ELECTRODE POTENTIALS OF METAL CHLORIDES IN BINARY AND TERNARY FUSED SALT SOLUTIONS WITH ALKALI CHLORIDES

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ABSTRACT

The standard formal electrode potentials of several metals have been determined from 700-900°C in NaCl, KCl, CsCl or the equimolar mixtures of these salts using galvanic or redox cells with a silver-silver chloride reference electrode. The activity coefficients and other partial molar properties of these solutions were calculated as a function of temperature from the emf measurements.

INTRODUCTION

In a previous publication from this laboratory, the standard electrode potentials and the associated thermodynamic properties for the dilute solutions of AlCl₃ in binary and ternary fused salts were reported (1). For those experiments, the electrode potential in the solvents NaCl, KCl, CsCl or in the equimolar mixtures of these salts, was determined using a silver-silver chloride reference electrode. For the present investigation, this method was extended to the chlorides of cobalt, nickel, thorium, iron, chromium and copper.

The electrode potentials of the dilute solutions of metal chlorides in alkali chlorides have been the subject of several electrochemical studies. However, data for various solvent systems are incomplete, especially for the multicomponent systems. It is the purpose of the present investigation to establish the thermodynamic behaviour and the emf series of metals in different binary and ternary alkali chloride molten salt electrolytes from 700°C to 900°C. Also, the validity of theoretical expressions for the prediction of the thermodynamic properties of the ternary solutions from binary solution data was confirmed.

When a metal, M, has two stable valence states at high temperatures, namely Mⁿ⁺ and Mⁿ⁺⁺ (where n>m), the electrode potentials to be determined are, respectively, E°ₘ and E°ₘ₊ⁿ of the electrodes M/Mⁿ⁺ and M/Mⁿ⁺⁺, and the redox potential E°ₘⁿ⁺/Mⁿ⁺ of the system Mⁿ⁺⁺/Mⁿ⁺. The expression

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relating the three potentials is easily calculated using a thermodynamic cycle as,

\[ nE_n^o - mE_m^o = (n-m)E_{m,n}^o \]  

When any two of the three potentials are known, the unknown potential can be calculated. In general, in fused salts \( E_n^o \) cannot be determined directly because of the reactivity of the metal with a solution containing the higher valence state chloride.

EXPERIMENTAL

The preparation and purification of the alkali chlorides has been described elsewhere (1). The metal chlorides were anhydrous and better than 99.9% pure. The metal electrodes had a purity of greater than 99.9%. Two different types of electrochemical cells were used for determining electrode potentials.

(a) A cell for measuring metal electrode potentials.

This cell, similar to that reported earlier (1), can be described schematically as,

\[
\begin{array}{c|c|c|c|c}
M & MCI - ACl & \text{asbestos} & AgCl - ACl & Ag \\
\hline
(-) & (X_m) & \text{diaphragm} & (X_i) & (+)
\end{array}
\]

where, \( M \) was respectively cobalt, nickel, iron, chromium, copper or thorium. \( MCI \) was respectively CoCl\(_2\), NiCl\(_2\), FeCl\(_2\), CuCl or ThCl\(_4\). ACl represents the salt components NaCl, KCl, CsCl or the binary equimolar mixtures of these salts. The concentration of AgCl in alkali chloride is fixed at \( X_i = 0.05 \). The spontaneous reaction for the Ag-M galvanic cell is,

\[ M + mAgCl \rightleftharpoons MCI_m + mAg \]

where the line under a salt species denotes a species in solution. The corresponding form of the Nernst equation for solutions dilute enough to obey Henry's law is written as,

\[ E_{\text{cell}} = E_f^{\circ}(\text{cell}) - \frac{2.303RT}{mF} \log \frac{x_{MCl_m}^m}{x_{AgCl}^m} \]  

where, \( X \)'s are mole fractions and, the standard formal cell potential, \( E_f^{\circ}(\text{cell}) \) is defined as,

\[ E_f^{\circ}(\text{cell}) = E_{MCl_m}^o - E_{AgCl}^o - \frac{2.303RT}{mF} \log \frac{y_{MCl_m}^m}{y_{AgCl}^m} \]  

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For this expression, \( E_{\text{MCl}_m}^\circ \) and \( E_{\text{AgCl}}^\circ \) are the standard formation cell potentials of pure liquid \( \text{MCl}_m \) and \( \text{AgCl} \). The values of \( E_{\text{MCl}_m}^\circ \) and \( E_{\text{MCl}_m}^\circ \) were obtained from the literature. \( F \) is the Faraday constant, given as 8.3144 J/K mol. The standard state in all cases was the pure liquid chloride at the temperature of the experiments.

(b) A cell for measuring redox potentials; this cell can be illustrated schematically as,

\[
\begin{align*}
\text{Ag} & | \text{AgCl} - \text{ACl} | \text{asbestos} | \text{MCl}_m - \text{MCl}_n - \text{ACl} | \text{Pt} \\
(-) & | (+)
\end{align*}
\]

where, \( \text{MCl}_m \) was, respectively, \( \text{FeCl}_2 \), \( \text{CrCl}_2 \) or \( \text{CuCl}_2 \) at mole fraction \( X_2 \), and \( \text{MCl}_n \) was, respectively, \( \text{FeCl}_3 \), \( \text{CrCl}_3 \) or \( \text{CuCl}_2 \) at mole fraction \( X_3 \). \( \text{ACl} \) had the same meaning as described above. The cell reaction is,

\[
\text{Ag} + \text{MCl}_n = \text{MCl}_m + \text{AgCl}
\]

where \( n = m + 1 \). For the redox cell, the corresponding form of the Nernst equation is,

\[
\begin{align*}
E_{\text{cell}} &= E_{\text{r(cell)}}^\circ - \frac{2.303 \ RT}{F} \log \frac{X_{\text{AgCl}} X_{\text{MCl}_m}}{X_{\text{MCl}_n}} \\
(4)
\end{align*}
\]

The standard formal redox cell potential is defined by:

\[
E_{\text{r(cell)}}^\circ = E_{\text{AgCl}}^\circ - E_{\text{MCl}_m}^\circ - E_{\text{MCl}_n}^\circ - \frac{2.303 \ RT}{\text{mF}} \log \frac{\gamma_{\text{AgCl}} \ \gamma_{\text{MCl}_m}}{\gamma_{\text{MCl}_n}}
\]

Formal formation potentials can also be defined by:

\[
E_{\text{f(MCl}_m)}^\circ = E_{\text{MCl}_m}^\circ - \frac{2.303 \ RT}{\text{mF}} \log \gamma_{\text{MCl}_m}
\]

Such formal formation potentials represent the free energy of formation of unit mole fraction of a hypothetical salt behaving thermodynamically as it would behave in an infinitely dilute state in a given solvent. Thus, for each solvent the formal potentials are a constant of the system from which emf series in fused salts may be tabulated.

