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CANADA

**ELECTROMOTIVE FORCE SERIES OF METALS  
IN FUSED SALTS  
AND  
ACTIVITIES OF METAL CHLORIDES IN 1:1  
MOLAR KCl-NaCl SOLUTIONS**

by

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**DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA**

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# Electromotive Force Series of Metals in Fused Salts and Activities of Metal Chlorides in 1:1 Molar KCl-NaCl Solutions

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## ABSTRACT

The potentials of a series of metal-metal chloride systems in an equimolar mixture of molten potassium and sodium chlorides have been measured against a silver-silver chloride reference electrode. An electromotive force series of metals at different temperatures has been established for this particular solvent. Experiments with a chlorine electrode have shown that the solutions of silver chloride in the KCl-NaCl solvent are ideal, and hence, deviations from ideality of the other chlorides in this solvent can be attributed directly to the formation of complexes in the melts. Three types of behavior have been observed for the salts studied in this solvent: ideality, and positive and negative deviations from ideality. The theoretical aspects of complex formation in melts are discussed.

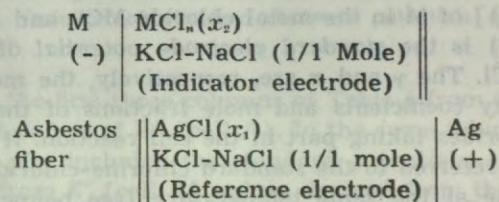
The work reported in this paper is the culmination of experiments begun in 1956 for the purpose of establishing electromotive force series of metal-metal chloride systems in a solvent consisting of 1:1M KCl-NaCl, at temperatures between 650° and 900°C. In the initial experimental work, a thermodynamically reversible, diffusion-free, silver-silver chloride reference electrode (1) was developed. This electrode was used to obtain the standard potentials of several systems (2-5). In this paper, the data have been used to establish emf series of metals at various temperatures.

A theoretical interpretation of these data required the definition of an "ideal" reference standard state. By choosing the pure metal chlorides at the temperatures of experiment as the standard state, it was observed that the experimental standard cell potentials showed pronounced deviations from ideality. To resolve the differences, a chlorine-chloride ion electrode was constructed, and the properties of the silver-silver chloride electrode were investigated in detail. Having established the properties and thermodynamic functions of the silver chloride solutions, the activity coefficients and other related thermodynamic properties of the remaining chlorides were calculated.

### Standard Electrode Potentials in Fused Salts

#### *Experimental*

The preparation of materials and the detailed experimental procedure for electrode potential measurements in fused salts has been described in detail in previous publications (1-5). The potentials of the systems Mn-MnCl<sub>2</sub>, Zn-ZnCl<sub>2</sub>, Cr-CrCl<sub>2</sub>, Ti-TiCl<sub>3</sub>, Cd-CdCl<sub>2</sub>, Fe-FeCl<sub>2</sub>, Pb-PbCl<sub>2</sub>, Sn-SnCl<sub>2</sub>, Co-CoCl<sub>2</sub>, Ni-NiCl<sub>2</sub>, and Cu-CuCl were investigated with cells of the type



[A]

A typical design of the all-silica cell is given in Fig. 1. In this cell the reference electrode solution is

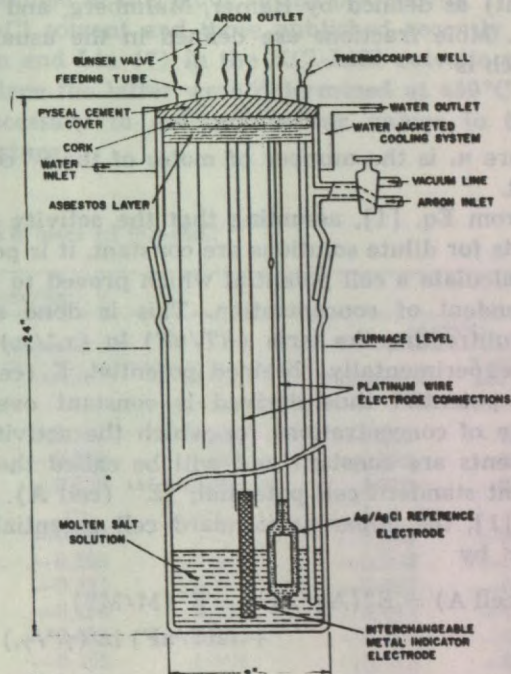
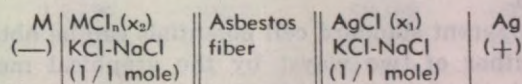
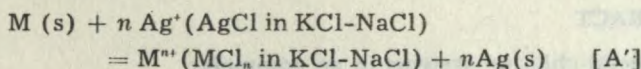


Fig. 1. Cell design for metal electrode potential measurements: Cell [A]



separated from the solution in the indicator electrode by a small asbestos fiber sealed into the end of the silica tubing of the reference electrode. The fiber absorbs the salts and makes a good electrical contact between the two solutions while hindering diffusion. Analysis of the solutions from both electrode compartments indicated that this method of separation was effective. For dilute salt solutions, the presence of a large excess of the same ionic melt on both sides of the junction effectively eliminated junction potentials.

