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3.53 ELECTROCHEMICAL PROCESSING OF MATERIALS

February 6, 2001 PROBLEM SET 1 due February 15

The e.m.f. of the $MnCl_2$ formation cell has been measured. For pure liquid $MnCl_2$ the standard potentials were

T (°C)	E° (mV)
671	1867
708	1852
743	1837
779	1822
813	1803

Mn (s) | $MnCl_2$ (l) | C, Cl_2 (g, 1 atm.)

For a solution of 1 mole % $MnCl_2$, 24.75 mole % NaCl, 74.25 mole % CsCl, the potentials were

T (C°)	E (mV)
754	2332
713	2342
663	2356
689	2349
646	2360

Mn (s) | $MnCl_2$ - NaCl - CsCl (l) | C, Cl_2 (g, 1 atm.)

(a) Plot E° and E versus T and draw the least-squares lines through the points.

(b) Calculate the temperature dependence of $\Delta G°$ in the temperature range 700-800°C for the reaction Mn (s) + Cl_2 (g, 1 atm.) = $MnCl_2$ (l). What are the values of $\Delta H°$ and $\Delta S°$?

(c) For the 1% $MnCl_2$ solution in 3:1 CsCl-NaCl determine the partial molar free energy of mixing $MnCl_2$, ΔG_{MnCl_2}, as a function of temperature. What are the values of ΔH_{MnCl_2} and ΔS_{MnCl_2} in this temperature range?

(d)(i) Calculate a_{MnCl_2} and γ_{MnCl_2} at 650°C and 750°C. Choose pure liquid $MnCl_2$ as both standard state and reference state for these calculations.

(ii) Does this solution show positive or negative deviation from ideality?

(iii) Calculate ΔS_{MnCl_2} for an ideal "molecular" solution and compare this value with ΔS_{MnCl_2} determined in part (c) of this question. Using the value of $\Delta S_{MnCl_2}^{excess}$ comment on the structure of this melt. Keep in mind the value of ΔH_{MnCl_2}.

(e) Plot a theoretical E vs $\log_{10} P_{Cl_2}$ curve at 700°C when the electrolyte is pure $MnCl_2$ and chlorine pressure varies from 1 atm. to 10^{-3} atm.

(f) If the pure Mn electrode is exchanged for a Mn alloy, does this change the e.m.f. measured in this cell? If so, how? If not, why is this the case?