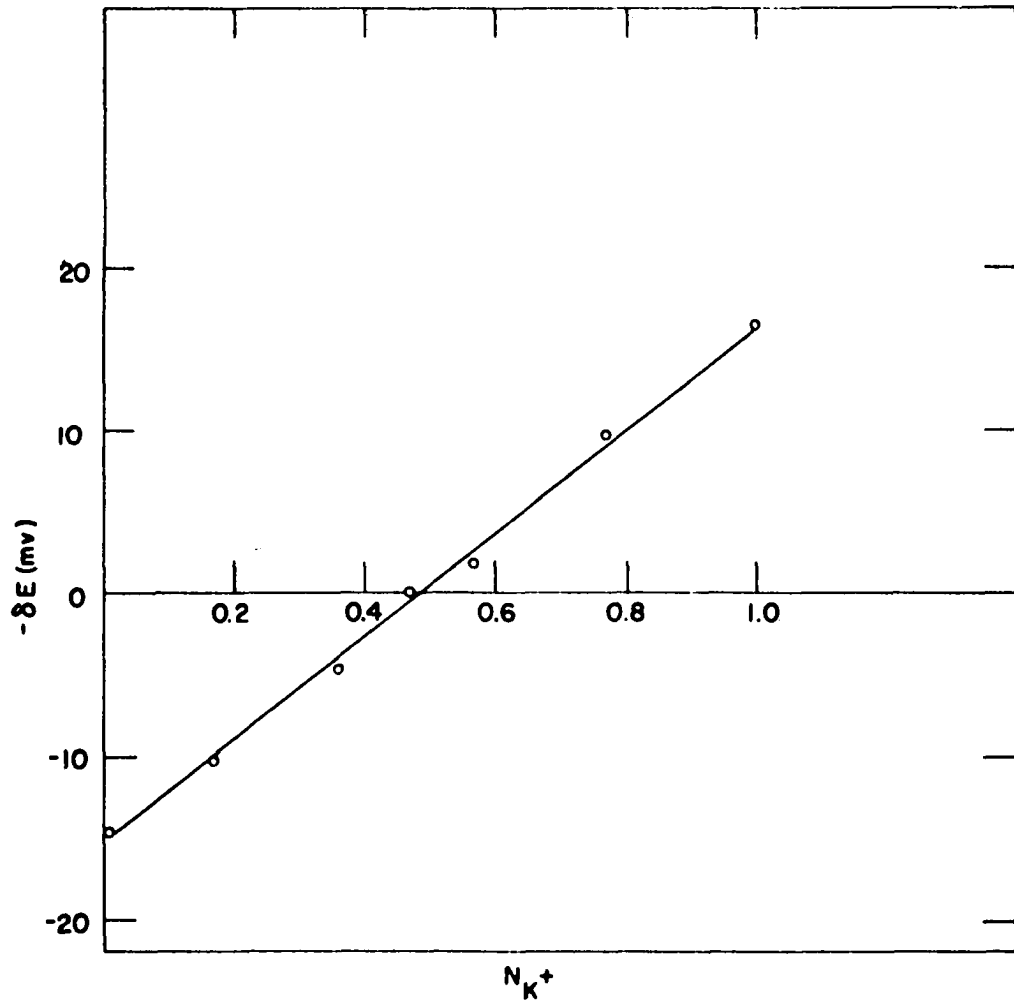
apparent liquid junction potential on the e.m.f. when MCl was added had to be ascertained. Runs were made in pure $NaNO_3$ and KNO_3 and the K_1 and K_2 determined from these runs were compared with those calculated from the data in the literature. The values determined experimentally agreed surprisingly well with those calculated from the data in the literature. Therefore, since it was the quantity $-\Delta E$, defined by equation 8, which was to be determined, it was evident that the apparent liquid junction potential was constant and was not affected by the added chloride, i.e., this δE would cancel when E_{obs} was subtracted from E with added chloride.

Runs were then made at various N_{K^+} and the constants were determined by graphing with a least squares technique. Some typical data are shown in Table 13. These plots are shown in Figure 14 and Figure 15 shows the concentration dependence of K_1; the data are summarized in Table 14. All these values were determined at $374°C$ and the temperature varied $\pm 0.5°C$ from run to run.

It is estimated that in the silver-chloride runs K_1 was determined with a precision of about 4 per cent and K_2 about 10 per cent. It is rather interesting that the slope of the plot for K_1 is 0.40; and the difference in the standard heats of reaction, or in the language of the quasi-lattice theory, the difference in the energies of interaction, for the pure solvents divided by 2.30 RT is 0.35. This would suggest an

Figure 14. Plot to show linearity of equation 15 for cell F

Table 13. Electromotive force as a function of chloride and potassium ion concentration at 374°C

| $N_{K^+} = 0.17$ | | | $N_{K^+} = 0.36$ | | |
| $m_{Ag^+} = 0.126 \times 10^{-2}$ | | | $m_{Ag^+} = 0.120 \times 10^{-2}$ | | |
$T_{Cl^-} \times 10^2$	$-\Delta E$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E$	θ
0.476	0.0052	20.6	0.487	0.0064	25.1
1.02	0.0113	22.2	1.12	0.0145	26.6
1.62	0.0176	23.0	1.69	0.0215	27.9
2.13	0.0227	23.7	2.15	0.0269	29.0
2.70	0.0284	24.7	2.64	0.0323	29.8
3.27	0.0340	25.8	3.20	0.0386	31.3
3.91	0.0397	26.7	3.82	0.0449	32.5
4.52	0.0450	27.6	4.38	0.0504	33.7
5.04	0.0494	28.4	4.92	0.0555	34.8
5.50	0.0532	29.2	5.44	0.0607	36.0

| $N_{K^+} = 0.77$ | | | $N_{K^+} = 1.00$ | | |
| $m_{Ag^+} = 0.124 \times 10^{-2}$ | | | $m_{Ag^+} = 0.120 \times 10^{-2}$ | | |
$T_{Cl^-} \times 10^2$	$-\Delta E$	θ	$T_{Cl^-} \times 10^2$	$-\Delta E$	θ
0.525	0.0105	39.6	0.488	0.0120	49.4
0.824	0.0159	40.2	1.02	0.0240	52.9
1.27	0.0239	42.3	1.57	0.0359	57.8
1.66	0.0305	44.0	2.08	0.0459	61.7
2.03	0.0364	45.6	2.59	0.0554	66.0
2.44	0.0424	46.9	3.11	0.0642	69.9
3.02	0.0500	49.5	3.69	0.0734	74.4
3.54	0.0580	51.9	4.29	0.0824	79.3
3.96	0.0638	54.3	4.93	0.0911	84.3
4.48	0.0705	57.0	5.44	0.0981	89.0

