3.020 – Thermodynamics of Materials Recitation 9

Problem 1

Consider a closed system with a block of pure Cr in a crucible and a liquid solution of Fe-Cr containing 1%Cr in another crucible. The oxygen partial pressure (P_{O_2}) in the closed system is fixed at 10^{-10} atm. You try to establish a process where you want to oxidize the solid Cr block, without oxidizing the Cr that is in solution with Fe. What is the temperature range to enable this process?

a) Let us first focus on the block of pure Cr. We know that solid Cr melts at 2171 K ($T_m(Cr)$) and that Cr_2O_3 melts at 2708K ($T_m(Cr_2O_3)$). We will not include molten Cr_2O_3 in our analysis. Furthermore, we know the enthalpy of formation ($\Delta H_f^o(Cr_2O_3)$) and the Gibbs free energy of formation ($\Delta G_f^o(Cr_2O_3)$) at 1900 K for the formation of 1 mole of Cr_2O_3. These values are respectively -270600 and -154100 cal. We also know the enthalpy of fusion ($\Delta H_{FUS}^o(Cr)$) for 1 mole of Cr which is 5000 cal. at the melting temperature $T_m(Cr)$.

   I. Write down the two necessary reactions that we need to consider for solving the problem of the pure Cr. *(Hint: there are multiple possibilities, but for sake of discussing the solutions in group, take one reaction as the oxidation reaction, and the other one as the phase transformation.)*
   II. Find an expression for the change in Gibbs free energy as a function of the temperature for both the reactions described in (a.I.).
   III. Depending on the temperature window, the total reaction that takes place is a specific linear combination of both reactions. Describe the two temperature windows together with their linear combinations and calculate the total changes in Gibbs free energy as a function of temperature for both windows.

b) Let us now focus on the liquid solution of Fe-Cr containing 1%Cr. We know that solid Fe melts at 1811 K ($T_m(Fe)$). We will only analyze the solution above this temperature (e.g. both Cr and Fe are hence liquid). Furthermore, we know that the solution behaves ideal and that the activity of Cr in the solution can be described by Henry's law with $\gamma_{Cr}^{\infty} = 1$.

   I. Write down the additional reaction that we need to consider for solving the problem of the Cr solution. *(Hint: liquid Cr going into a liquid solution.)*
   II. Find an expression for the change in Gibbs free energy as a function of the temperature for this reaction.
   III. Similarly, the total reaction that takes place is a specific linear combination of all three reactions. Write down this linear combination and specify the appropriate temperature window, and calculate the total change in Gibbs free energy as a function of temperature.

c) Use the given equilibrium oxygen partial pressure (P_{O_2}) (that applies to both the Cr block and the Fe-Cr solution) to calculate the Gibbs free energy change for the oxidation reaction in function of the temperature.

d) Make the Ellingham diagram based on the results found in (a)-(b) and (c) and calculate the temperature window where it is possible to oxidize the solid Cr block, without oxidizing the Cr that is in solution with Fe.

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