The complete experimental apparatus and procedure have been described in detail elsewhere. Reversibility was confirmed by temperature cycling and by polarization tests. For the latter, l mA was passed through the cell, in each case the emf returned to the original value in less than one minute. Cell emf's were stable and reproducible to within l mV over a 24 h period. The adjustment for thermoelectric potentials was established by connecting the electrode tips in the absence of the electrolyte, and measuring the resulting emf at various temperatures.
RESULTS AND DISCUSSION

Tables 1 to 9 summarize the measured cell emf's which have been expressed as least squares lines of the form \( E = A T + B \), where, \( E \) is the cell potential in volts, and \( T \) is the temperature in K. Cell emf's have been adjusted for thermoelectric effects. Melt compositions have been expressed in terms of the mole fractions of the metal chloride. Also, for the ternary solutions, the composition variable \( t \) has been defined as,

\[
t = \frac{x_{\text{CsCl}}}{x_{\text{CsCl}} + x_{\text{NaCl}}}
\]

or

\[
t = \frac{x_{\text{CsCl}}}{x_{\text{CsCl}} + x_{\text{KCl}}}
\]

for the CsCl ternary solutions, and as,

\[
t = \frac{x_{\text{KCl}}}{x_{\text{KCl}} + x_{\text{NaCl}}}
\]

for the solutions containing only KCl and NaCl. The correlation coefficients in Tables 1 through 9 indicate that the plots of cell emf versus temperature are linear. Also, the estimate for the standard deviation of a cell potential for the regression of cell emf on temperature is smaller than 4 mV, for all cases.

A typical Nernst plot for the ThCl\(_4\) system is given in Figure 1. For this metal chloride, the Nernst slope indicates a four electron transfer within a 99.9% confidence level. Thus, the tetravalent thorium ion is present in these melts, although it should be less stable for the NaCl solvents. For the FeCl\(_2\), NiCl\(_2\), CoCl\(_2\), and CrCl\(_2\) solutes the linear regression analysis for the Nernst plots gave correlation coefficients of almost unity in all cases. Within a 99.9% confidence level, there is a two electron transfer. For all the redox cells and for the CuCl galvanic cell, there is a one electron transfer reaction. The linear regression analysis for these Nernst plots also gave correlation coefficients of close to unit for every case. Since for all systems the Nernst relationship is obeyed, Henry's law is followed over a range of concentrations up to approximately \( 10^{-2} \) mole fraction.

Values of \( E^\circ_{\text{f(cell)}} \) and \( E^\circ_{\text{f(cell)}} \) determined graphically as well as the formal formation potentials of the higher valence state metal chlorides calculated from equation \([1]\), are recorded in accordance with the IUPAC convention in Tables 10 a to 10c for three temperatures \([3]\). The values have been adjusted to correspond to the chlorine gas reference electrode reported in a previous investigation \([1]\). The results in the present study agree with values found in the literature \([4-14]\). It can be seen that the magnitude of the formal potentials increase as CsCl is added, showing the pronounced effect of CsCl is creating thermodynamically stable solutions. In general, the magnitude of the formal potentials decrease as the temperature is...
increased which indicates a decrease in thermodynamic stability at the higher temperatures. Included in Tables 10a to 10c are values of the standard formal potentials in the ternary solutions as calculated from the previously derived expression (15-17),

\[ E^\circ_{f(123)} = (1-t) E^\circ_{f(12)} + t E^\circ_{f(13)} \]  

where, \( E^\circ_{f(12)} \) is the standard formal potential in the ternary solution, and \( E^\circ_{f(12)} \) and \( E^\circ_{f(13)} \) are the standard formal potentials in the component binary systems. The \( t \) parameter was defined in equation (7). The experimental results for \( t = 1/2 \) are in agreement to approximately ± 6% of the predicted values.

Tables 11 to 13 summarize the thermodynamic properties. The thermodynamic properties for CuCl\(_2\) were not calculated because the standard formation potential of liquid CuCl\(_2\) is not available. Tables 11a to 11c list activity coefficients for three temperatures. The very low values of the activity coefficients when combined with exothermic enthalpies of mixing and negative excess entropies of mixing, to be discussed subsequently, are indicative of strong interactions in these solutions which are usually associated with the formation of complex species. With the exception of several NaCl solvents, the activity coefficients increase with temperature increase, indicating the dissociation of the complexes at higher temperatures. For a few NaCl solvents, the activity coefficients decrease as the temperature is increased which could be taken as due to clustering of the ionic species, rather than to any complex formation. Also included in Table 11 are the predicted values of the activity coefficients for the ternary solutions according to the equation given as (15-17),

\[ \log Y_{123} = (1-t) \log Y_{12} + t \log Y_{13} \]  

The partial molar enthalpies of mixing are summarized in Table 12. The solutions become increasingly exothermic as the radius of the alkali chloride changes from Na\(^+\) to Cs\(^+\). This is commonly explained on the basis of the competition for anions between the solute and solvent cations. Furthermore, the predicted values for the partial molar enthalpies of mixing in the ternary solutions, calculated from (15-17),

\[ \Delta H_{123} = (1-t) \Delta H_{12} + t \Delta H_{13} \]  

are given in Table 12. The comparison between the measured and predicted value is better in the systems without NaCl where there is a minimum of extrapolation.

Table 13 lists the excess partial molar entropies of mixing. In general, the values are negative, and the magnitude increases in the order NaCl + KCl + CsCl. This indicates that part of the total entropy of mixing should be related to the change in frequency of the characteristic vibrations of the species in solution.
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REFERENCES

1. P.J. Tumidajski and S.N. Flengas, Can. J. Chem. 63, 1080 (1985).
2. W.H. Hamer, M.S. Malmberg and B. Rubin, J. Electrochem. Soc. 103, 8 (1956).
3. T. Licht and A. de Bethune, J. Chem. Educ. 34, 443 (1957).
4. D.C. Hamby and A.B. Scott, J. Electrochem. Soc. 117, 319 (1970).
5. R. Combesc, J. Vedel and B. Tremillon, J. Electroanal. Chem. 27, 174 (1970).
6. S.N. Flengas and T.R. Ingraham, Can. J. Chem. 35, 1139 (1957).
7. D.C. Hamby and A.B. Scott, J. Electrochem. Soc. 115, 704 (1968).
8. D.C. Hamby and A.R. Hohimer, J. Electrochem. Soc. 121, 104 (1974).
9. S.N. Flengas and T.R. Ingraham, Can. J. Chem. 35, 1254 (1957).
10. H. Kuhnl, M. Wittner and W. Simon, Electrochimica Acta 24, 55 (1979).
11. M.V. Smirnov, A.V. Pokrovskii and N.A. Loginov, Russ. J. Inor. Chem. 15, 1644 (1970).
12. S.N. Flengas and T.R. Ingraham, Can. J. Chem. 36, 1103 (1958).
13. M.V. Smirnov, A.V. Pokrovskii and N.A. Loginov, Zh. Prikl. Kh. 43, 2334 (1970).
14. R. Srinivasan and S.N. Flengas, Can. J. Chem. 42, 1315 (1964).
15. D.R. Sadoway and S.N. Flengas, J. Electrochem. Soc. 122, 515 (1975).
16. D.R. Sadoway and S.N. Flengas, in "Extractive Metallurgy of Retractory Metals", edited by H. Shohn, N. Carlson and J. Smith, AIME, Warrendale, Pa., pp. 315-339 (1981).
17. S.N. Flengas and D.R. Sadoway, in "Proceedings of the Third International Symposium on Molten Salts", edited by G. Mamantov, M. Blander and G.P. Smith, The Electrochemical Society, N.J., pp. 68-94 (1981).
Table 1. $E_{cell}$ versus temperature for the CoCl$_2$ system