Figure 15. Logarithmic dependence of K_1 on the concentration of the solvent cation in the silver-chloride system
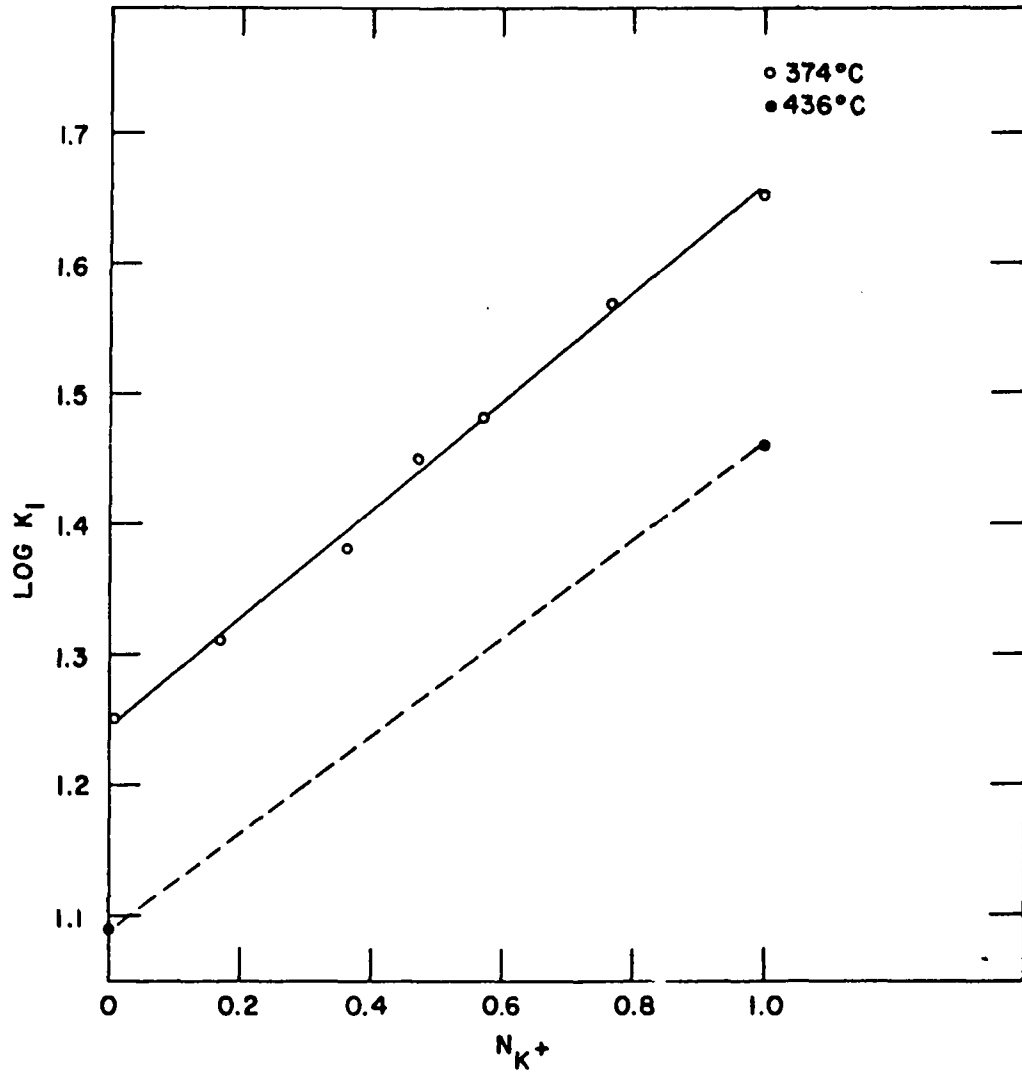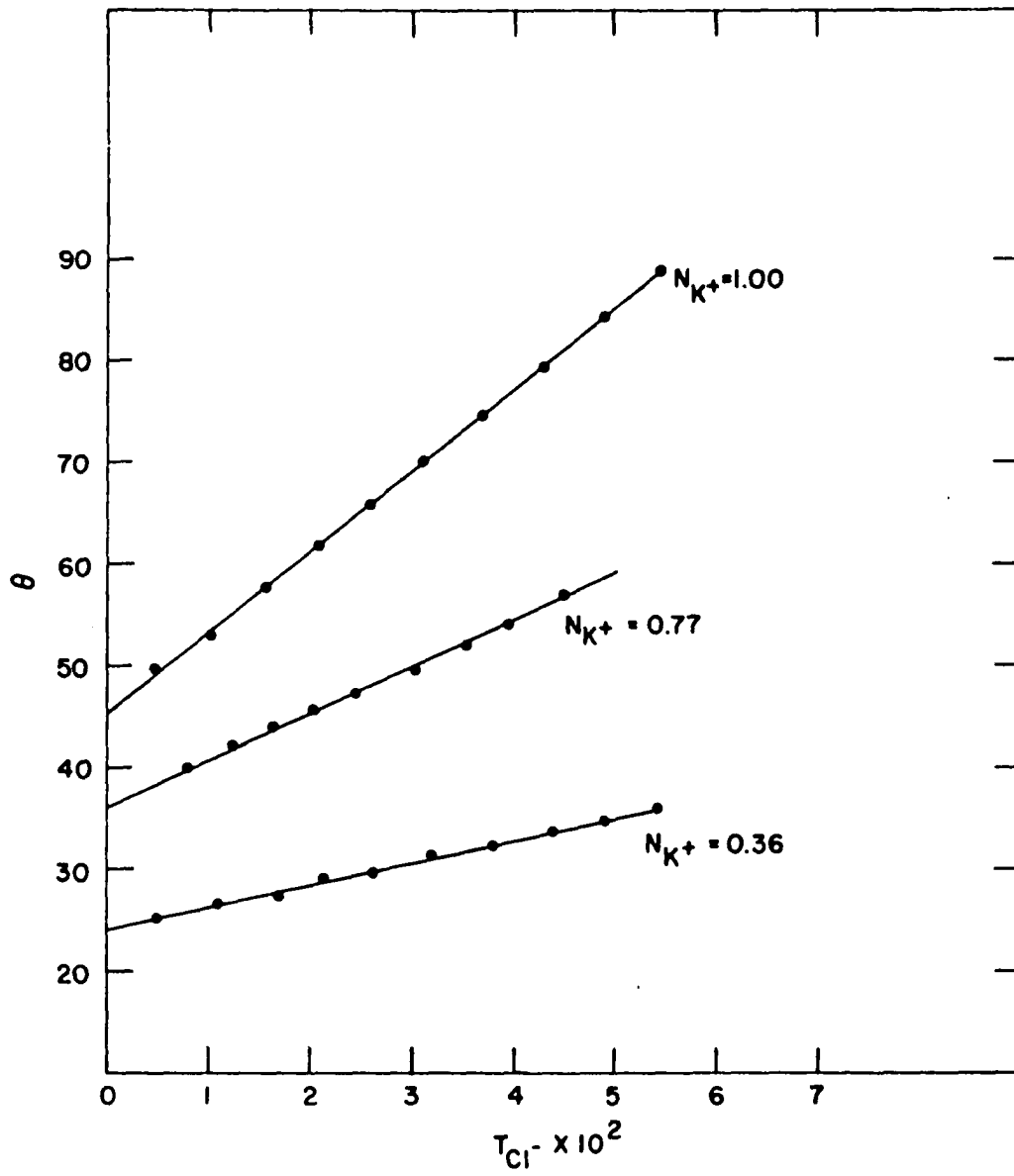
Table 14. Variation of K_1 and K_2 with N_{K^+} at 374°C