The reaction for a cell of the type shown above is:



The relationship between the cell potential and salt concentrations in the melt is given by the Nernst equation in the expanded form

$$E(\text{cell A}) = E^\circ(Ag/Ag^+) - E^\circ(M/M^{n+}) \\ + (RT/nF) \ln \frac{x_2}{x_1^n} - (RT/nF) \ln \frac{\gamma_2}{\gamma_1^n} \quad [1]$$

where  $E^\circ(M/M^{n+})$  is the standard electrode potential [with the IUPAC Stockholm sign convention (16)] of M in the metal chloride  $MCl_n$  and  $E^\circ(Ag/Ag^+)$  is the standard electrode potential of Ag in  $AgCl$ . The  $\gamma$  and  $x$  are, respectively, the mean activity coefficients and mole fractions of the metal chlorides taking part in the cell reaction. If the  $E^\circ$  are referred to the standard chlorine-chloride electrode at the same temperature (see below), they become equal to minus the formation potentials of  $MCl_n$  and  $AgCl$ , respectively, in their standard states (pure salt at the temperature of the experiment) as defined by Hamer, Malmberg, and Rubin (6). Mole fractions are defined in the usual way, which is

$$x_i = n_i / \sum n_j \quad [2]$$

where  $n_i$  is the number of moles of the  $i^{\text{th}}$  constituent.

From Eq. [1], assuming that the activity coefficients for dilute solutions are constant, it is possible to calculate a cell potential which proved to be independent of concentration. This is done simply by subtracting the term  $(RT/nF) \ln (x_1^n/x_2)$  from the experimentally obtained potential,  $E(\text{cell A})$ . The potential thus derived is constant over the range of concentrations for which the activity coefficients are constant and will be called the "apparent standard cell potential,"  $E^{\circ'}(\text{cell A})$ . From Eq. [1], the apparent standard cell potentials are given by

$$E^{\circ'}(\text{cell A}) = E^\circ(Ag/Ag^+) - E^\circ(M/M^{n+}) \\ + (RT/nF) \ln (\gamma_1^n/\gamma_2) \quad [3]$$

The standard cell potential  $E^\circ(\text{cell A})$  would be given by Eq. [3] without the activity coefficient term.

Apparent standard cell potentials can be obtained in either of two ways: by the graphical method, which involves the interpolation (or extrapolation) of the  $\log x_2/x_1^n$  vs.  $E(\text{cell A})$  curve to zero log-

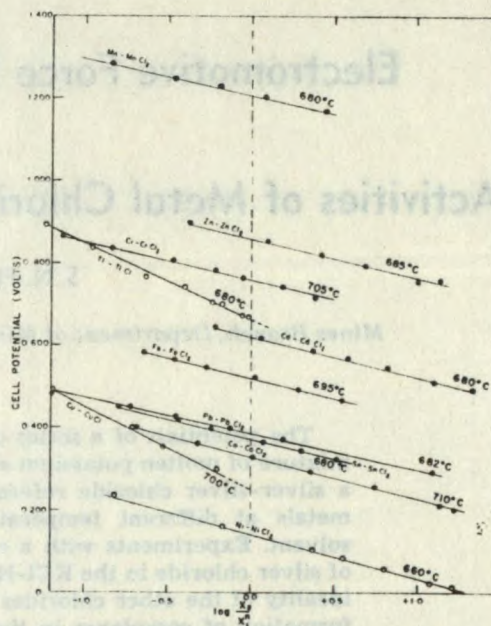


Fig. 2. Electromotive force of Cell [A] for different metals as a function of  $\log (x_2/x_1^n)$  at constant temperature. ( $x_1 = 6.235 \times 10^{-2}$ ).

value (Fig. 2), or by calculation from the Nernst equation. In the latter method the Nernst curves must be linear, and the slopes of the straight lines must be identical with the theoretical values of  $(2.303 RT/nF)$ . From Eq. [3] it is seen that the experimentally derived apparent standard cell potential  $E^{\circ'}(\text{cell A})$  includes, in addition to the standard electrode potentials, the dilution effect as an activity coefficient term. Since standard electrode potentials are known (6), Eq. [3] can be used to calculate activity coefficients in melts.

### Results

The results of potential measurements with these cells at different salt concentrations are given in Fig. 2. In this graph the experimentally obtained cell potentials  $E(\text{cell A})$  are plotted vs. the logarithm of the mole fraction ratio in the two half-cells, following the Nernst equation [1]. It will be observed that the relationship is linear, which justifies the assumption made for the definition of the apparent standard cell potential  $E^{\circ'}(\text{cell A})$  of Eq. [3]. This linearity indicates that the activity coefficients of the metal chlorides are either unity or constant for the concentration range of the experiments. The apparent standard cell potentials for each system, obtained by graphical interpolation or extrapolation at zero log-term, are indicated by the intercepts with the dotted line in the center of Fig. 2.

The slopes of the straight lines are in most cases in good agreement with the Nernst equation, with the exception of the Ni-NiCl<sub>2</sub> system in which a slope of 0.107 is obtained instead of 0.096. Cell potentials in Fig. 2 are corrected for small thermoelectric forces. These were measured separately on the bimetallic systems of the electrodes (with their connections) and are given in Fig. 3.<sup>1</sup>

<sup>1</sup> Potentials given in some of our previous publications (1-4) have not been corrected for thermoelectric effects. For such corrections, reference should be made to Fig. 3.