| Solvent          | $X_{CoCl_2}$ | $E = AT + B$ (V) | C Coeff. | Range (K)  |
|------------------|--------------|------------------|----------|------------|
|                  |              | $A \times 10^3$  | $B$      |            |
| NaCl             | 2.02 x $10^{-3}$ | -0.471          | 0.343    | -0.999     | 1108-1178  |
|                  | 3.88 x $10^{-3}$ | -7.550          | 0.344    | -0.999     | 1107-1166  |
|                  | 6.56 x $10^{-3}$ | -9.840          | 0.344    | -0.999     | 1111-1186  |
|                  | 8.55 x $10^{-3}$ | -1.096          | 0.344    | -0.999     | 1107-1181  |
| KC1              | 3.55 x $10^{-3}$ | -1.272          | 0.426    | -0.996     | 1081-1174  |
|                  | 5.63 x $10^{-3}$ | -1.504          | 0.430    | -0.999     | 1091-1174  |
|                  | 7.61 x $10^{-3}$ | -1.627          | 0.429    | -0.998     | 1100-1197  |
|                  | 1.03 x $10^{-2}$ | -1.753          | 0.428    | -0.999     | 1075-1181  |
| CsCl             | 6.11 x $10^{-3}$ | -1.804          | 0.497    | -0.999     | 961-1118   |
|                  | 1.01 x $10^{-2}$ | -2.023          | 0.498    | -0.999     | 965-1107   |
|                  | 1.31 x $10^{-2}$ | -2.137          | 0.498    | -0.999     | 957-1104   |
|                  | 1.87 x $10^{-2}$ | -2.291          | 0.498    | -0.999     | 941-1096   |
| NaCl-KCl*        | 1.72 x $10^{-3}$ | -1.207          | 0.453    | -0.999     | 985-1101   |
| (t=1/2)          | 3.04 x $10^{-3}$ | -1.454          | 0.453    | -0.999     | 957-1106   |
|                  | 5.20 x $10^{-3}$ | -1.678          | 0.452    | -0.999     | 957-1109   |
|                  | 7.87 x $10^{-3}$ | -1.865          | 0.453    | -0.999     | 946-1105   |
| NaCl-CsCl*       | 2.98 x $10^{-3}$ | -0.929          | 0.406    | -0.999     | 966-1103   |
| (t=1/2)          | 7.35 x $10^{-3}$ | -1.320          | 0.406    | -0.999     | 968-1102   |
|                  | 1.02 x $10^{-2}$ | -1.453          | 0.405    | -0.999     | 969-1102   |
|                  | 1.26 x $10^{-2}$ | -1.545          | 0.405    | -0.999     | 961-1105   |
| KC1-CsCl*        | 4.91 x $10^{-3}$ | -2.354          | 0.538    | -0.999     | 990-1136   |
| (t=1/2)          | 8.11 x $10^{-3}$ | -2.550          | 0.538    | -0.999     | 974-1109   |
|                  | 1.05 x $10^{-2}$ | -2.664          | 0.538    | -0.999     | 960-1109   |
|                  | 1.43 x $10^{-2}$ | -2.800          | 0.539    | -0.999     | 960-1102   |

*Equimolar.*
Table 2. \( E_{\text{cell}} \) versus temperature for the NiCl\(_2\) system

| Solvent      | \( X_{\text{NiCl}_2} \) | \( E = AT + B \) (V) | C Coeff. | Range (K)  |
|--------------|--------------------------|----------------------|----------|------------|
|              |                          | \( A \times 10^4 \)  | \( B \)  |            |
| NaCl         | 1.36 \( \times 10^{-3} \) | -0.050               | 0.120    | -0.972     | 1131-1189  |
|              | 2.00 \( \times 10^{-3} \) | -0.206               | 0.118    | -0.999     | 1128-1185  |
|              | 3.94 \( \times 10^{-3} \) | -0.495               | 0.118    | -0.999     | 1123-1186  |
|              | 4.61 \( \times 10^{-3} \) | -0.559               | 0.117    | -0.998     | 1126-1191  |
| KCl          | 2.00 \( \times 10^{-3} \) | -0.041               | 0.106    | -0.985     | 1078-1152  |
|              | 3.43 \( \times 10^{-3} \) | -0.256               | 0.104    | -0.998     | 1068-1110  |
|              | 5.23 \( \times 10^{-3} \) | -0.440               | 0.104    | -0.999     | 1048-1105  |
|              | 6.78 \( \times 10^{-3} \) | -0.565               | 0.106    | -0.994     | 1077-1107  |
| CsCl         | 5.25 \( \times 10^{-3} \) | -1.016               | 0.170    | -0.999     | 968-1100   |
|              | 8.19 \( \times 10^{-2} \) | -1.211               | 0.171    | -0.999     | 937-1094   |
|              | 1.19 \( \times 10^{-2} \) | -1.574               | 0.172    | -0.999     | 937-1094   |
|              | 1.51 \( \times 10^{-2} \) | -1.476               | 0.172    | -0.999     | 940-1094   |
| NaCl-KCl*    | 1.27 \( \times 10^{-3} \) | -1.801               | 0.335    | -0.999     | 978-1093   |
| \((t=1/2)\)  | 2.92 \( \times 10^{-3} \) | -2.209               | 0.340    | -0.997     | 973-1098   |
|              | 4.46 \( \times 10^{-3} \) | -2.855               | 0.336    | -0.999     | 976-1101   |
|              | 6.06 \( \times 10^{-3} \) | -2.479               | 0.335    | -0.998     | 970-1095   |
| NaCl-CsCl*   | 3.23 \( \times 10^{-3} \) | -1.229               | 0.210    | -0.999     | 953-1087   |
| \((t=1/2)\)  | 6.96 \( \times 10^{-3} \) | -1.555               | 0.209    | -0.999     | 950-1087   |
|              | 9.52 \( \times 10^{-3} \) | -1.699               | 0.210    | -0.999     | 954-1091   |
|              | 1.27 \( \times 10^{-2} \) | -1.817               | 0.209    | -0.999     | 916-1091   |
| KCl-CsCl*    | 3.88 \( \times 10^{-3} \) | -0.389               | 0.134    | -0.998     | 947-1109   |
| \((t=1/2)\)  | 7.60 \( \times 10^{-3} \) | -0.680               | 0.134    | -0.998     | 934-1109   |
|              | 1.05 \( \times 10^{-2} \) | -0.813               | 0.135    | -0.999     | 934-1100   |
|              | 1.32 \( \times 10^{-2} \) | -0.917               | 0.134    | -0.999     | 940-1100   |