N_{K^+}	K_1	Log K_1	K_2	Log K_2
0.00	17.7	1.25	6.78	0.831
0.17	20.3	1.31	7.98	0.902
0.36	24.2	1.38	8.97	0.953
0.47	28.0	1.45	8.93	0.951
0.57	30.3	1.48	8.91	0.951
0.77	36.9	1.57	11.6	1.06
1.00	44.9	1.65	18.0	1.26

equation of the form

$$\log \frac{K_1}{K_1^{\bullet}} = -N_{K^+} \frac{\Delta H}{2.30\ RT} \tag{42}$$

where $K_1^{\bullet}$ is the constant for the reaction defined by equation 5 in pure $NaNO_3$. This equation is similar in form to that proposed by the proponents of the quasi-lattice and quasi-thermodynamic theories for the variation of log γ_{AgNO_3}.

One experiment was performed at 374°C with a solvent composition of 0.47 mole fraction of $CsNO_3$ and 0.53 mole fraction of $NaNO_3$ both in the reference and reaction compartments. Although the plot of Θ versus T_{Cl^-} showed some

scatter at low T_{Cl^-}, the plot gave a fairly good straight line. By means of a least squares treatment the constants were found to be 50.0 and 9.64 for K_1 and K_2, respectively. Examination of Table 4 will show that the $NaNO_3$-$CsNO_3$ mixture is almost as good a complexing solvent as pure KNO_3.

IV. DISCUSSION

A. Comparison of the Quasi-Lattice to
the "Chemical" Approach

Generally three methods of describing thermodynamic behavior in molten salt solutions have been used in the past. The first two are the so-called physical theories, the quasi-thermodynamic theory of Flood et al. (27), and the quasi-lattice theory of Blander (3); the third is the "chemical" approach. The word "chemical" as employed here is used to imply only the use of the law of mass action to describe the data and does not imply anything about the type of bonding involved.

The Temkin (67) model for fused salts when statistically interpreted corresponds to an ionic mixture in which the anions are randomly distributed between themselves and similarly for the cations. The above authors feel that deviations from this ideal model can arise from restrictions in mixing which need not be a result of complex ion formation.
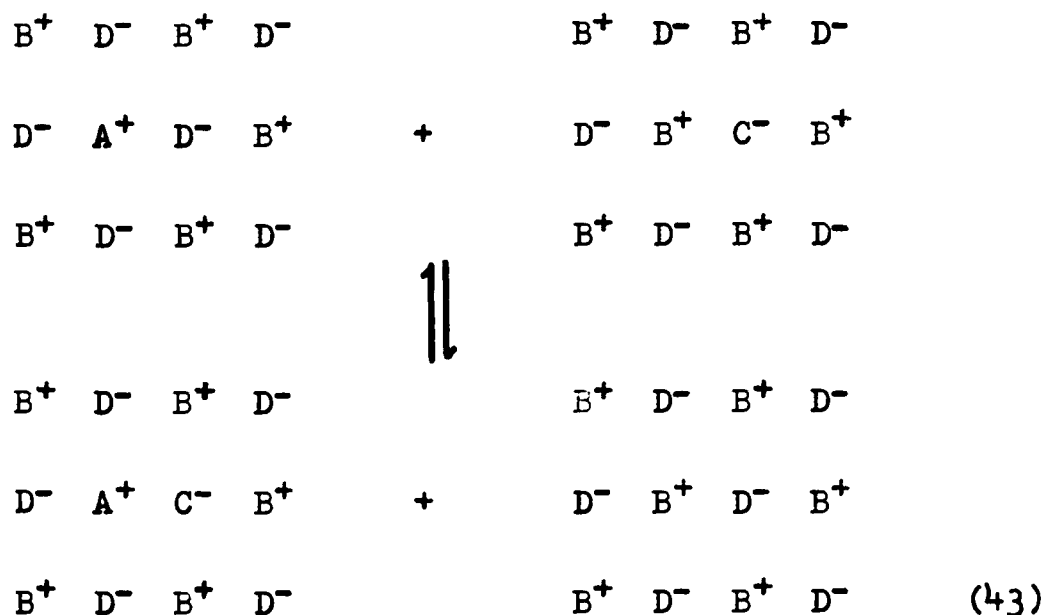
At this point, because of their similarity, it might be instructive to discuss some of the salient features of the quasi-lattice theory and point out some of its differences from the quasi-thermodynamic theory.

The quasi-lattice theory is applied to reciprocal molten salt mixtures; these are mixtures containing at least two cations and two anions and, as noted above, the equations for the solution behavior of an ideal reciprocal salt solution are given by Temkin. In general the method of calculation, as pointed out by the author, used in the lattice theory is similar in some respects to that used by Guggenheim (37) in the quasi-chemical approach to strictly regular, or s-regular, solutions. To digress for a moment, an s-regular solution is any mixture of molecules satisfying all the conditions for forming an ideal mixture except that the interchange energy is not zero. This implies that the mutual energies of an AB pair formed by mixing is not equal to the arithmetic mean of the mutual energies of AA and BB pairs.

