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Thermodynamic properties of the $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$ system

Peter J. Tumidajski and Christopher A. Pickles

Abstract: The thermodynamic behavior of NiCl_2 in $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$ ternary solutions was investigated using formation cells of the type, $(-)\text{Ni}/\text{NiCl}_2\text{-CoCl}_2\text{-KCl}/\text{C}, \text{Cl}_2(\text{gas}, 1 \text{ atm})/(+)$. The values of the NiCl_2 activity coefficients indicate a non-ideal system consonant with the formation of complex species. The NiCl_2 activity coefficients at 1000 K were fitted to the polynomial equation,

$$\ln \gamma = (-1225 + 363t - 3186t^2 + 8385t^3 - 6369t^4)Y^2 + (6776 - 1639t + 14803t^2 - 41112t^3 + 32405t^4)Y^3 + (-8665 + 1842t - 16964t^2 + 48873t^3 - 39440t^4)Y^4$$

where

$$Y = 1 - X_{\text{KCl}} \text{ and } t = \frac{X_{\text{CoCl}_2}}{X_{\text{CoCl}_2} + X_{\text{NiCl}_2}}$$

The experimental data were limited to the ranges $0 \leq t \leq 0.80$ and $0.10 \leq Y \leq 0.5$.

Key words: molten salt, thermodynamic properties, nickel chloride, non-ideal solution, complex species.

Résumé : Utilisant des cellules de formation du type $(-)\text{Ni}/\text{NiCl}_2\text{-CoCl}_2\text{-KCl}/\text{C}, \text{Cl}_2(\text{gaz}, 1 \text{ atm})/(+)$, on a étudié le comportement thermodynamique du NiCl_2 dans des solutions ternaires de $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$. Les valeurs des coefficients d'activité du NiCl_2 indiquent que le système n'est pas idéal, ce qui est en accord avec la formation d'espèces complexes. Les coefficients d'activité du NiCl_2 à 1000 K peuvent être ajustés à l'équation polynomiale

$$\ln \gamma = (-1225 + 363t - 3186t^2 + 8385t^3 - 6369t^4)Y^2 + (6776 - 1639t + 14803t^2 - 41112t^3 + 32405t^4)Y^3 + (-8665 + 1842t - 16964t^2 + 48873t^3 - 39440t^4)Y^4$$

dans laquelle $Y = 1 - X_{\text{KCl}}$ et

$$t = \frac{X_{\text{CoCl}_2}}{X_{\text{CoCl}_2} + X_{\text{NiCl}_2}}$$

Les données expérimentales sont limitées par $0 \leq t \leq 0.80$ et $0.10 \leq Y \leq 0.5$.

Mots clés : sels fondus, propriétés thermodynamiques, chlorure de nickel, solution non idéale, espèces complexes.

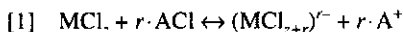
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Introduction

In previous publications from the authors, the thermodynamic properties of charge asymmetric molten salt solutions of metal chlorides with alkali halide solvents have been investigated by EMF measurements (1-7). The measurements provide valuable and practical information on: the feasibility of new pro-

cesses for the recovery of metals by fused salt electrolysis, and high-temperature batteries and energy storage devices.

The thermodynamic properties of the charge asymmetric molten salt solutions, such as the exothermic enthalpies and activities with pronounced negative deviations from ideality, indicate the formation of complex species. The concept of complex formation in molten salts has been described in detail elsewhere (1, 6). Briefly, a molten salt complex like $(\text{MCl}_{z+r})^-$ is a local configuration where a cation M^{z+} is surrounded by $(z+r)\text{Cl}^-$ anions.



Within the complex itself, the M-Cl bond distances and, accordingly, the corresponding bond energies, are different from the M-Cl bond distances in the noncomplexed pure molten MCl_z state. However, because of overall electrical neu-

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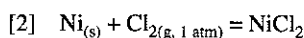
trality, the anions and cations occupy single anionic and cationic lattice sites within the quasi-lattice structure of the ionic solution. Thus, the $(\text{MCl}_{2+r})^r$ entities are not discrete ions on single anionic sites. A perturbation in the cation to anion bond distance within the continuum of the molten ionic phase is regarded as evidence of a complex species.