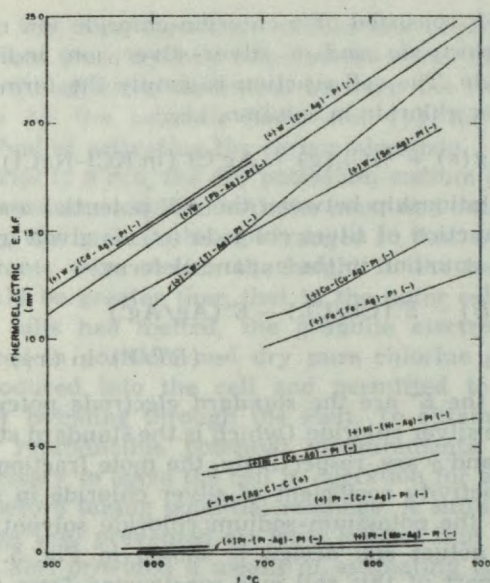


Fig. 3. Thermoelectric electromotive forces of the bimetallic systems of the various types of electrodes used in this study.

The effect of temperature change on the apparent standard cell potentials  $E^{\circ}$  (cell A) was also measured; the results are summarized in Fig. 4. It is seen that between 650° to 900°C the relationship of temperature and apparent standard cell potential is linear and the temperature coefficient is small. Standard cell potentials for the systems Cu-CuCl<sub>2</sub> and Cr-CrCl<sub>2</sub> are shown in the graph by dotted lines to indicate that these values were not obtained experimentally but were calculated using a process described previously (4). In fact, neither of these potentials could be measured directly because of a spontaneous reduction of the higher valency chlorides by the corresponding metal electrodes.

The emf series derived in the present investigation at temperatures of 700°, 800°, and 900°C are

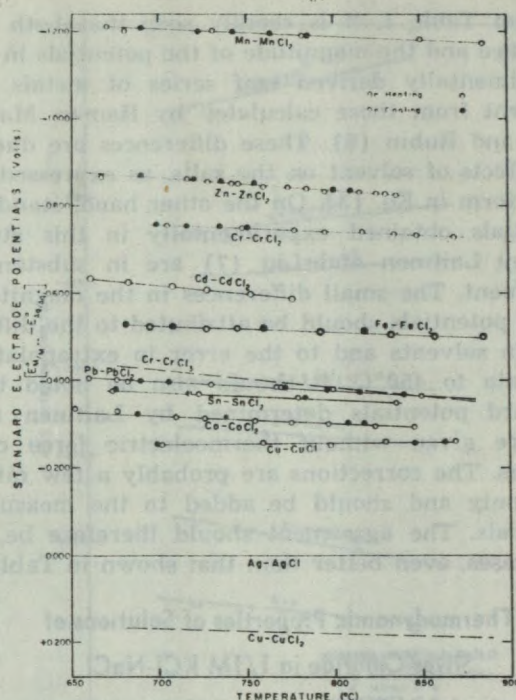


Fig. 4. Variation of standard electrode potentials with temperature.

given in the first three columns of Table I from our observed values of  $E^{\circ}$  (cell A). In the same tabulation are also included the standard potentials, calculated from  $E^{\circ}$  (cell A) values derived from thermal data by Hamer, Malmberg, and Rubin (6). A third set of data is included to demonstrate the agreement between the standard electrode potentials obtained in this study in the presence of 1/1M KCl-NaCl solvent and those published recently by Laitinen and Liu (7) in the KCl-LiCl eutectic solvent. Since the latter were determined at 450°C, it was necessary to extrapolate our values to this temperature.

Table I. Standard electrode potentials<sup>a</sup> of metals in fused 1:1 KCl-NaCl

Electrode	$E^{\circ}(M/M^{n+}) - E^{\circ}(Ag/Ag^{+}), v$							
	This study			Hamer, et al. <sup>b</sup>			At 450°C	
	700°C	800°C	900°C	700°C	800°C	900°C	This study <sup>c</sup>	Laitinen and Liu <sup>d</sup>
Mn, MnCl <sub>2</sub>	-1.206	-1.190	-1.172	-1.010	-0.981	-0.955	-1.230	-1.212
Zn, ZnCl <sub>2</sub>	-0.860	-0.835	-0.810	-0.665	-0.650	-0.630	-0.930	-0.929
Cr, CrCl <sub>2</sub>	-0.758	-0.740	-0.728	-0.565	-0.526	-0.505	-0.810	-0.788
Tl, TlCl	-0.665	—	—	-0.665	—	—	—	—
Cd, CdCl <sub>2</sub>	-0.620	-0.580	—	-0.415	-0.367	—	-0.630	-0.679
Fe, FeCl <sub>2</sub>	-0.520	-0.510	-0.498	-0.305	-0.292	-0.270	-0.560	-0.534
Cr, CrCl <sub>3</sub>	-0.425	-0.385	-0.345	-0.385	-0.380	-0.375	-0.525	-0.523
Pb, PbCl <sub>2</sub>	-0.390	-0.376	-0.355	-0.315	-0.286	-0.270	-0.447	-0.464
Sn, SnCl <sub>2</sub>	-0.370	-0.354	-0.340	-0.405	-0.435	-0.450	-0.410	-0.445
Co, CoCl <sub>2</sub>	-0.324	-0.300	-0.275	-0.195	-0.155	-0.135	-0.372	-0.354
Cu, CuCl	-0.260	-0.256	-0.260	-0.140	-0.145	-0.152	-0.240	-0.214
Ni, NiCl <sub>2</sub>	-0.140	—	—	-0.095	—	—	—	-0.158
Ag, AgCl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu, CuCl <sub>2</sub>	+0.170	+0.180	+0.192	+0.410	+0.430	+0.450	+0.200	+0.189
Cl <sub>2</sub> , Cl <sup>-</sup>	+0.845	+0.820	+0.795	+0.850	+0.826	+0.794	+0.905	+0.853

<sup>a</sup> It will be noted that the sign of the electrode potentials is in accord with the recommendations of the IUPAC Stockholm Convention [See Licht and deBethune (16)]. The potentials are referred to Ag/AgCl.