At any rate although no precise lattice exists for the liquid, X-ray analysis by many investigators has shown the liquid to be more like a solid than like a gas. In the quasi-lattice treatment, since free-energy differences were calculated between two liquid states, each of which was approximated by a lattice, it was argued that most of the errors stemming from the use of the lattice model were eliminated.

Now the simplest reciprocal salt system in one which contains two cations A^+ and B^+, and two anions, C^- and D^-. The lattice model is an assembly of these ions in a vacuum

consisting of two interlocking sublattices one of cations and the other of anions. All the ions are assumed to have the same coordination number, Z, which for a simple cubic lattice would be six; this then corresponds to the number of first nearest neighbors. This model is restricted to the case in which cations and anions, respectively, have the same size and charge. This implies that there is no difference in the Coulombic interactions of A^+ and B^+ ions or C^- and D^- ions. Thus the model is limited to short-range extra-Coulombic interactions. Moreover a nearest-neighbor relative inter-action between A^+ and C^- ions is postulated such that the energy of interaction of an A^+ and C^- ion pair that are nearest neighbors is not zero. Consider the process represented by equation 43. This interchange of the circled D^- ion that is adjacent to one A^+ and

$$
\begin{array}{cccc}
B^+ & D^- & B^+ & D^- \\
D^- & A^+ & D^- & B^+ \\
B^+ & D^- & B^+ & D^-
\end{array}
\quad + \quad
\begin{array}{cccc}
B^+ & D^- & B^+ & D^- \\
D^- & B^+ & C^- & B^+ \\
B^+ & D^- & B^+ & D^-
\end{array}
$$

$$\Updownarrow$$

$$
\begin{array}{cccc}
B^+ & D^- & B^+ & D^- \\
D^- & A^+ & C^- & B^+ \\
B^+ & D^- & B^+ & D^-
\end{array}
\quad + \quad
\begin{array}{cccc}
B^+ & D^- & B^+ & D^- \\
D^- & B^+ & D^- & B^+ \\
B^+ & D^- & B^+ & D^-
\end{array}
\tag{43}
$$

$(Z-1)B^+$ ions with the C^- ion that is adjacent to ZB^+ ions gives rise to an energy change $\Delta\epsilon = (\Delta E/N)$ where N is Avogadro's number.

Two approximations are used. First there is the assymetric approximation in which the groupings $AC_n^{+(1-n)}$ are included where $n \leqslant Z$. Thus this approximation neglects groupings such as A_2C^+. The most probable distribution of C^- and D^- ions was determined by maximizing the total number of ways of distributing C^- and D^- ions under the restriction of constant total energy and at constant number of C^- ions. This leads to the relation

$$\gamma_{AD} = \frac{(1-X)^Z \left[1 - \alpha \frac{X}{(1-X)}\right]^{Z-1}}{N_{D^-}} \tag{44}$$

where $\alpha = e^{-\Delta E/RT}$, and X is the fraction of positions adjacent to an A^+ ion that are occupied by C^- ions; X can be calculated from the distribution function. Second is the symmetric approximation, following the method of Guggenheim, which includes the groupings $A_mC_n^{+(m-n)}$ where m and n are any integers. This leads to the relation

$$\gamma_{AD} = \left(\frac{1-Y}{1-N_{C^-}}\right)^Z \tag{45}$$

where Y is calculated from the distribution function for the

symmetric approximation in terms of Z, $\triangle E$ and the concentration of ions in solution.

Flood et al. (27) originally proposed a crude approximation to $\triangle E$, the interaction energy. That is, $\triangle E = 2\triangle H'/Z$, where $\triangle H'$ is the heat change for the reaction

$$AD_{(1)} + BC_{(1)} \rightleftharpoons AC_{(1)} + BD_{(1)} \qquad (46)$$
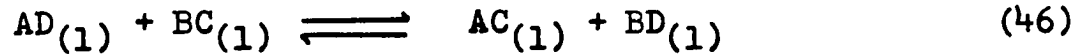
The expression for γ_{AD} in the quasi-thermodynamic theory is

$$\log \gamma_{AD} = N_{B^+} \cdot N_{C^-} \frac{\triangle F^O}{2.30\ RT} \qquad (47)$$

where N_{B^+} is the ion fraction of B^+ and similarly for C^-; and $\triangle F^O$ is the free-energy change for the metathetical reaction 45. In the asymmetric approximation for small values of $ZN_{A^+}\alpha$ it was shown that equation 43 reduced to

$$\log \gamma_{AD} = \frac{-ZN_{C^-}(\alpha - 1)\left[1 - ZN_A(\alpha - 1)\right]}{2.30} = -\frac{bN_{C^-}}{2.30} \qquad (48)$$

which is similar to equation 46. However the results are the same only for $\alpha \sim 1$. From both the asymmetric and symmetric calculations, based on the lattice model, it has been shown that

$$\lim_{N_{C^-} \to 0} \left(\frac{\partial \ln \gamma_{AD}}{\partial N_{C^-}}\right) = -Z(\alpha - 1) \tag{49}$$

so that

$$K_1 = Z(\alpha - 1) \tag{50}$$

Using equation 50 association constants for Ag^+Cl^- were calculated. However the lattice theory in its present form, is not correct for the higher association constants.

Since the "chemical" approach has been described earlier in great detail, it will suffice to say that it is based mainly upon the law of mass action. Since the PV term for liquids is small, $\Delta H \cong \Delta E$; therefore, as is shown in Table 5, there is excellent agreement in the value for the interaction energy calculated from the "chemical" and physical theories for the Ag^+Cl^- ion pair. Furthermore there is excellent agreement for the value of K_1 calculated from both the theories as is shown in Table 4. There are certain limitations to the lattice model besides the fact that it does not correctly predict the higher association constants. This becomes evident in the system $AgNO_3-K_2SO_4-KNO_3$. The authors point out in several of the papers that the fact that the lattice model worked so well for the $AgNO_3-KCl-KNO_3$ was surprising since the model consists of charged rigid spheres in a two-dimensional lattice with cations and anions of the

same charge and size, respectively, although at $N_{Ag}+$ greater than 0.720×10^{-3} and X greater than 0.15, the error due to the approximations made in the derivation of the theory became significant. Nitrate ion, of course, is planar with an average crystal radius of 4.37 $\overset{o}{A}$ while chloride is spherical with a crystal radius of 1.81 $\overset{o}{A}$. Now in the sulfate system not only are the sizes of the anions different but also the charges. Again the concentration dependence of the deviations from ideality were explained equally well by the two approaches. And both failed to predict correctly the temperature dependence of the deviations from ideality. In addition Blander and Braunstein (5) found that the deviation in the system $AgNO_3$-KCl-KNO_3 were best fitted to the asymmetric approximation at low concentrations of Ag^+ and Cl^- and that the deviations in the system $AgNO_3$-NaCl-$NaNO_3$ were between the two approximations but were best fitted to the symmetric approximation. The constants calculated by the two approaches are shown in Tables 4 and 6 for comparison. In all the calculations made by the proponents of the lattice model it was found that ΔE was "slightly" sensitive to the arbitrary choice of Z. The authors assumed Z = 6; however Levy et al. (60) have shown that the coordination numbers in molten alkali halides were relatively low ranging from about 3.5 to 5.6 as compared with 6 or 8 in crystals.