Previous work has focused on the thermodynamic state of the metal ions (and the complex) by control of the solvent composition with mixed halide solvents. The situation where the thermodynamic behavior of solutions in which two metal cations compete for the available chloride anionic ligands has not heretofore been reported. Accordingly, this paper reports on the thermodynamic behavior of the $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$ solutions.

Experimental

The NiCl_2 , CoCl_2 , and KCl were spectroscopic grade and anhydrous. They were received in sealed ampoules from APL Engineered Materials (Urbana, Illinois). They were packed under argon gas. The chemicals were used without further purification. Nickel electrodes were polished with fine emery paper, and then washed several times with a 10 volume percent HF solution, distilled water, and acetone. Weighing, handling, and the transfer of all chemicals was conducted inside a glove box filled with anhydrous argon gas where the oxygen and moisture were always kept below 5 ppm.

The cell design was similar to the chloride formation cells described elsewhere (3, 4, 7). The cell consisted of a nickel metal electrode immersed in the $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$ molten solution of known composition and a graphite chlorine electrode which also dipped into a molten solution of the same composition. The two cell compartments were separated by an asbestos fiber diaphragm fused into silica glass. The cell reaction is



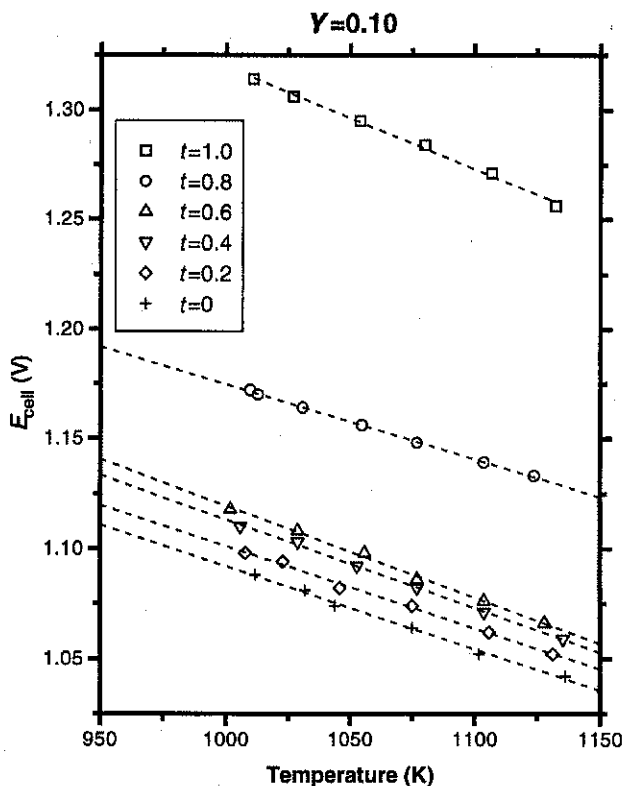
where, NiCl_2 represents the NiCl_2 in the $\text{NiCl}_2\text{-CoCl}_2\text{-KCl}$ solution. The corresponding Nernst equation is

$$[3] \quad E_{\text{cell}} = E_{\text{NiCl}_2}^0 - \frac{RT}{2F} \ln(\gamma_{\text{NiCl}_2} X_{\text{NiCl}_2})$$

where F is Faraday's constant of $96487 \text{ J V}^{-1} \text{ mol}^{-1}$, R is the universal gas constant given as $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$, and T is the absolute temperature in Kelvin. The standard state in all cases is pure liquid NiCl_2 at the temperature of the experiments. $E_{\text{NiCl}_2}^0$ is the standard potential for the formation of pure liquid NiCl_2 . Values for $E_{\text{NiCl}_2}^0$ were obtained from a previous investigation (8).