<sup>b</sup> Standard potentials calculated from thermal data.

<sup>c</sup> Extrapolated values from our experimental data obtained at temperatures between 650° to 900°C in 1:1 KCl-NaCl.

<sup>d</sup> Values obtained by Laitinen and Liu (7) in KCl-LiCl at 450°C.

From Table I, it is readily seen that both the sequence and the magnitude of the potentials in the experimentally derived emf series of metals are different from those calculated by Hamer, Malmberg, and Rubin (6). These differences are due to the effects of solvent on the salts, as expressed by the  $\gamma$  term in Eq. [3]. On the other hand, standard potentials obtained experimentally in this study and by Laitinen and Liu (7) are in substantial agreement. The small differences in the magnitude of the potentials should be attributed to the difference in solvents and to the error in extrapolating our data to 450°C. It should also be noted that standard potentials determined by Laitinen and Liu are given without thermoelectric force corrections. The corrections are probably a few millivolts only and should be added to the measured potentials. The agreement should therefore be, in most cases, even better than that shown in Table I.

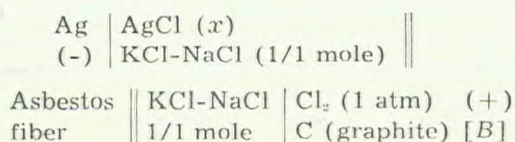
### Thermodynamic Properties of Solutions of Silver Chloride in 1/1M KCl-NaCl

The standard cell potentials obtained in cell [A] represent the difference between the individual standard electrode potentials of the reference and indicator electrode systems. Consequently, it is not possible to calculate individual activities of the metal chlorides in solution unless the thermodynamic properties of one species are known. Although preliminary results (1) indicated ideality of the AgCl (KCl-NaCl) system, it was necessary to confirm this by determining the activities of silver chloride in solution. The thermodynamic properties of pure silver chloride have been studied by several investigators (8-10, 17), using silver-chlorine cells of various designs. The agreement between the different data is quite good. On the other hand, there is little information on the properties of solutions of silver chloride in fused salt solvents. Stern (11, 12) investigated the systems AgCl-KCl and AgCl-NaCl, at 800°C and showed that, whereas the former deviates from ideality positively, the latter deviates negatively. Takahashi (13) investigated the system AgCl(KCl-LiCl) and found a small deviation from ideality. In these studies the pure silver chloride state was also chosen as the standard state for reference.

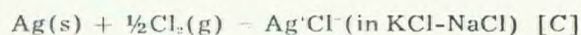
In the present investigation, a cell consisting of silver-silver ion and chlorine-chloride ion electrodes was developed and used to measure the thermodynamic properties of solutions of silver chloride in the 1/1M KCl-NaCl solvent at temperatures varying between 650°-900°C.

### Experimental

The cell used to measure the potentials of silver chloride in the molten salt solution was of the following type:



The cell consisted of a chlorine-chloride ion reference electrode and a silver-silver ion indicator electrode. The cell reaction is simply the formation of silver chloride in solution, i.e.:



The relationship between the cell potential and the mole fraction of silver chloride ( $x$ ), is given by the Nernst equation in the expanded form:

$$E(\text{cell B}) = E^\circ(\text{Cl}^-/\text{Cl}_2) - E^\circ(\text{Ag}/\text{Ag}^+) - (RT/F) \ln(x\gamma) [4]$$

where the  $E^\circ$  are the standard electrode potentials in pure silver chloride (which is the standard state), and  $x$  and  $\gamma$  are, respectively, the mole fraction and mean activity coefficient of silver chloride in solution in the potassium-sodium chloride solvent.

The actual cell design is shown in Fig. 5. The lower part of this cell was constructed from silica tubing and the upper part from Pyrex tubing. The two parts were joined by a graded seal. The over-all dimensions of the cell were 2 in. x 20 in. The silver electrode was a rod of pure silver wire (99.99%) connected to the potentiometer by platinum wire.