One of the main objections to the "chemical" approach

has been that, if the associated species behave non-ideally, the values of the equilibrium quotients defined by equations 5 and 6 would not be constant. However since the ion fraction of the silver ion in all the experiments reported here was of the order of 10^{-4} to 10^{-5}, thus limiting the concentration of the complex species to some value less than this, the assumption that the species behave ideally seems to be a rather good one. Moreover analagous to equation 50 one may define the constants such that this difficulty is overcome. Consider equation 13; differentiating after T_{Cl^-} one obtains

$$\left(\frac{\partial \beta}{\partial T_{Cl^-}}\right)_{T,P} = K_1 + 2K_1K_2T_{Cl^-} \tag{51}$$

and

$$\lim_{T_{Cl^-} \to 0} \left(\frac{\partial \beta}{\partial T_{Cl^-}}\right)_{T,P} = K_1 \tag{52}$$

Then K_1 is a true constant since there is only one limit of the continuous-single valued function $(\partial \beta / \partial T_{Cl^-})_{T,P}$. K_2 can be defined in terms of the second derivative. Any other method of extrapolation to infinite dilution to obtain an equilibrium constant would be equivalent.

One obvious advantage of the quasi-lattice model is that it takes into account interactions of the solvent ions with that of the solute ions. The "chemical" approach, on the

other hand, is concerned only with the interactions of the
solute ions and neglects all other interactions between
solute and solvent. Duke and Iverson (19) pointed out that
interpretation of the data on the basis of stable complex ions
did not indicate whether the complex is of the ionic type or
the chemical type since, among other things, the role of the
solvent is not known.

Indeed it becomes quite apparent that measurements of the
type described here do not distinguish between the physical
and "chemical" approaches since they both arrive essentially
at the same conclusions. To be sure the "chemical" method
takes higher interactions into account. For example to
complete the silver-chloride system, once the Ksp has been
determined in a particular solvent, K_3, as previously
defined by equation 17, could be determined by noting the
increase in solubility of AgCl(s) upon addition of silver
nitrate. In this case one could fit the data very nicely by
assuming species such as Ag^+Cl^- and Ag_2Cl^+. If K_3 were
small, as previously indicated, one could, in order to
increase the sensitivity of the method, employ a radiotracer
technique.

It seems rather fortuitous that, with all the
restrictions put on the lattice model the experimental
results agree with the theoretical conclusion as well as they
do. Someone is attributed to have said that it appears as

though the quasi-lattice approach is nothing more than a
statistical derivation of the law of mass action; and the
results reported herein seem to add salt to the wound, as it
were.

In conclusion, then, from the data compiled here in
addition to the overwhelming data in the literature in favor
of the complex ion terminology, the "chemical" approach in
describing the thermodynamic properties of reciprocal molten
salt solutions would seem to be a fruitful one. This is
especially true in view of the simplicity of the approach as
compared to that of the lattice models.

B. Complex Ions in Fused Salts

It is interesting, if not somewhat surprising, to find
the striking similarity between the fused salt solvents and
water as a complexing medium. Association constants for
complex ions in water are included in Table 15 and stability
constants for complex ions in various fused salt solvents
are shown in Table 16, for comparison.

In view of the complexing ability of silver ion with
chloride and bromide, it would appear as though the solubility
products for AgCl and AgBr, determined by Flengas and Rideal
(26), should be slightly in error since they did not take the
complexing into account. It was found that when the

Table 15. Stability constants of complex ions in water at 25°C

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

Complex	$K_n(mol/1)^{-1} \times 10^{-2}$	Reference
$PbCl^+$	38	66
$PbBr^+$	70.6	66
PbI^+	83	66
$CdCl^+$	91 ± 5	66
$CdBr^+$	142 ± 7	66
CdI^+	300 ± 15	66
$AgNO_3$	0.67	11
$CdNO_3^+$	1.3	11
$HgNO_3^+$	1.2	11
$Hg(NO_3)_2$	1.0	11
$PbNO_3^+$	2.5	11
$Pb(NO_3)_2$	0.8	11
$SnCl^+$	11.3 ± 0.2	18
$AgC_2O_4^-$	260 ± 1	14

complexing was considered, the Ksp was smaller than the reported values for AgCl and AgBr. The silver-iodide system was not investigated in this work since AgI is so insoluble

Table 16. Stability constants of complex ions in various fused salt solvents

$$K_n = \frac{(MX_n^{2-n})}{(MX_{n-1}^{3-1})\,(X^-)}$$

Solvent	Complex	$K_n(molal^{-1})$	t^oC	Reference
Li-KNO$_3$	PbCl$^+$	42	180	13
	PbCl$_2$	3	180	13
	CdCl$^+$	200	180	13
	CdCl$_2$	15	180	13
	CdCl$_3^-$	40	180	13
	CdCl$_4^{--}$	5	180	13
	NiCl$^+$	26	180	13
	NiCl$_2$	2	180	13
	NiCl$_3^-$	10	180	13
Na-KNO$_3$	CdCl$^+$	20	250	48
	CdCl$_2$	5	250	48
	ZnBr$^+$	250	250	21
	ZnBr$_2$	40	250	21
	ZnBr$_3^-$	10.4	250	21
LiClO$_4$	PbCl$^+$	30 $\pm$ 5	275	20
	PbCl$_2$	9 $\pm$ 5	275	20
	PbCl$_3^-$	5 $\pm$ 5	275	20
	CdCl$^+$	40 $\pm$ 15	275	20

Table 16. (Continued)

$$K_n = \frac{(MX_n^{2-n})}{(MX_{n-1}^{3-1})\ (X^-)}$$

Solvent	Complex	$K_n(\text{molal}^{-1})$	$t°C$	Reference
Li-KNO$_3$	CoCl$^+$	12.5	160	-[a]
	CoCl$_2$	4.0	160	-[a]
	CoCl$_3^-$	4.0	160	-[a]

[a]Gruen, D. M. Argonne National Laboratory, Lemont, Ill. Complex Ion Formation. Talk given at Iowa State University of Science and Technology, Ames, Iowa. 1959.

in the melt that one would have to work in solutions much more dilute than the chloride and bromide systems.