*Equimolar.*
Table 3. $E_{\text{cell}}$ versus temperature for the FeCl$_2$ system

| Solvent          | $E_{\text{FeCl}_2}$  | $E = AT + B$ (V) | C Coeff,     | Range (K) |
|------------------|----------------------|------------------|-------------|-----------|
|                  | $A \times 10^4$ | $B$               |             |           |
| CsCl             | $3.41 \times 10^{-3}$ | -1.713           | 0.683       | -0.992    | 969-1044 |
|                  | $8.46 \times 10^{-3}$ | -2.105           | 0.683       | -0.999    | 967-1070 |
|                  | $1.26 \times 10^{-2}$ | -2.231           | 0.678       | -0.997    | 958-1053 |
|                  | $1.68 \times 10^{-2}$ | -2.400           | 0.683       | -0.994    | 968-1051 |
| NaCl-KCl*        | $2.79 \times 10^{-3}$ | -1.279           | 0.614       | -0.995    | 966-1029 |
|                  | $6.25 \times 10^{-3}$ | -1.779           | 0.629       | -0.998    | 953-1033 |
|                  | $9.18 \times 10^{-3}$ | -1.849           | 0.619       | -0.998    | 965-1036 |
|                  | $1.18 \times 10^{-2}$ | -1.875           | 0.611       | -0.998    | 957-1035 |
| KCl-CsCl*        | $3.06 \times 10^{-3}$ | -1.789           | 0.679       | -0.997    | 974-1036 |
|                  | $6.25 \times 10^{-3}$ | -2.119           | 0.682       | -0.998    | 967-1036 |
|                  | $9.70 \times 10^{-3}$ | -2.184           | 0.669       | -0.999    | 962-1036 |
|                  | $1.26 \times 10^{-2}$ | -2.438           | 0.684       | -0.998    | 962-1031 |

*Equimolar.*
Table 4. \( E_{\text{cell}} \) versus temperature for the CrCl\(_2\) system

| Solvent | \( x_{\text{CrCl}_2} \) | \( E = AT + B \text{(V)} \) | C Coeff. | Range (K) |
|---------|-----------------|-----------------|----------|-----------|
|         | \( A \times 10^4 \) | \( B \)          |          |           |
| NaCl    | 6.90 x 10\(^{-4}\) | 1.234           | 0.660    | 0.999     | 1115-1172 |
|         | 1.24 x 10\(^{-3}\) | 1.356           | 0.619    | 0.999     | 1122-1173 |
|         | 2.16 x 10\(^{-3}\) | 1.035           | 0.630    | 0.999     | 1117-1175 |
|         | 2.80 x 10\(^{-3}\) | 1.105           | 0.609    | 0.999     | 1110-1166 |
| KCl     | 7.01 x 10\(^{-4}\) | -2.695          | 1.076    | -0.999    | 1082-1173 |
|         | 1.21 x 10\(^{-3}\) | -1.552          | 0.925    | -1.000    | 1086-1166 |
|         | 1.72 x 10\(^{-3}\) | -1.611          | 0.914    | -0.999    | 1092-1169 |
|         | 2.29 x 10\(^{-3}\) | -2.234          | 0.970    | -0.999    | 1084-1172 |
| CsCl    | 1.65 x 10\(^{-3}\) | -3.459          | 1.071    | -0.999    | 980-1114  |
|         | 3.29 x 10\(^{-3}\) | -3.768          | 1.072    | -0.999    | 980-1109  |
|         | 5.03 x 10\(^{-3}\) | -3.949          | 1.072    | -0.999    | 980-1107  |
|         | 6.99 x 10\(^{-3}\) | -4.088          | 1.071    | -0.999    | 980-1107  |
| NaCl-KCl* | 6.67 x 10\(^{-4}\) | -1.152          | 0.929    | -0.993    | 984-1122  |
| (t=1/2) | 1.09 x 10\(^{-3}\) | -1.416          | 0.935    | -0.998    | 984-1122  |
|         | 1.76 x 10\(^{-3}\) | -1.691          | 0.940    | -0.998    | 984-1131  |
|         | 2.36 x 10\(^{-3}\) | -1.833          | 0.940    | -0.998    | 978-1131  |
| NaCl-CsCl* | 1.48 x 10\(^{-3}\) | -1.951          | 0.925    | -0.998    | 1010-1132 |
| (t=1/2) | 2.51 x 10\(^{-3}\) | -2.166          | 0.924    | -0.999    | 977-1136  |
|         | 3.38 x 10\(^{-3}\) | -2.269          | 0.921    | -0.984    | 979-1118  |
|         | 4.24 x 10\(^{-2}\) | -2.398          | 0.925    | -0.999    | 978-1118  |
| KCl-CsCl* | 9.76 x 10\(^{-4}\) | -2.758          | 1.016    | -0.999    | 981-1105  |
| (t=1/2) | 1.76 x 10\(^{-3}\) | -3.007          | 1.015    | -0.999    | 978-1129  |
|         | 2.83 x 10\(^{-3}\) | -3.217          | 1.016    | -0.999    | 981-1118  |
|         | 3.60 x 10\(^{-3}\) | -3.321          | 1.016    | -0.999    | 979-1110  |

*Equimolar.*
| Solvent   | $X_{CuCl}$ | $E = AT + B$ (V) | C Coeff. | Range (K) |
|-----------|------------|-----------------|----------|-----------|
|           | A x $10^4$ | B               |          |           |
| NaCl      | 1.01 x $10^{-3}$ | 2.687 | 0.335 | 0.999 | 1090-1176 |
|           | 1.93 x $10^{-3}$ | 2.121 | 0.335 | 0.999 | 1087-1171 |
|           | 2.64 x $10^{-3}$ | 1.780 | 0.336 | 0.999 | 1082-1178 |
|           | 3.68 x $10^{-3}$ | 1.563 | 0.335 | 0.999 | 1084-1178 |
| KCl       | 9.58 x $10^{-4}$ | 2.228 | 0.432 | 0.999 | 1057-1156 |
|           | 1.91 x $10^{-3}$ | 1.623 | 0.433 | 0.999 | 1072-1181 |
|           | 3.34 x $10^{-3}$ | 1.150 | 0.432 | 0.999 | 1075-1173 |
|           | 4.68 x $10^{-3}$ | 0.858 | 0.432 | 0.998 | 1068-1181 |
| CsCl      | 9.54 x $10^{-4}$ | 1.642 | 0.511 | 0.998 | 962-1172  |
|           | 1.91 x $10^{-3}$ | 1.042 | 0.511 | 0.998 | 965-1175  |
|           | 3.05 x $10^{-3}$ | 0.633 | 0.512 | 0.997 | 986-1176  |
|           | 4.94 x $10^{-3}$ | 0.186 | 0.515 | 0.978 | 944-1181  |
| NaCl-KCl* | 9.00 x $10^{-4}$ | 1.036 | 0.548 | 0.999 | 983-1181  |
| (t=1/2)   | 1.60 x $10^{-3}$ | 4.370 | 0.549 | 1.000 | 994-1177  |
|           | 3.09 x $10^{-3}$ | -0.025 | 0.548 | -0.999 | 954-1173  |
|           | 4.24 x $10^{-3}$ | -0.301 | 0.549 | -0.999 | 942-1175  |
| NaCl-CsCl*| 9.25 x $10^{-4}$ | 1.659 | 0.419 | 0.999 | 976-1175  |
| (t=1/2)   | 1.70 x $10^{-3}$ | 1.140 | 0.418 | 0.999 | 966-1173  |
|           | 2.77 x $10^{-3}$ | 0.712 | 0.419 | 0.999 | 976-1173  |
|           | 3.84 x $10^{-3}$ | 0.432 | 0.419 | 0.999 | 964-1171  |
| KCl-CsCl* | 1.02 x $10^{-3}$ | 1.661 | 0.497 | 0.999 | 979-1174  |
| (t=1/2)   | 2.04 x $10^{-3}$ | 1.068 | 0.496 | 0.999 | 980-1169  |
|           | 3.05 x $10^{-3}$ | 0.714 | 0.497 | 0.999 | 975-1174  |
|           | 4.40 x $10^{-3}$ | 0.395 | 0.497 | 0.985 | 976-1180  |