The inert electrode for the chlorine-chloride ion system was a 1/4 in. diameter rod of spectrographically pure graphite. A 20,000-ohm resistance in series with the electrodes was used as an additional precaution to reduce the potentiometric current and prevent any polarization phenomena. One of the features of this cell is the activation of the graphite electrode before use. The end of the rod was coated with a concentrated sucrose solution and then carbonized in a chlorine atmosphere at 800°C for 24 hr. The result was a thin, porous, and highly absorbent carbon deposit. This cell, like all the others used in this investigation, was fitted with a small asbestos fiber to separate the two solutions. It will be noted

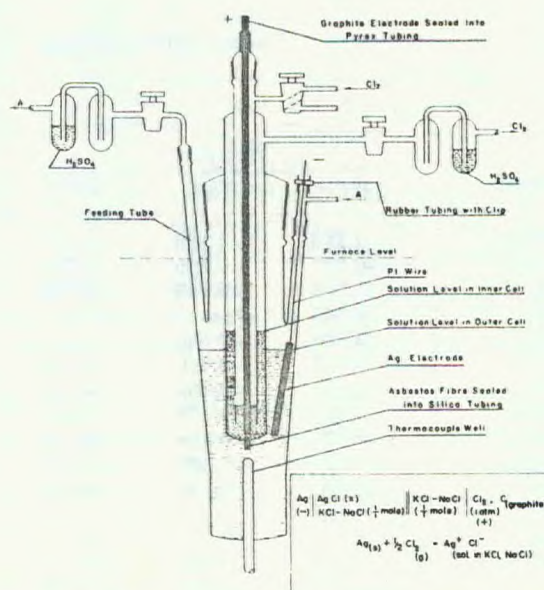
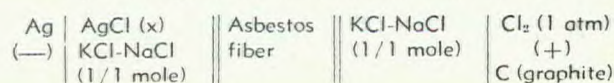


Fig. 5. Design of the silver-chlorine cell: Cell [B]



that the main significant differences between this cell and those used by other investigators (8, 9) are (a) the effective separation between the two half-cells by the asbestos fiber, and (b) the simple method of activating the carbon electrode.

Prior to a run, the dry potassium-sodium chloride mixture was added to both the inner and outer half-cells, the amounts being arranged so that when the contents were molten the height in the inner cell would be greater than that in the outer cell. After the salts had melted, the graphite electrode was placed in position, and dry pure chlorine gas was introduced into the cell and permitted to escape after bubbling through the melt. To obtain steady and reproducible potential measurements, it was necessary to leave the cell in operation for about 24 hr before taking potential readings. A sulfuric acid outlet trap prevented air from leaking into the cell and also provided a means of estimating the chlorine gas flow. It was found that the cell potential was independent of the rate of chlorine gas flow, and the cell was operated normally under a very slow flow (about 30 cc/min).

Solutions of silver chloride were prepared *in situ* by adding weighed amounts of silver chloride to the molten salt solvent and mixing well with a small electrically-operated platinum stirrer. To insure that true equilibrium had been attained after each addition of solute, the cell was allowed to stand for about 24 hr during which the potentials were checked several times. It was observed that with vigorous stirring, equilibrium was attained in a short time and that afterward the potentials remained practically unchanged. Small fluctuations of the potentials, of the order of  $\pm 0.4$  mv, did actually occur and were attributed to local temperature changes in the cell. Thus, a complete run lasted several days, during which the chlorine electrode was in continuous use. The silver electrode was immersed in the solution only while potential measurements were being made. It was then withdrawn into the space above the solution. Purified argon was used to provide an inert gas protection for the silver electrode compartment.

The chlorine-chloride ion electrode may be regarded as a standard reference electrode for potential measurements in fused chloride salts. Unfortunately, in comparison with the silver-silver chloride electrode, it has the disadvantage of being rather fragile and complicated in design.

### Results

The results of the experiments in which the electromotive forces of the silver-chlorine cell were measured as a function of temperature at various mole fractions of silver chloride, are shown in Fig. 6. All potentials have been corrected for small thermoelectric effects. It is apparent that the cell potential varies linearly with temperature over the temperature range between 650° to 900°C.

The variation of  $E$  (cell B) with  $\log x$ , according to the Nernst equation [4], is shown in Fig. 7, for 700°, 800°, and 900°C. The relationship over most of the curves is linear, and the slopes of the straight

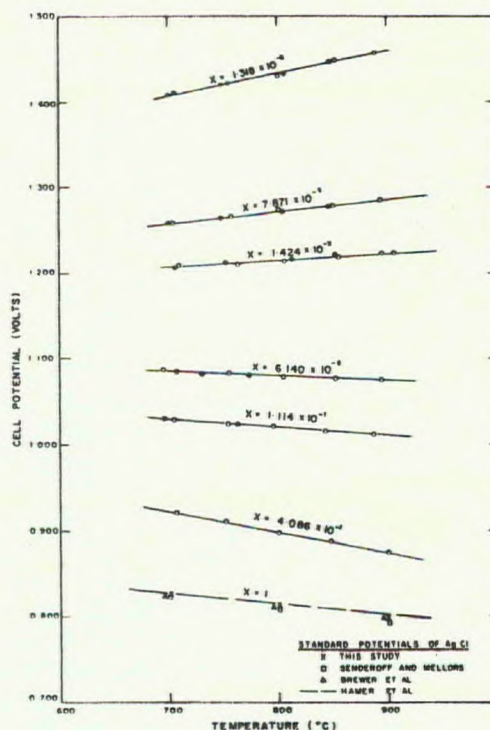


Fig. 6. Variation of emf with temperature for Cell [B]

lines agree very well with the calculated slopes from the Nernst equation at these temperatures for a one-electron electrode reaction. The standard cell [B] potential is obtained by graphical extrapolation of the straight lines in Fig. 7, to zero  $\log x$ . These potentials, according to Eq. [4], would include the activity coefficient term of the Nernst equation, if any. It will be observed, in Fig. 7, that one of the experiments was continued to higher concentrations of silver chloride than the others. At a mole fraction of about 0.5, which corresponds to a  $\log x$  term of about  $-0.2$ , the curve deviates from linearity. This is attributed mainly to the generation