The work on the silver halide system, then, has illustrated a general method for the evaluation of equilibrium constants of complex ions in fused salts when the positive ion of the complex participates in a reversible electrode reaction. Essentially this is an extension of the procedure of Duke and Courtney (18) in aqueous solution to molten salts.

Moreover the results with cadmium and lead point up the utility of the Ag, AgBr(s) electrode in fused nitrate melts as a suitable reference electrode. It should be noted that the silver-silver bromide electrode followed the Nernst limiting

law somewhat better as ε $\sim$ectrode of the second kind,
Ag, AgBr(s), than as an electrode of the first kind, i.e., a
silver wire dipping into a saturated solution of silver
bromide.

The species postulated for the lead-bromide system agree
quite well with the work of Christie and Osteryoung (13) who
performed polarographic determinations of formation constants
of complex ions in fused Li-KNO$_3$. They found that only the
mono- and dichloro-complexes were important for lead. The
values of the constants are listed in Table 16. In the
cadmium-chloride system they found that there were four
important species. As already mentioned it appeared as if
the species CdBr$_4^{-2}$ might be important as indicated by the
concentration dependence of K$_3$ shown in Table 11. In
attempting to determine the constants for the bromo-complexes
of lead and cadmium the above investigators found that the
polarographic waves for lead and cadmium exhibited maxima in
the presence of bromide. Unfortunately this precluded any
accurate determination of the half-wave potentials with the
addition of KBr to the melt. However they were able to
estimate that the bromo-complexes were more stable than the
chloro-complexes.

This work on cadmium and lead along with other data
seems to indicate that the conclusions of Van Artsdalen (71)
were in error. He found that the mono- and tribromo-complexes

were not thermodynamically important since he could not get a consistent fit of his data upon assuming the mono- and tri-species. The work herein does not substantiate this conclusion. From cryoscopic measurements he found that the association constant for the dibromo-complex of cadmium in $NaNO_3$ was 2900 at $310^\circ C$.

Irving (47) has divided the periodic table into essentially three groups with respect to coordination excluding, of course, the inert gases:

(a) essentially electrostatic such that $F^- \gg Cl^- > Br > I$;

(b) the small exceptional case where $F^- < Cl^- < Br < I$; and

(c) the borderline classes.

Because of the small size of F^- and because the differences between F^- and Cl^- are greater than those between the heavier halide ions, the order given in (a) is readily explicable. For aqueous solutions silver and cadmium are in class (b) and lead is in class (c). This same ordering seems apparent in the fused nitrate solvents. In the fused nitrate solvents the differences between the silver-chloride and silver-bromide complexes and cadmium-chloride and bromide complexes indicate that they are definitely of the extra-Coulombic type (b) since in both cases the chloride complexes are much weaker than the corresponding bromide complexes. The lead chloride complexes, on the other hand, are only slightly less stable than the

corresponding bromides and thus belong in class (c). The tendency of Ag^+ to form complex ions with the halides in aqueous solution is generally greater than that of Cd^{++} (Table 17). This same trend is exhibited in the fused salt solvents. Although Cd^{++} and Ag^+ are isoelectronic and certainly of type (b), the ionic charge of the former is twice that of the latter. Thus one may postulate that the electrons in Cd^{++} will be more strongly held and, in particular, will not be so readily available for dative π -bonding. The lead-halide complexes are probably more Coulombic than the corresponding silver and cadmium complexes since the chloro-complex is only slightly less stable than the bromo-complex but definitely of type (c).

Table 17. Comparison of complexing ability of silver and cadmium in aqueous halide solutions

	F^-	Cl^-	Br^-	I^-
log K_1 (Ag)	-0.32	3.08	4.38	8.13
log K_1 (Cd)	0.46	1.59	1.76	2.08

C. Effect of the Solvent Cation Size on
the Complexing Constants

As noted earlier there seemed to be a regular trend in the complexing ability of silver and chloride with change in the ratio of the two solvent cations.

In view of this one might be tempted to explain the apparent liquid junction potential, or contact potential, on the basis of differences in association in the mixed solvent. Table 15 shows that silver (I) is weakly associated in aqueous nitrate solutions. Gruen and McBeth (35) have shown that Co^{+2} is hexacoordinated and Ni^{+2} is tetracoordinated in $Li-KNO_3$ solvent. Ubbelohde (69), in defining the association entropy, stated that on melting of a solid such as silver nitrate complexes of the type $Ag(NO_3)_2^-$ or $Ag_2(NO_3)^+$ can form because the precise symmetry of crystal arrangement is destroyed owing to the increase in positional randomization. He also argued, using considerations of the entropy of fusion of nitrates and other low melting ionic solids, for the formation of complex ions of the type $Na_2NO_3^+$ and $Na(NO_3)_2^-$. Then with respect to the reference solution (0.47 N_{K^+}) as the concentration of potassium increased the association between Ag^+ and NO_3^- increased causing an increase in $-$ E and, conversely, as N_{K^+} became less than that of the reference cell the association decreased, paralleling the behavior of Ag^+Cl^-

as the concentration of potassium was varied. In short then this implies that silver ion is more highly associated in KNO_3 than in $NaNO_3$ resulting in a difference in the mobility of the nitrate ion. However as much can be said against as for this approach. Owens (62) has shown that since the mobility of the nitrate ion is essentially constant through-out the $AgNO_3$-KNO_3 and $AgNO_3$-$NaNO_3$ systems, independent of the composition of the melt, there must be complete dissociation in the melt. Danilov and Krasnitskii (15) have shown by X-ray diffraction studies in molten nitrates that there are discrete nitrate ions. And Doucet and Le Duc (17) carried out a cryoscopic study of the $AgNO_3$-KNO_3 system; they concluded that there was complete dissociation in the melt. In addition it must be conceded that the concept of association in the above case is not so well defined as that in a reciprocal salt solution.