*Equimolar.*
Table 6. $E_{cell}$ versus temperature for the ThCl$_4$ system

| Solvent         | $X_{ThCl_4}$ | $E = AT + B$ (V) | C Coeff. | Range (K) |
|-----------------|--------------|-----------------|----------|-----------|
|                 |              | $A \times 10^n$ | $B$      |           |
| NaCl            | $3.04 \times 10^{-4}$ | 1.371 | 1.246 | 0.999 | 1113-1177 |
|                 | $1.13 \times 10^{-3}$ | 1.090 | 1.247 | 0.999 | 1101-1177 |
|                 | $1.52 \times 10^{-3}$ | 1.038 | 1.246 | 0.995 | 1103-1175 |
|                 | $2.20 \times 10^{-3}$ | 0.961 | 1.246 | 0.997 | 1093-1175 |
| KCl             | $7.75 \times 10^{-4}$ | -2.230 | 1.750 | -0.999 | 1100-1179 |
|                 | $1.55 \times 10^{-3}$ | -2.587 | 1.752 | -0.999 | 1071-1174 |
|                 | $2.12 \times 10^{-3}$ | -2.455 | 1.751 | -0.999 | 1072-1173 |
|                 | $2.70 \times 10^{-3}$ | -2.510 | 1.752 | -0.999 | 1076-1173 |
| CsCl            | $2.64 \times 10^{-3}$ | -5.981 | 2.207 | -0.999 | 981-1087 |
|                 | $4.13 \times 10^{-3}$ | -6.082 | 2.208 | -0.999 | 972-1085 |
|                 | $5.52 \times 10^{-3}$ | -6.144 | 2.208 | -0.999 | 955-1080 |
|                 | $7.74 \times 10^{-3}$ | -6.207 | 2.206 | -0.999 | 960-1079 |
| NaCl-KCl*       | $6.73 \times 10^{-4}$ | -4.007 | 1.936 | -0.999 | 1009-1111 |
| $(t=1/2)$       | $8.22 \times 10^{-4}$ | -4.064 | 1.937 | -0.999 | 982-1092 |
|                 | $2.09 \times 10^{-3}$ | -4.260 | 1.937 | -0.999 | 982-1101 |
|                 | $2.88 \times 10^{-3}$ | -4.324 | 1.936 | -0.999 | 982-1101 |
|                 | $5.87 \times 10^{-3}$ | -4.592 | 1.937 | -0.999 | 981-1100 |
| NaCl-CsCl*      | $1.71 \times 10^{-3}$ | -0.489 | 1.590 | -0.999 | 953-1083 |
| $(t=1/2)$       | $4.18 \times 10^{-3}$ | -0.663 | 1.588 | -0.999 | 948-1079 |
|                 | $6.81 \times 10^{-3}$ | -0.777 | 1.589 | -0.999 | 950-1085 |
|                 | $8.85 \times 10^{-3}$ | -0.836 | 1.589 | -0.999 | 952-1085 |
| KCl-CsCl*       | $1.84 \times 10^{-3}$ | -3.614 | 1.903 | -0.999 | 961-1095 |
| $(t=1/2)$       | $3.68 \times 10^{-3}$ | -3.769 | 1.904 | -0.999 | 963-1092 |
|                 | $5.65 \times 10^{-3}$ | -3.861 | 1.904 | -0.998 | 963-1093 |
|                 | $8.35 \times 10^{-3}$ | -3.944 | 1.903 | -0.996 | 948-1093 |

*Equimolar.*
## Table 7. \( E_{\text{cell}} \) versus temperature for the FeCl\(_2\)-FeCl\(_3\) system

| Solvent     | \( x_{\text{FeCl}_2} \) | \( x_{\text{FeCl}_3} \) | \( E = AT + B (V) \) | \( C \) Coeff, Range (K) |
|-------------|-----------------|-----------------|-------------------|-------------------------|
| CsCl        | 3.46 x 10\(^{-3}\) | 2.58 x 10\(^{-3}\) | 1.010 x 10\(^{-4}\) | 0.097 955-1024          |
|             | 3.45 x 10\(^{-3}\) | 6.29 x 10\(^{-3}\) | 1.897 x 10\(^{-4}\) | 0.197 950-1024          |
|             | 3.44 x 10\(^{-3}\) | 9.73 x 10\(^{-3}\) | 2.344 x 10\(^{-4}\) | 0.099 950-1026          |
|             | 3.43 x 10\(^{-3}\) | 1.21 x 10\(^{-2}\) | 2.430 x 10\(^{-4}\) | 0.198 960-1026          |
| NaCl-KCl*   | 3.17 x 10\(^{-3}\) | 4.33 x 10\(^{-3}\) | 1.433 x 10\(^{-4}\) | 0.998 962-1026          |
|             | 3.16 x 10\(^{-3}\) | 8.73 x 10\(^{-3}\) | 2.065 x 10\(^{-4}\) | 0.999 953-1031          |
|             | 3.14 x 10\(^{-3}\) | 1.31 x 10\(^{-2}\) | 2.452 x 10\(^{-4}\) | 0.998 953-1021          |
|             | 3.13 x 10\(^{-3}\) | 1.53 x 10\(^{-2}\) | 2.532 x 10\(^{-4}\) | 0.998 945-1017          |
| KCl-CsCl*   | 3.57 x 10\(^{-3}\) | 2.79 x 10\(^{-3}\) | 0.425 x 10\(^{-4}\) | 0.969 953-1024          |
|             | 3.56 x 10\(^{-3}\) | 4.94 x 10\(^{-3}\) | 1.208 x 10\(^{-4}\) | 0.997 948-1024          |
|             | 3.55 x 10\(^{-3}\) | 7.19 x 10\(^{-3}\) | 1.409 x 10\(^{-4}\) | 0.996 948-1019          |
|             | 3.53 x 10\(^{-3}\) | 1.20 x 10\(^{-2}\) | 1.937 x 10\(^{-4}\) | 0.998 950-1019          |