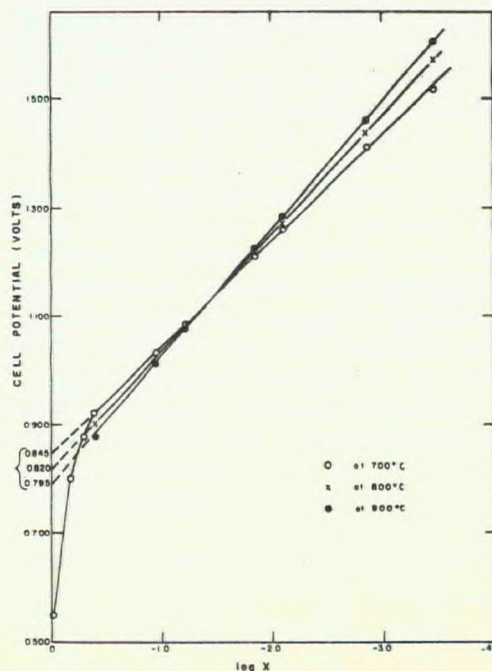


Fig. 7. EMF of Cell [B] as a function of  $\log x$  at constant temperature.

of a junction potential at high silver chloride concentration. On this basis, it can be calculated that the junction potential between pure silver chloride and the potassium-sodium chlorides is about 300 mv. This junction potential decreases rapidly as soon as some of the potassium-sodium chloride mixture has been added to the silver chloride side, and at a mole fraction of about 0.5 it disappears completely.

However, it should be pointed out that part of this potential, which is termed a junction potential, could be due to a difference in the chloride ion activities in the two half-cell solutions. The activity of chloride ion in the potassium-sodium chloride half-cell, is equal to the activity of chloride ion in the silver chloride half-cell only for dilute silver chloride solutions.

To investigate the combined effects of chloride ion activity and junction potential, a silver-chlorine cell without transference was operated. This was done by simply removing the asbestos fiber that separated the two half-cells and thus permitting free mixing of the solutions. The observed electromotive force initially was only 2 mv less than in the corresponding cell of the closed type, for the same chloride ion concentration (0.32M). After a short time, however, the potential of the open cell became erratic and this was attributed to the chemical depolarization of the silver electrode caused by small amounts of chlorine gas dissolving and migrating in the molten mixture. Hence, further experiments with this type of cell were discontinued. However, the initially observed difference of 2 mv, which is almost within the area of experimental error for the method, indicates that the effects of chloride ion activity coefficient had almost disappeared even in this rather concentrated silver chloride solution.

In Fig. 6 the dashed line at a mole fraction  $x = 1$  indicates the formation potential of pure silver chloride at different temperatures, as calculated from thermal data by Hamer, Malmberg, and Rubin (6). The triangular and square points along this line represent the experimental results obtained by Senderoff and Mellors (9), and the potentials calculated from the free energy functions as tabulated by Brewer, *et al.* (10) for the Ag-AgCl system. It is evident from Fig. 6 that the potentials calculated by Hamer and co-workers are a little larger than the experimental ones, although the agreement with the calculations of Brewer is good. Deviations between the potential data are probably due to the uncertainty of the thermal data. The crosses along this line represent standard formation potentials derived experimentally in the present study, in the presence of solvent, and the agreement between the experimental data by the different methods is striking.

From the data in Fig. 6, using the well-known equations,

$$\Delta F^\circ = -E^\circ F = -RT \ln K \quad [5]$$

$$d \ln K / dT = \Delta H / RT^2 \quad [6]$$

$$\Delta F = \Delta H - T\Delta S \quad [7]$$

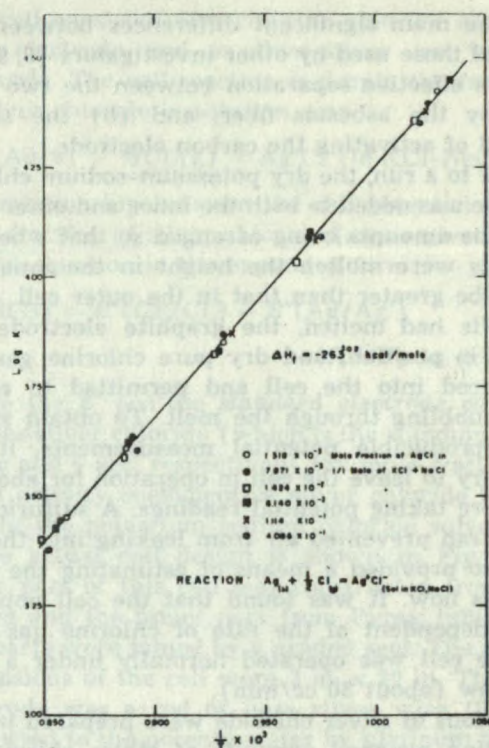
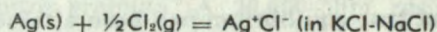


Fig. 8. Variation of  $\log K$  with the reciprocal of absolute temperature of the reaction:



it is possible to calculate the enthalpies and entropies of formation of silver chloride in the presence of solvent. The results of the calculations are shown in Fig. 8, in which the logarithm of the equilibrium constant for the formation reaction of silver chloride is plotted against the reciprocal of absolute temperature. It will be noted that the agreement between the different sets of data from which these points were calculated is very good. The relationship is linear for the range of temperature, i.e., between 650°-900°C. From the slope of the straight line the heat of formation of silver chloride is calculated as:  $\Delta H_f = -26.3 \pm 0.2$  kcal mole<sup>-1</sup>. The summary of all thermal data for silver chloride is given in Table II.