On the other hand this contact potential between the two phases might be explained more satisfactorily by noting that the standard electrode potential for the silver-nitrate electrode is probably different in the two solutions. Consider once again cell F with no added chloride. It has been shown that γ_{AgNO_3} = 1 in pure sodium and potassium nitrate and for the eutectic mixture, all solutions dilute in silver nitrate. One may write two half-reactions, one for the reference

$$E' = E^{O'} + \frac{RT}{F} \ln \frac{1}{N'_{Ag^+}} \tag{53}$$

and one for the indicator

$$E = E^{O} + \frac{RT}{F} \ln \frac{1}{N_{Ag^+}} \tag{54}$$

Since $E^{O'} \neq E^{O}$ it follows that

$$E - E' = E_{cell} = (E^{O} - E^{O'}) - \frac{RT}{F} \ln \frac{N_{Ag^+}}{N'_{Ag^+}} \tag{55}$$

Thus it is readily apparent that the difference, $-\delta E$, might result from the difference in $E^{O'}$s in the two solvents. In the calculations, described in section II, A, $-\Delta E$ was used for the calculation, where, as in the above case, $-\Delta E$ was the difference in the e.m.f. without chloride from that with added chloride. Thus in the computation of $-\Delta E$ the quantity $(E^{O} - E^{O'})$ would cancel and thus reduce to the case where any deviation from ideality on the indicator side on addition of chloride could be ascribed to association in the melt. To insure that this was indeed the case, several runs were made using cell F with $N_{K^+} = 1.00$ and $N_{K^+} = 0.00$ and the calculated complexing constants were compared to those calculated from the data in the literature. The agreement was excellent with respect to the estimated uncertainties in

K_1 and K_2 (see Tables 4 and 14 for comparison). The values independently determined here were included in Figure 8. Graham (33) in discussing several types of electrical potential differences stated that the "absolute" a "true" potential difference between dissimilar phases is an undefined concept. Guggenheim (38) has demonstrated that true potential differences between dissimilar phases are unmeasurable since they are not defined. Moreover he pointed out that any attempt to define an absolute potential difference is unnecessary because it is possible to describe all experimental observations in terms of potential differences of the types already known. In a subsequent paper Guggenheim (39) allowed that it was possible to define new types of potential differences which might prove to be convenient for some purposes, but that there was no necessity for doing so.

The difference in the solute interactions with change in the solvent, as reflected in the change in K_1 and K_2 with N_{K+}, might be related to the field effect of the solvent cation. Since the potassium ion is larger than the sodium ion, and as nearest neighbor to a chloride ion that is part of an Ag^+Cl^- pair bond, it will polarize the electrons in the bond less than the sodium ion because of its weaker field. If the bond strength is related to the electron density in the bond between the two "ions", then the energy of ion-pair formation should be more negative in pure KNO_3 solvent than

in the pure $NaNO_3$ solvent, which was the observed situation for both Ag^+Cl^- and $AgCl_2^-$. Basolo and Pearson (1) have claimed that sometimes the bond strength is related to the penetration of ligand electrons through the outer shell of the central ion, leading to a higher effective ionic charge; the penetration would be less the stronger the positive field of the solvent cation, and hence the smaller would be the energy of interaction of an Ag^+Cl^- pair. This would explain, qualitatively at least, the observed deviations in alkali nitrates, alkali chlorides, and alkaline earth chlorides.

However Kleppa and Hersh (51) and Kleppa (50) in determining the heats of mixing in liquid alkali nitrate systems proposed that the principal source of the enthalpy of mixing is the reduction in Coulombic repulsion between the second nearest neighbor cations. They showed that the quantity

$$\Delta H^M / N_{Na^+} (1 - N_{Na^+})$$

was proportional to the quotient of the difference and the sum of the interionic (crystal) distances, characteristic of the two pure components, squared, the so-called Tobolsky (68) parameter. Here ΔH^M is the molar enthalpy of mixing.

In the reaction represented by equation 42 for an A^+C^- ion to form it seems reasonable to expect that before an A^+ ion can react with a C^- it will have to overcome the potential barrier presented by the cation sheath about C^-, i.e., it is

more reasonable that C^- will have B^+ ions about it in the melt than A^+ and similarly for A^+ and D^-. Now consider the difference in the Coulombic interactions between the situations $Ag^+.....Cl^-Na^+$ and $Ag^+.....Cl^-K^+$. This might represent the situation before any non polar quantum bonds are formed. This situation could be represented by means of a crude structural model for molten salts proposed by Forland (28) or the model proposed by Fuoss and Kraus (31, 32) for ion triple formation in aqueous solution.

Consider a triple ion consisting of two positive and one negative ion and assume the ions to be charged rigid unpolarizable spheres contained in a medium of macroscopic dielectric constant, D. Of the various ways by which a triple ion can form, consider the approach of a positive ion to the dipole (ion-pair). Let r_0 be the distance of the approaching positive ion from the center of the dipole and let $2 \Delta r$ be the distance between the ions in the pair. Since the minimum in potential energy determines the maximum stability, the most favorable condition for triple ion formation occurs when all three ions lie on the same line. Then it can be shown that the potential energy, U, is given by

$$U = - \frac{Ne^2}{D} \left(\frac{1}{r_0 - \Delta r} - \frac{1}{r_0 + \Delta r} \right) \qquad (56)$$

It is assumed that the difference in the standard free energy change for reaction 5 in KNO_3 and $NaNO_3$ is a result of the difference in the Coulombic stability of the triple ion in the two solvents such that

$$\Delta F_a^O - \Delta F_b^O = U_a - U_b \tag{57}$$

where a and b refer to KNO_3 and $NaNO_3$, respectively. Since

$$-\Delta F^O = RT \ln K \tag{58}$$

one finds that

$$\ln \frac{K_{1a}}{K_{1b}} = \frac{2e^2}{kT} \left[\frac{1}{D_a} \left(\frac{\Delta r_a}{r_{oa}^2 - (\Delta r_a)^2} \right) - \frac{1}{D_b} \left(\frac{\Delta r_b}{r_{ob}^2 - (\Delta r_b)^2} \right) \right] \tag{59}$$

where $k = R/N$ is the Boltzman constant.

Unfortunately the dielectric constants of these fused nitrates have not been measured. Harned and Owen (41) point out that measurement of a high dielectric constant, in a liquid possessing appreciable conductance is not easy, especially at high temperatures. However D may be estimated by means of the equation first derived by Born (7) for aqueous solutions.

$$-\Delta F_{solv} = \frac{N(Ze)^2}{2r_i} \left(1 - \frac{1}{D}\right) \tag{60}$$

where r_i is the radius of a spherical ion of charge Ze and $-\Delta F_{solv}$ is the free energy of the solvation of the ion, i, and D is the macroscopic dielectric constant. The energies of solvation of the individual ions in aqueous solution can be derived if (a) The magnitude of the radii of the ions in aqueous solution are known. These radii, however, differ from the crystal lattice values since they refer to the distance from the center of the ion to the center of the water dipole. Körtum and Bockris (53) have stated that the calculation is complicated further by the different orientation of water molecules around cation and anion. (b) The variation of the dielectric constant in the high electrical field of the ion is known.