*Equlmolar.*
Table 8. $E_{cell}$ versus temperature for the CrCl$_2$-CrCl$_3$ system

| Solvent | $X_{CrCl_2}$ | $X_{CrCl_3}$ | $E = AT + B$ (V) | C Coeff. Range (K) |
|---------|--------------|--------------|------------------|--------------------|
|         |              |              | $A \times 10^4$  | $B$                |
| NaCl    | $1.11 \times 10^{-3}$ | $1.72 \times 10^{-3}$ | 10.98 | -0.491 | 0.999 | 1098-1181 |
|         | $1.10 \times 10^{-3}$ | $3.51 \times 10^{-3}$ | 11.60 | -0.492 | 0.999 | 1093-1180 |
|         | $1.10 \times 10^{-3}$ | $5.13 \times 10^{-3}$ | 11.91 | -0.490 | 0.999 | 1093-1184 |
|         | $1.10 \times 10^{-3}$ | $6.95 \times 10^{-3}$ | 12.18 | -0.491 | 0.999 | 1091-1182 |
|         | $2.41 \times 10^{-3}$ | $6.94 \times 10^{-3}$ | 11.51 | -0.491 | 0.999 | 1091-1187 |
| KCl     | $6.75 \times 10^{-4}$ | $1.51 \times 10^{-3}$ | 6.286 | -0.034 | 0.999 | 1097-1184 |
|         | $6.72 \times 10^{-4}$ | $4.54 \times 10^{-3}$ | 7.374 | -0.036 | 0.999 | 1089-1179 |
|         | $6.71 \times 10^{-4}$ | $6.82 \times 10^{-3}$ | 7.731 | -0.036 | 0.999 | 1080-1181 |
|         | $6.69 \times 10^{-4}$ | $8.93 \times 10^{-3}$ | 7.958 | -0.036 | 0.999 | 1083-1180 |
|         | $1.67 \times 10^{-3}$ | $8.92 \times 10^{-3}$ | 7.169 | -0.035 | 0.999 | 1076-1175 |
| CsCl    | $2.21 \times 10^{-3}$ | $3.06 \times 10^{-3}$ | 3.618 | 0.178  | 0.999 | 996-1103  |
|         | $2.20 \times 10^{-3}$ | $6.11 \times 10^{-3}$ | 4.220 | 0.178  | 0.999 | 976-1103  |
|         | $2.19 \times 10^{-3}$ | $9.85 \times 10^{-3}$ | 4.619 | 0.180  | 0.999 | 983-1109  |
|         | $2.18 \times 10^{-3}$ | $1.49 \times 10^{-2}$ | 5.000 | 0.177  | 0.999 | 983-1115  |
|         | $3.74 \times 10^{-3}$ | $1.48 \times 10^{-2}$ | 4.531 | 0.178  | 0.999 | 979-1109  |
| NaCl-KCl* (t=1/2) | $9.68 \times 10^{-4}$ | $2.39 \times 10^{-3}$ | 10.83 | -0.484 | 0.999 | 986-1126  |
|         | $9.66 \times 10^{-4}$ | $4.03 \times 10^{-3}$ | 11.30 | -0.485 | 0.999 | 985-1126  |
|         | $9.65 \times 10^{-4}$ | $5.20 \times 10^{-3}$ | 11.54 | -0.485 | 0.999 | 985-1130  |
|         | $9.63 \times 10^{-4}$ | $7.80 \times 10^{-3}$ | 11.86 | -0.484 | 0.999 | 978-1130  |
|         | $2.40 \times 10^{-3}$ | $7.78 \times 10^{-3}$ | 11.08 | -0.485 | 0.999 | 978-1135  |
| NaCl-CsCl* (t=1/2) | $7.80 \times 10^{-4}$ | $3.48 \times 10^{-3}$ | 8.189 | -0.145 | 0.999 | 902-1098  |
|         | $7.76 \times 10^{-4}$ | $8.65 \times 10^{-3}$ | 8.978 | -0.145 | 0.999 | 917-1098  |
|         | $7.73 \times 10^{-4}$ | $1.18 \times 10^{-2}$ | 9.248 | -0.145 | 0.999 | 925-1131  |
|         | $7.70 \times 10^{-4}$ | $1.56 \times 10^{-2}$ | 9.501 | -0.146 | 0.999 | 923-1127  |
|         | $3.36 \times 10^{-3}$ | $1.55 \times 10^{-2}$ | 8.223 | -0.145 | 0.999 | 893-1127  |
| KCl-CsCl* (t=1/2) | $1.46 \times 10^{-3}$ | $4.22 \times 10^{-3}$ | 5.500 | 0.055  | 0.999 | 924-1118  |
|         | $1.45 \times 10^{-3}$ | $8.34 \times 10^{-3}$ | 6.082 | 0.056  | 0.999 | 905-1086  |
|         | $1.44 \times 10^{-3}$ | $1.34 \times 10^{-2}$ | 6.503 | 0.055  | 0.999 | 943-1086  |
|         | $1.43 \times 10^{-3}$ | $1.70 \times 10^{-2}$ | 6.704 | 0.058  | 0.999 | 943-1120  |
|         | $3.25 \times 10^{-3}$ | $1.70 \times 10^{-2}$ | 5.995 | 0.056  | 0.999 | 923-1120  |

*Equimolar.
Table 9. $E_{cell}$ versus temperature for the CuCl-CuCl$_2$ systems

| Solvent   | $X_{CuCl}$ ($10^{-4}$) | $X_{CuCl_2}$ ($10^{-3}$) | $E = AT + B$ (V) | A ($10^{-4}$) | B | C Coeff. Range (K) |
|-----------|-------------------------|---------------------------|------------------|---------------|---|--------------------|
| NaCl      | 8.57                    | 4.86                      | 1.642            | 0.633         | 0.999 | 1096-1183          |
|           | 8.56                    | 9.71                      | 2.260            | 0.631         | 0.999 | 1101-1174          |
|           | 8.56                    | 1.50                      | 2.625            | 0.632         | 0.999 | 1092-1177          |
|           | 8.55                    | 2.23                      | 2.977            | 0.631         | 0.999 | 1093-1179          |
| KCl       | 8.84                    | 9.40                      | -0.556           | 0.986         | -0.999 | 1079-1171          |
|           | 8.83                    | 1.73                      | -0.031           | 0.986         | -0.995 | 1071-1169          |
|           | 8.82                    | 2.82                      | 0.394            | 0.985         | 0.999  | 1069-1165          |
|           | 8.81                    | 3.68                      | 0.621            | 0.986         | 0.999  | 1068-1163          |
| CsCl      | 1.48                    | 1.72                      | -3.866           | 1.401         | -1.000 | 988-1170           |
|           | 1.48                    | 4.04                      | -3.121           | 1.400         | -0.999 | 985-1166           |
|           | 1.48                    | 6.36                      | -2.727           | 1.400         | -0.999 | 990-1162           |
|           | 1.47                    | 8.98                      | -2.435           | 1.401         | -0.998 | 987-1164           |
| NaCl-KCl* | 4.03                    | 3.46                      | 4.048            | 0.440         | 0.999  | 985-1171           |
| (t=1/2)   | 4.03                    | 7.16                      | 4.678            | 0.439         | 0.999  | 984-1164           |
|           | 4.02                    | 1.11                      | 5.053            | 0.440         | 0.999  | 998-1167           |
|           | 4.02                    | 1.51                      | 5.318            | 0.439         | 0.999  | 989-1172           |
| NaCl-CsCl*| 1.13                    | 1.25                      | -0.840           | 1.014         | -0.999 | 962-1099           |
| (t=1/2)   | 1.13                    | 2.60                      | -0.205           | 1.014         | -0.996 | 963-1105           |
|           | 1.12                    | 4.05                      | 0.186            | 1.013         | 0.992  | 963-1103           |
|           | 1.12                    | 5.49                      | 0.440            | 1.014         | 0.999  | 962-1103           |
| KCl-CsCl* | 1.06                    | 1.33                      | -2.096           | 1.197         | -0.999 | 953-1095           |
| (t=1/2)   | 1.06                    | 2.80                      | -1.459           | 1.197         | -0.999 | 948-1102           |
|           | 1.06                    | 4.25                      | -1.094           | 1.197         | -0.999 | 961-1099           |
|           | 1.06                    | 5.69                      | -0.832           | 1.196         | -0.999 | 961-1100           |