From Table II it can be readily derived that the standard partial molal free energy of mixing of silver chloride with the potassium-sodium chloride

Table II. Thermal data for silver chloride

Temp. °C	Standard free energy of formation, kcal mole <sup>-1</sup>	Standard enthalpy of formation, kcal mole <sup>-1</sup>	Standard entropy of formation, cal. deg <sup>-1</sup> mole <sup>-1</sup>
700	-19.48 <sup>a</sup>	-26.3 <sup>a</sup>	-7.1 <sup>a</sup>
	-19.42 <sup>b</sup>	-25.3 <sup>b</sup>	-6.1 <sup>b</sup>
	-19.35 <sup>c</sup>	-26.0 <sup>c</sup>	-6.8 <sup>c</sup>
800	-18.91 <sup>a</sup>	-26.3 <sup>a</sup>	-7.0 <sup>a</sup>
	-18.79 <sup>b</sup>	-25.3 <sup>b</sup>	-6.1 <sup>b</sup>
	-18.84 <sup>c</sup>	-26.0 <sup>c</sup>	-6.7 <sup>c</sup>
900	-18.33 <sup>a</sup>	-26.3 <sup>a</sup>	-6.9 <sup>a</sup>
	-18.19 <sup>b</sup>	-25.3 <sup>b</sup>	-6.1 <sup>b</sup>
	-18.31 <sup>c</sup>	-26.0 <sup>c</sup>	-6.6 <sup>c</sup>

<sup>a</sup> This study. Data obtained from solutions of silver chloride in KCl-NaCl solvent.

<sup>b</sup> Senderoff and Mellors (9). Data obtained on pure silver chloride.

<sup>c</sup> Brewer, *et al.* (10). Data obtained on pure silver chloride.

molten salt solvent is of the order of only  $-0.05$  to  $-0.15$  kcal mole $^{-1}$ , a value surprisingly low and well within the area of experimental error of the data used for comparison. Accordingly, for all practical purposes, the activity coefficient of silver chloride in the 1/1M KCl-NaCl solution is unity ( $\gamma = 1.0$ ). From the data in Table II, it can also be derived that the standard partial molal entropy of mixing is of the order of  $-0.9$  to  $-0.3$  cal/deg mole, the value again depending on the data used for the comparison. The indication is that the standard entropy change accompanying the process of solution is very small and in the area of experimental error of these measurements. Thus, the solution of silver chloride will be considered to be ideal over the temperature range of  $650^{\circ}$ - $900^{\circ}$ C and for the range of concentrations from very dilute up to  $0.5M$ .

### Discussion

By taking the state of the pure metal chlorides at the temperature of the experiments as the standard state, Eq. [3] can be applied to measure the activity coefficients of the metal chlorides in the fused salt solution. By setting the activity coefficient of silver chloride ( $\gamma_1$ ) equal to unity, Eq. [3] can be rearranged to read

$$\log \gamma (\text{MCl}_n) = (nF/2.303RT) [E^{\circ} - E^{\circ}] \quad [8]$$

where  $E^{\circ}$  is the apparent standard cell [A] potential experimentally obtained in this study, and  $E^{\circ}$  is the calculated standard cell [A] potential from tabulated formation potentials given by Hamer, Malmberg, and Rubin (6) (cf. Table I).

Hence, the activity coefficients can be readily calculated by using Eq. [8] and the data given in Tables I and II. The accuracy of the values thus obtained depends on the accuracy of our observed potentials and on the accuracy of the thermal data from which Hamer's standard potentials have been calculated. The results of these calculations are given in Table III. Also shown in Table III are the range of concentration, for which the activity coefficients were found to be constant and the variation of activity coefficient with temperature. It is obvious from the table that only the solutions of

silver chloride and thallos chloride in this solvent behave ideally. For all the other metal chloride solutions studied, a marked deviation from ideality is observed.

For metal chloride solutions such as  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ , and all the others for which the activity coefficients are less than unity, the formation of complexes can be postulated. It would appear that these salts in solution are complexed to the extent that only about 1/100 to 1/1000 of the amount present is free to contribute to the electrode potential. For these chlorides the activity coefficients show the expected behavior, i.e., they increase with increasing temperature. The constancy of the activity coefficients in dilute solutions, for the range of concentrations investigated, indicates that in these solutions the complex species remain unchanged.

Two notable exceptions to the general pattern of complex formation are represented by chromic and stannous chloride. For these salts the activity coefficients are larger than unity. On the assumption that no phase changes are involved, this behavior would indicate that the solvent has a bond-loosening effect on the solute.