Initially, the cell was heated for 24 h in a furnace while anhydrous argon gas passed over the salts to remove any residual moisture. Then, EMFs were measured with a Hewlett Packard model 3468B multimeter. Reversibility was confirmed by temperature cycling and with polarization tests. For a complete description of the temperature cycling procedure and the polarization test refer to previous reports (1, 4). In all cases, the cell EMF returned to within $\pm 2 \text{ mV}$ of the original cell EMF. Cell EMFs were also corrected for the thermoelectric potential between the nickel and the graphite electrodes.

Fig. 1. Cell voltage versus temperature for the $Y = 0.10$ composition.



The values ranged from 1 to 5 mV over the range of experimental temperatures. The temperature upper limit was determined by subjective observation of vapor loss from the melt.

Results and discussion

Cell EMFs have been plotted against temperature in Figs. 1–3 for $Y = 0.1$, $Y = 0.25$, and $Y = 0.50$, respectively. The broken lines in Fig. 1–3 indicate the least-squares lines through the experimental data points. Table 1 summarizes the statistical treatment of the least-squares lines, which have been expressed in the form $E = A + BT$, where E is the cell EMF in volts and T is the temperature in Kelvin. Melt compositions have been expressed in terms of the following variables:

$$[4] \quad Y = 1 - X_{\text{KCl}}$$

$$[5] \quad t = \frac{X_{\text{CoCl}_2}}{X_{\text{CoCl}_2} + X_{\text{NiCl}_2}}$$

All measured cell potentials are reported with a positive sign as they represent spontaneous overall cell reactions. The correlation coefficients in Table 1 indicate that the relationship between EMF and temperature is linear. The estimate for the standard deviations of cell EMF for the regression of cell EMF on temperature is less than $\pm 2 \text{ mV}$ for all points. Further, the measured EMF values were stable and reproducible to within $\pm 1 \text{ mV}$.

Values for $\ln \gamma_{\text{NiCl}_2}$ at 1000 K were calculated with eq. [3]. The values are summarized in Table 2. It can be seen that γ_{NiCl_2} deviates markedly from ideal behavior in consonance

Table 2. Values of $\ln \gamma_{\text{NiCl}_2}$ for the $\text{NiCl}_2\text{--CoCl}_2\text{--KCl}$ ternary system at 1000 K.

t	Y	$\ln \gamma_{\text{NiCl}_2}$
0	0.10	-6.340
0	0.25	-4.535
0	0.50	-0.815
0.20	0.10	-6.331
0.20	0.25	-4.538
0.20	0.50	-0.785
0.40	0.10	-6.325
0.40	0.25	-4.809
0.40	0.50	-0.858
0.60	0.10	-6.066
0.60	0.25	-4.506
0.60	0.50	-0.860
0.80	0.10	-6.651
0.80	0.25	-4.545
0.80	0.50	-0.875

Therefore, eq. [6] can be used to calculate the NiCl_2 thermodynamic properties for any composition in the ternary $\text{NiCl}_2\text{--CoCl}_2\text{--KCl}$ solution at 1000 K. And, in conjunction with the Gibbs-Duhem equation, the integral thermodynamic properties at 1000 K can be calculated for the ternary solution.

Conclusions

1. The thermodynamic properties of NiCl_2 in the $\text{NiCl}_2\text{--}$

- $\text{CoCl}_2\text{--KCl}$ ternary solution indicate marked deviations from ideality in consonance with nickel complex formation.
2. The addition of CoCl_2 to the $\text{NiCl}_2\text{--KCl}$ solution has a minor influence on the nickel chloride activity.
3. Values of $\ln \gamma_{\text{NiCl}_2}$ were fitted to a polynomial equation at 1000 K. The equation can be used to calculate the thermodynamic properties of NiCl_2 for any composition in the ternary melt within the composition range $0 \leq t \leq 0.80$ and $0.10 \leq Y \leq 0.5$.

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