*Equimolar.*
|        | NaCl | KCl | CsCl | NaCl-KCl* | NaCl-CsCl* | KCl-CsCl* |
|--------|------|-----|------|-----------|------------|-----------|
| ThCl₄  | -2.265 | -2.516 | -2.653 | -2.433 | -2.391 | -2.357 | -2.499 | -2.357 | -2.385 |
| AlCl₃** | -1.851 | -1.872 | -1.910 | |          |          |          |          |          |          |
| CrCl₂  | -1.513 | -1.615 | -1.629 | -1.560 | -1.564 | -1.560 | -1.571 | -1.586 | -1.562 |
| FeCl₂  | | -1.464 | | -1.352 | |          |          |          |          |          |
| CrCl₃  | -1.145 | -1.275 | -1.316 | -1.206 | -1.210 | -1.224 | -1.231 | -1.271 | -1.196 |
| CoCl₂  | -1.062 | -1.199 | -1.295 | -1.125 | -1.131 | -1.183 | -1.179 | -1.229 | -1.247 |
| CuCl   | -1.041 | -1.198 | -1.270 | -1.107 | -1.120 | -1.161 | -1.156 | -1.225 | -1.234 |
| FeCl₃  | | -1.118 | | -1.027 | |          |          |          |          |
| NiCl₂  | -0.865 | -0.984 | -1.046 | -0.929 | -0.925 | -0.956 | -0.955 | -1.023 | -1.015 |
| AgCl** | -0.779 | -0.893 | -0.950 | |          |          |          |          |          |
| CuCl₂  | -0.618 | -0.724 | -0.763 | -0.658 | -0.671 | -0.697 | -0.691 | -0.731 | -0.744 |
| CrCl₂/CrCl₃ | -0.409 | -0.591 | -0.690 | -0.500 | -0.500 | -0.550 | -0.550 | -0.639 | -0.641 |
| FeCl₂/FeCl₃ | | -0.426 | | -0.379 | |          |          |          |          |
| CuCl/CuCl₂ | -0.194 | -0.250 | -0.256 | -0.207 | -0.222 | -0.233 | -0.225 | -0.237 | -0.253 |

*Equimolar
**Reference (1)
|                | NaCl | KCl | CsCl | NaCl-KCl* | NaCl-CsCl* | KCl-CsCl* |
|----------------|------|-----|------|-----------|------------|----------|
| ThCl₄          | -2.259 | -2.502 | -2.632 | -2.420 | -2.381 | -2.528 | -2.446 | -2.541 | -2.567 |
| AlCl₃*         | -1.827 | -1.849 | -1.884 |          | -1.845 | -1.856 | -1.868 | -1.866 |
| CrCl₂          | -1.505 | -1.600 | -1.610 | -1.549 | -1.553 | -1.544 | -1.558 | -1.568 | -1.605 |
| FeCl₂          |       | -1.450 |          | -1.338 |          | -1.393 |          |          |          |
| CrCl₃          | -1.129 | -1.258 | -1.299 | -1.191 | -1.194 | -1.206 | -1.214 | -1.253 | -1.279 |
| CoCl₂          | -1.049 | -1.185 | -1.281 | -1.115 | -1.117 | -1.170 | -1.165 | -1.213 | -1.233 |
| CuCl           | -1.028 | -1.184 | -1.256 | -1.095 | -1.106 | -1.147 | -1.142 | -1.210 | -1.220 |
| FeCl₃          |       | -1.106 |          | -1.015 |          | -1.063 |          |          |          |
| NiCl₂          | -0.853 | -0.972 | -1.034 | -0.917 | -0.913 | -0.946 | -0.944 | -1.012 | -1.003 |
| AgCl**         | -0.768 | -0.882 | -0.940 |          | -0.859 | -0.854 | -0.900 | -0.911 |          |
| CuCl₂          | -0.606 | -0.716 | -0.759 | -0.646 | -0.661 | -0.689 | -0.683 | -0.724 | -0.738 |
| CrCl₂/CrCl₃    | -0.377 | -0.572 | -0.678 | -0.474 | -0.475 | -0.525 | -0.528 | -0.623 | -0.625 |
| FeCl₂/FeCl₃    |       | -0.419 |          | -0.371 |          | -0.402 |          |          |          |
| CuCl/CuCl₂     | -0.184 | -0.247 | -0.262 | -0.197 | -0.216 | -0.231 | -0.223 | -0.239 | -0.255 |

*Equimolar

**Reference (1)
|          | $E_{+}^{*}$ (+ 0.003 V) | \( \Delta G \) | \( \Delta H \) | \( \Delta S \) |
|----------|-------------------------|----------------|----------------|----------------|
| $E^*$    |                        |                |                |                |
| KCl      | -2.487                  | -2.610         |                |                |
| CaCl     | -2.520                  | -2.570         |                |                |
| NaCl     | -2.466                  | -2.443         |                |                |
| TlCl$_{4}^{-}$ | -1.803                  | -1.858         |                |                |
| AlCl$_{3}^{-}$ | -1.825                  | -1.831         |                |                |
| CrCl$_{3}$ | -1.113                  | -1.228         |                |                |
| CrCl$_{2}$ | -1.057                  | -1.104         |                |                |
| CoCl$_{2}$ | -1.016                  | -1.095         |                |                |
| CuCl     | -1.016                  | -1.095         |                |                |
| FeCl$_{3}$ | -0.841                  | -1.022         |                |                |
| NiCl$_{2}$ | -0.757                  | -0.920         |                |                |
| AgCl     | -0.346                  | -0.449         |                |                |
| $\text{FeCl}_2/\text{FeCl}_3$ | -0.174                  | -0.244         |                |                |