In Table III, the standard partial molal free energies of mixing are calculated from the data, using the equation:

$$\Delta F_{\text{mix}}^{\circ} = RT \ln \gamma = + nF$$

$$[E^{\circ}(\text{cell A}) - E^{\circ}(\text{cell A})] \quad [9]$$

The quantity defined by Eq. [9] represents the difference between the free energy of the salt in its hypothetical standard state as a solute [i.e., a solution containing unit mole fraction of the salt but having in all other respects the thermodynamic properties of the state of infinite attenuation of the solute, as defined by Lewis and Randall (18)] minus the free energy of the salt in its actual standard state as the pure salt. It is of interest to note that the effect of temperature on the standard partial molal free energies of mixing is, in most cases, very small. Only in the cases of stannous chloride and chromic chloride is the change significant. For chromic chloride the "ideality" of the solutions is closely

Table III. Activity coefficients, standard partial molal free energies and entropies of mixing of metal chlorides in 1:1M KCl-NaCl

Salts	Range of mole fractions, $10^4 x$	Activity coefficients $\gamma_x$			$\Delta F^{\circ}(\text{mixing})$ , cal mole $^{-1}$			$\Delta S^{\circ}(\text{mixing})$ , cal deg $^{-1}$ mole $^{-1}$		
		700°C	800°C	900°C	700°C	800°C	900°C	700°C	800°C	900°C
MnCl $_2$	5.87-107.0	0.0093	0.011	0.014	-9,040	-9,640	-10,000	3.6	3.7	3.5
ZnCl $_2$	22.20-717.0	0.0091	0.018	0.028	-8,990	-8,530	-8,300	-2.0	-2.3	-2.0
CrCl $_2$	2.84-93.5	0.010	0.010	0.013	-8,900	-9,820	-10,280	8.9	8.9	8.8
TlCl	36.10-603.0	1.0	—	—	0.0	—	—	—	—	—
CdCl $_2$	23.40-835.0	0.0075	0.010	—	-9,460	-9,820	—	6.1	5.8	—
FeCl $_2$	8.85-138.0	0.0059	0.0089	0.011	-9,920	-10,050	-10,520	4.4	4.1	4.4
CrCl $_3$	4.00-90.0	0.24	1.18	2.4	-2,770	+350	+2,070	-22.0	-22.2	-22.0
PbCl $_2$	3.25-628.0	0.17	0.14	0.19	-3,460	-4,150	-3,920	3.7	3.8	3.9
SnCl $_2$	6.32-125.0	2.3	5.7	8.9	+1,610	+3,730	+5,070	-15.1	-11.7	-9.8
CoCl $_2$	7.60-612.0	0.046	0.043	0.063	-5,950	-6,690	-6,460	3.9	4.2	3.9
CuCl	10.80-391.0	0.24	0.30	0.34	-2,770	-2,570	-2,560	-0.7	-0.8	-0.8
NiCl $_2$	5.94-666.0	0.34	—	—	-2,080	—	—	—	—	—
AgCl	3.37-6850.0	1.0	1.0	1.0	0.0	0.0	0.0	(-0.5)	(-0.5)	(-0.5)
CuCl $_2$	10.0-390.0	0.0033	0.0045	0.0061	-11,070	-11,530	-11,900	5.5	5.4	5.5



related to temperature. At about 800°C the solutions are almost "ideal," but with increasing temperature a positive deviation from ideality is evident.

From the dependence of the standard partial molal free energies of mixing on temperature, the standard partial molal enthalpies and entropies of mixing can be calculated for the systems shown in Table III. The latter are also given in this table.

The standard partial molal entropies of mixing, as shown in the last three columns of Table III, also suggest that complex ions are present in all of these systems. It is necessary here to define the term "complex" as used throughout this study. In a very broad sense a "complex" in an ionic melt should be defined as a group of atoms for which the binding forces are stronger than the forces tending to separate them. The latter type of forces obviously includes the interactions between similar groups of atomic aggregates and also the interactions with the solvent. In terms of structure, a "complex" in solution should be a group of atoms in which the immediate neighbors of any atom are arranged in some orderly way, but the arrangement becomes more random gradually with increasing distance from the center of the complex. The definition is almost that on a liquid, with the difference that there is a distinction between the random distribution of atoms or ions in the solvent, and the locally more ordered distribution of atoms in a complex.

Although the presence of finite complexes in melts has been demonstrated both by potentiometric (14) and by spectrophotometric measurements (15), it seems reasonable that in ionic metals there should exist several intermediate states of aggregation between the so-called "noncomplexed" ionic state and the type of finite complexes found in aqueous solutions.

The actual values of the activity coefficients, and of other thermodynamic functions which characterize these complexes in solution will depend entirely on the definition of a noncomplexed state. A completely different set of data would be obtained if, instead of choosing the pure metal salt as the standard state, the state of infinite dilution were chosen. In fact, only the existing differences between any two states are measured directly, and a thermodynamic definition of a noncomplexed state is quite arbitrary. Even the "ideal solution" appears to arise from cancelling out of opposing effects in the binding forces within the complex itself.

In support of this view is the behavior of the solutions of silver chloride in alkali chlorides. Stern (11,12) found that the partial molal free energy of mixing of silver chloride in potassium chlo-

ride is negative, and that of silver chloride in sodium chloride is positive. In the present investigation it was found that in a solution of silver chloride in 1/1M mixture of potassium and sodium chlorides, the standard partial free energy of mixing is zero and the solutions are "ideal." It is apparent that by regulating the composition of the solvent and temperature it is possible to obtain solutions with positive, negative, or zero deviation from ideality. Thus, one may conclude that what is thermodynamically an "ideal" state is not necessarily a non-complexed state.

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