Levy et al. (60) among others, by means of X-ray and neutron diffraction studies of molten alkali halides have shown that the ionic radii are approximately the same as in the crystal, at least near the melting point. Since the crystal radii are known accurately the Born equation should be more applicable to a melt than to aqueous solutions.

Flengas and Rideal (26) calculated free energies of solvation in a eutectic mixture of $NaNO_3$-KNO_3 for the compounds AgCl, AgBr, and AgI, by applying,

$$-U_{AgX} = (\Delta F_{sol})_{AgX} - (\Delta F_{solv})_{AgX} \qquad (61)$$

from lattice free energies and free energies of solution in melts; and ΔF_{sol} was calculated from the measured Ksp. Moreover lattice free energies can be calculated by equation 61 from data of free energies of solvation in aqueous solutions given by Benjamin and Gold (2) and the known free energies of solution in water calculated from solubility data. The above authors showed that the temperature correction to the lattice free energies obtained at 25°C were negligibly small.

Using the data of Hill (45) on the Ksp of AgCl in molten $NaNO_3$ and KNO_3, and the data of the above authors, it was found that the free energy of solvation of AgCl in KNO_3 and $NaNO_3$ was -191 kcal/mole and -190 kcal/mole, respectively. Thus from equation 60 it is evident that D_a is approximately equal to D_b. With the ionic radii of Ag^+ and Cl^-, given by Pauling (64) the dielectric constant, D, was calculated and found to be approximately 6.5 which is similar to the values listed in the International Critical Tables for the solids at room temperature. It is also similar to the value of 6.44 for an equimolar mixture of molten KNO_3-$NaNO_3$. Using the calculated value of D and the crystal radii of Ag^+, Cl^-, Na^+, and K^+, it was found from equation 59 that K_{1a}/K_{1b} was approximately 1.6 and the value determined experimentally was

2.5. Thus it seems apparent that, in part lat least, the difference between the $AgNO_3$-KCl-KNO_3 and $AgNO_3$-$NaCl$-$NaNO_3$ systems is a Coulombic effect.

It is clearly fortuitous that the above "model" which neglects the 3-dimensional character of the problem and such possible effects as polarization, influence of van der Waals' forces and possible variations in the repulsive potential, gives an expression for the difference in the formation constant of the Ag^+Cl^- pair in KNO_3 and $NaNO_3$ which is correct as to order of magnitude.

V. SUMMARY

Complexing constants for the species Ag^+Cl^-, $AgCl_2^-$, Ag^+Br^-, $AgBr_2^-$, $PbBr^+$, $PbBr_2$, $CdBr^+$, $CdBr_2$, and $CdBr_3^-$ have been determined in the eutectic mixture of $NaNO_3-KNO_3$ at various temperatures by electromotive force measurements on concentration cells. Constants were determined also for Ag^+Cl^- and $AgCl_2^-$ in pure KNO_3 and $NaNO_3$ at 374^oC. Moreover constants were calculated for the chloro-silver complexes in potassium nitrate and sodium nitrate and for $AgSO_4^-$ in potassium nitrate from data in the literature. The values of K_1 determined from the quasi-lattice theory were compared to the values determined herein and found to agree quite well.

A reversible Ag, AgBr(s) electrode for use in molten alkali nitrates was reported and found to be quite satisfactory as a reference electrode for use in these solvents.

It was found that the values of K_n, previously defined, for these various associated species in the molten solvents were of the same order of magnitude as those in aqueous solutions. The silver and cadmium complexes are of the extra-Coulombic type and the lead complexes fall in the borderline class as is the case for these metal-halide species in aqueous media.

The influence of the solvent cation size on the

stability of the chloro-silver complexes was investigated; it was found that the stability increased with increase in the size of the solvent cation. This effect was ascribed, in part, to a reduction in the Coulombic repulsion between the solvent cation around chloride and the silver ion as the solvent was changed from sodium nitrate to potassium nitrate. In addition the difference in the field effect of the solvent cations must contribute to the difference in stability as observed in these various solvents. In the $NaNO_3$-KNO_3 the change in ΔF^0 for Ag^+Cl^- from pure sodium nitrate to pure potassium nitrate was a linear function of the ion fraction of potassium.

The "chemical" and physical approaches were compared and found to be consistent. Thus it has been shown how two different approaches to the formulation of the specific interactions which produce deviations from ideal behavior in reciprocal molten salt solutions lead to equations which, while mathematically different, are hardly distinguishable when applied to the experimental data. It should be borne in mind, however, that the fact that a model, which has a theoretical basis, can be made to fit the facts by a proper choice of constants is not proof of the correctness of the underlying theory. To be sure this has been pointed out by Blander and Braunstein (5). At this point it seems fitting to quote a statement made by Hildebrand and Scott (43) in a

of course, complicate the situation. Moreover the effect of the solvent cation on the deviation from ideal behavior warrants further investigation from both a theoretical and experimental viewpoint.

discussion concerning the relative merits of the physical and "chemical" approaches. They stated that the fact that two approaches explain the data equally well

> ".....leads to the suspicion that the difference between the physical and chemical approaches may be largely a matter of viewpoint, and that when properly formulated, they might prove to be identical. If this be true, then adecision between the two is a matter of personal choice and the question is devoid of any real substance".

They also felt that to distinguish between them one must look beyond thermodynamics.

It would be of particular interest to investigate some other systems by a technique analagous to the one described herein. For example the behavior of selected solutes in molten nitrites and in lithium perchlorate might be of interest. Adaption of the carbon/Cl_2 electrode, which has proved to be a useful reference electrode in molten halides, to molten alkali metal nitrates would enable one to investigate the behavior of metal nitrates in mixtures of MCl-MNO$_3$. This would work for the complex Ag_2Cl^+ and chloro-complexes of lead, cadmium, cobalt (II), zinc, copper (II), etc. It would be of further interest to investigate the behavior of $Zn(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$ and some of the more unstable, but nevertheless interesting, metal nitrates in MBr-MNO$_3$ systems using the silver-silver bromide electrodes along with the procedure outlined herein. The fact that some of these nitrates are unstable at high temperatures would,

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VII. ACKNOWLEDGEMENT