

1. (20pts) Answer the following questions related to phase diagram in a one component system.

(a) (5pts) Schematically represent the variation of the molar Gibbs free energy $\Delta G_{(s \rightarrow l)}$ of melting of water with temperature at constant pressure of 1 atm. Explain the reason for your representation briefly.

(b) (10pts) Derive the Clausius-Clapeyron equation, $d \ln P = \frac{\Delta H}{RT^2} dT$

and show that this equation can explain an exponential increase in the saturation vapor pressure exerted by a condensed phase with increasing temperature.

(c) (5pts) The vapor pressure of zinc have been written as

$$\ln p \text{ (atm)} = -15,780/T - 0.755 \ln T + 19.25$$

and $\ln p \text{ (atm)} = -15,250/T - 1.255 \ln T + 21.79$

Which of the two equations is for solid zinc?

2. (25pts) Answer the following questions related to the behavior of solutions

(a) (5pts) Prove that the solvent A obeys Raoult's law in the composition range over which the solute B obeys Henry's law.

(b) (10pts) Show that the heat, Gibbs free energy, and entropy of mixing of two ideal gases, respectively, are given as

$$\Delta \bar{H}_i^{M, id} = 0$$

$$\Delta G^{M, id} = RT(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta S^{M, id} = -R(X_A \ln X_A + X_B \ln X_B)$$

(c) (5pts) Prove that the entropy of mixing of an ideal solution is a measure of the increase in the number of spatial configurations.

(d) (5pts) A hypothetical solution known as "regular solution" has been suggested in order to explain the behavior of a nonideal solution. Explain the $\Delta \bar{H}_i^M$ and $\Delta \bar{S}_i^M$ of the regular solution in comparison with those of an ideal solution.

3. (25pts) Answer the following equations.

(a) (10pts) The molar Gibbs free energy of formation of binary solution $A-B$ is given by

$$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B) \quad \text{and for a regular solution,}$$

$$\Delta G^M - \Delta G^{M, id} = G^{XS} = RT\alpha X_A X_B = \Omega X_A X_B = \Delta H^M$$

Show that immiscibility becomes imminent in a regular solution at the critical value of $\alpha = 2$. Also show that the critical temperature, below which immiscibility occurs in a regular system, is given by $T_{cr} = \Omega/2R$.

(b) (10pts) For the A - B binary phase diagram showing a complete solid solution (i.e., eye lens shape phase diagram), schematically draw ΔG^M versus composition (X_B) for both liquid and solid solutions, and also a_B versus X_B at the temperature T ($T_{m(A)} < T < T_{m(B)}$). On the ΔG^M versus X_B plot, represent the molar Gibbs free energy of melting of pure A and B at T . Explain your schematic drawings briefly.

(c) (5pts) Draw schematically the ΔG^M versus composition (X_B) for both liquid and solid solutions at the temperature T ($T_{m(A)} > T > T_{m(B)}$) for a binary eutectic system exhibiting complete liquid miscibility and virtually complete solid immiscibility. Also draw a_B versus X_B at the same temperature. Explain your schematic drawings briefly.

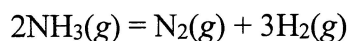
4. (20pts) Answer the questions related to reactions involving gases.

(a) (10pts) Derive the *van't Hoff equation*
$$\frac{\partial \ln K_p}{\partial \left(\frac{1}{T}\right)} = -\frac{\Delta H^\circ}{R}$$

by using the Gibbs-Helmholtz equation
$$\left(\frac{\partial(\Delta G^\circ / T)}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2}$$

Also, explain the effects of temperature on K_p for endothermic (positive ΔH°) and exothermic (negative ΔH°) reactions, respectively.

(b) (10pts) Consider the cracking of gaseous ammonia according to the reaction



$$\text{where } \Delta G^\circ = 87,030 - 25.8T \ln T - 31.7T \text{ (J)}$$

under the conditions of a constant total pressure of 1 atm and at 400°C. Calculate the equilibrium partial pressures of each gas, respectively.

5. (25pts) Answer the following questions on the basis of their Ellingham diagrams shown in Fig. 12.13.

(a) (10pts) Calculate the temperature at which pure Ag₂O decomposes to Ag metal and O₂ gas when heated in (i) pure oxygen at 1 atm pressure, and (ii) in air.

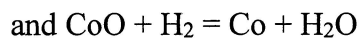
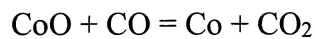
$$\text{For } 2\text{Ag} + \text{O}_2/2 = \text{Ag}_2\text{O}, \Delta G^\circ = -30,540 + 66.11T \text{ (J) at the range of 298-463K}$$

(b) (5pts) Compare the relative efficiencies of H₂ and CO as reducing agents for metal oxides.

$$\text{For } \text{CO} + \text{O}_2/2 = \text{CO}_2, \Delta G^\circ = -282,400 + 86.81 T \text{ (J)}$$

$$\text{For } \text{H}_2 + \text{O}_2/2 = \text{H}_2\text{O}, \Delta G^\circ = -247,500 + 55.85 T \text{ (J)}$$

(c) (10pts) Consider the reduction of CoO by each of H₂ and CO by the following reactions;



$$\text{where, } \Delta G^\circ = +233,900 - 71.85T \text{ (J) for } \text{CoO(s)} = \text{Co(s)} + \text{O}_2\text{(g)}/2.$$

Calculate how much (in moles) CoO can be reduced with 1 mole of H₂ at 1673 K and at 873 K, respectively. Also calculate how much (in moles) CoO can be reduced with 1 mole of CO at 1673 K and at 873 K, respectively.