\* Equimolar
\*\* Reference (1)
|        | NaCl | KCl | CsCl | NaCl-KCl* | NaCl-CsCl* | KCl-CsCl* |
|--------|------|-----|------|-----------|------------|-----------|
|        | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. |
| ThCl₄  | -0.065 | -4.732 | -7.323 | -3.196 | -2.399 | -5.137 | -3.694 | -5.509 | -6.028 |
| AlCl₃** | -2.014 | -2.319 | -3.025 | -2.375 | -2.520 | -2.722 | -2.672 |
| CrCl₂  | -1.360 | -2.318 | -2.453 | -1.803 | -1.839 | -1.812 | -1.907 | -2.053 | -2.386 |
| FeCl₂  | -3.093 | -3.093 | -2.047 | -2.047 | -2.569 |
| CrCl₃  | -0.230 | -2.047 | -2.637 | -1.097 | -1.139 | -1.342 | -1.434 | -2.000 | -2.342 |
| CoCl₂  | -1.831 | -4.103 | -4.033 | -2.471 | -2.967 | -2.988 | -2.932 | -3.418 | -4.068 |
| CuCl   | -0.562 | -1.300 | -1.647 | -0.878 | -0.931 | -1.132 | -1.105 | -1.432 | -1.474 |
| FeCl₃  | -5.041 | -5.041 | 3.769 | -4.434 |
| NiCl₂  | -1.660 | -2.794 | -3.361 | -2.299 | -2.227 | -2.529 | -2.511 | -3.150 | -3.078 |
| AgCl** | 0.204 | 0.529 | 0.595 | 0.218 | 0.196 | 0.410 | 0.462 |

*Equimolar
**Reference (1)
| Compound     | NaCl | KCl | CsCl | NaCl-KCl* | NaCl-CsCl* | KCl-CsCl* |
|--------------|------|-----|------|-----------|------------|----------|
|              | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| TeCl₄        | -0.247 | -4.688 | -7.025 | -3.117 | -2.468 | -5.171 | -3.636 | -5.385 | -5.857 |
| AlCl₃**      | -1.637 | -1.929 | -2.365 | -1.861 | -2.001 | -2.170 | -2.147 |
| CrCl₂        | -1.344 | -2.227 | -2.310 | -1.752 | -1.786 | -1.711 | -1.827 | -1.926 | -2.269 |
| FeCl₂        | -2.934 | -1.920 | -2.422 |
| CrCl₃        | -0.240 | -2.014 | -2.561 | -1.093 | -1.127 | -1.288 | -1.401 | -1.946 | -2.288 |
| CoCl₂        | -1.771 | -4.009 | -3.900 | -2.418 | -2.890 | -2.888 | -2.836 | -3.285 | -3.955 |
| CuCl         | -0.522 | -1.235 | -1.563 | -0.826 | -0.879 | -1.067 | -1.043 | -1.353 | -1.399 |
| FeCl₃        | -4.878 | -3.636 | -4.286 |
| NiCl₂        | -1.611 | -2.701 | -3.244 | -2.228 | -2.156 | -2.454 | -2.428 | -3.025 | -2.973 |
| AgCl**       | 0.224 | -0.298 | -0.562 | -0.191 | -0.169 | -0.381 | -0.430 |

*Equimolar
**Reference (1)
|        | NaCl | KCl  | CsCl | NaCl-KCl* | NaCl-OsCl* | KCl-OsCl* |
|--------|------|------|------|-----------|------------|-----------|
|        | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. |
| ThCl₄  | -0.427 | -4.629 | -6.733 | -3.158 | -2.528 | -5.202 | -3.580 | -5.260 | -5.681 |
| AlCl₃**| -1.438 | -1.726 | -2.115 | -1.633 | -1.777 | -1.934 | -1.921 |
| CrCl₂  | -1.329 | -2.128 | -2.151 | -1.699 | -1.729 | -1.604 | -1.740 | -1.790 | -2.140 |
| FeCl₂  | -2.775 |         | -1.793 | -1.793 |         | -2.274 |
| CrCl₃  | -0.249 | -1.973 | -2.504 | -1.090 | -1.111 | -1.238 | -1.377 | -1.886 | -2.239 |
| CoCl₂  | -1.711 | -3.917 | -3.743 | -2.359 | -2.814 | -2.771 | -2.727 | -3.131 | -3.830 |
| CuCl   | -0.481 | -1.173 | -1.493 | -0.781 | -0.827 | -1.011 | -0.987 | -1.287 | -1.333 |
| FeCl₃  | 4.716  |         | -3.504 | -4.138 |
| NiCl₂  | -1.562 | -2.651 | -3.132 | -2.158 | -2.107 | -2.383 | -2.347 | -2.913 | -2.892 |
| AgCl** | 0.242  | -0.269 | -0.531 | -0.165 | -0.145 | -0.354 | -0.400 |

* Equimolar

** Reference (1)
Table 12. Partial molar enthalpies of mixing

|        | NaCl | KCl | CsCl | NaCl-KCl* Expt. | Calc. | NaCl-CsCl* Expt. | Calc. | KCl-CsCl* Expt. | Calc. |
|--------|------|-----|------|-----------------|-------|------------------|-------|-----------------|-------|
| ThCl₄  | 184  | -50.7| -270 | -15.5           | 66.7  | 24.6             | -43.0 | -106            | -160  |
| AlCl₃**| -179 | -182| -227 |                 |       | -207             | -203  | -214            | -205  |
| CoCl₂  | -60.6| -95.3| -119 | -46.0           | -78.0 | -89.1            | -89.8 | -118            | -107  |
| CrCl₂  | -15.6| -92.7| -128 | -44.1           | -54.2 | -87.7            | -71.8 | -111            | -110  |
| FeCl₂  |      | -125 |       | -100            |       |                  |       | -115            |       |
| NiCl₂  | -49.4| -66.2| -89.6 | -55.6           | -57.8 | -55.3            | -69.5 | -87.8           | -77.9 |
| CuCl   | -40.0| -58.8| -67.8 | -42.5           | -49.4 | -53.3            | -53.9 | -63.8           | -63.3 |
| FeCl₃  |      | -55.4|       | -45.2           |       |                  |       | -50.3           |       |
| CrCl₃  | 9.5  | -34.2| -52.5 | -29.3           | -12.4 | -37.7            | -21.5 | -45.8           | -43.4 |
| AgCl** | -17.6| -27.7| -28.9 |                 |       | -23.7            | -23.3 | -27.9           | -28.3 |

* Equimolar
** Reference (1)
|        | NaCl | KCl | CsCl | NaCl-KCl* | NaCl-CsCl* | KCl-CsCl* |
|--------|------|-----|------|-----------|------------|-----------|
| ThCl₄  | 172  | 43.7| -110 | 46.8      | 121        | 6.7       |
| AlCl₃* | -130 | -127| -159 |           |            |           |
| CoCl₂  | -21.1| -28.9| -33.9| 4.5       | -25.7      | -44.3     |
| CrCl₂  | 11.6 | -41.6| -72.2| -6.5      | -47.0      | -64.1     |
| FeCl₂  |      | -56.4|      | -53.1     | -57.8      |           |
| NiCl₂  | -13.9| -8.2 | -19.1| -7.7      | -5.0       | -21.6     |
| CuCl   | -26.3| -29.8| -31.7| -22.8     | -28.1      | -32.2     |
| FeCl₃  |      |      | -9.3 | -10.5     | 9.8        |           |
| CrCl₃  | 13.2 | 7.4 | 1.4  | 18.3      | -9.3       | -4.3      |
| AgCl** | -20.3| -19.5| -15.5|           | -17.9      | -18.0     |

*Equimolar
**Reference (1)
Figure 1. Nernst plot for the ThCl₄ systems.