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3.53 ELECTROCHEMICAL PROCESSING OF MATERIALS

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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

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

$\text{Mn (s)} \mid \text{MnCl}_2 \text{ (l)} \mid \text{C, Cl}_2 \text{ (g, 1 atm.)}$

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

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

$\text{Mn (s)} \mid \text{MnCl}_2 - \text{NaCl} - \text{CsCl (l)} \mid \text{C, Cl}_2 \text{ (g, 1 atm.)}$

- (a) Plot E° and E versus T and draw the least-squares lines through the points.
- (b) Calculate the temperature dependence of ΔG° in the temperature range 700-800°C for the reaction $\text{Mn (s)} + \text{Cl}_2 \text{ (g, 1 atm.)} = \text{MnCl}_2 \text{ (l)}$. What are the values of ΔH° and ΔS° ?
- (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 $\Delta S_{\text{MnCl}_2}^{\text{excess}}$ comment on the structure of this melt. Keep in mind the value of ΔH_{MnCl_2} .
- (e) Plot a theoretical E vs $\log_{10} P_{\text{Cl}_2}$ 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?