6. (25pts) Answer the following questions.

(a) (10pts) For the general reaction, $aA + bB = cC + dD$, containing components in condensed solution and occurring at the temperature T and the pressure P , prove that the criterion for reaction equilibrium is given by $Q^{\text{eq}} = K$.

Where $Q^{\text{eq}} = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$ is called the activity quotient, and K is the equilibrium constant.

(b) (5pts) Calculate the activity of FeO in an FeO-Al₂O₃-SiO₂ melt below which the FeO cannot be reduced to pure liquid iron by a CO-CO₂ mixture of $\frac{P_{\text{CO}}}{P_{\text{CO}_2}} = 10^5$ at 1600°C.

$$\text{Where, } \Delta G^\circ = -232,700 + 45.13 T \text{ (J) for the reaction } \text{Fe(l)} + \text{O}_2\text{(g)}/2 = \text{FeO(l)}$$

$$\Delta G^\circ = -394,100 - 0.84T \text{ (J) for the reaction } \text{C(gr)} + \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$$

$$\Delta G^\circ = -223,400 - 175.3T \text{ (J) for the reaction } 2\text{C(gr)} + \text{O}_2\text{(g)} = 2\text{CO(g)}$$

(c) (10pts) Prove that the Gibbs phase rule is given by $F = C - P + 2$, where F is degrees of freedom, $C = \#$ of components, and $P = \#$ of phases.

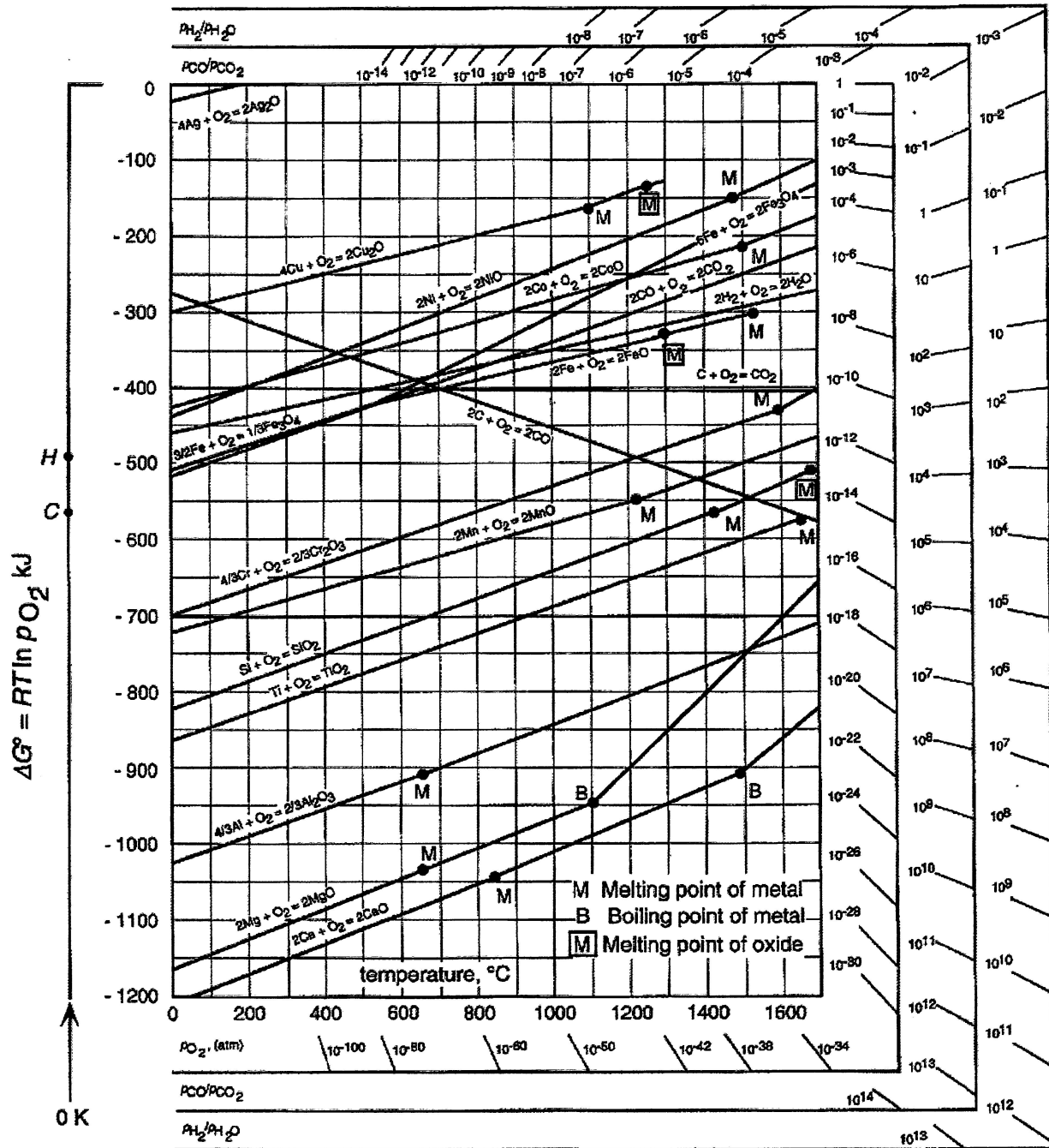


Figure 12.13 The Ellingham diagram for selected oxides.