

國立高雄大學 104 學年度研究所碩士班招生考試試題

科目：材料熱力學  
考試時間：100 分鐘

系所：化學工程及材料工程學系  
(乙組)  
本科原始成績：100 分

是否使用計算機：是

1. For  $\text{Zn} + \text{CuSO}_4 = \text{Cu} + \text{ZnSO}_4$ ,  $\Delta G^\circ = -208,800 - 13.9T$  J. What are the non-PV works done and the heat flow in the follow conditions?
  - (a) Placing pure solid zinc into saturated copper sulfate solution at  $25^\circ\text{C}$ . (5 points)
  - (b) Reversible process in a Daniell cell. (5 points)
2. How to know the activity of a metal oxide (e.g. PbO) which is dissolved in an inert oxide solvent (e.g.  $\text{SiO}_2$ ). Please design two kinds of electrochemical experiments to calculate the activity of PbO as a function of its molar fraction in liquid PbO- $\text{SiO}_2$ . (16 points)
3. When an Fe-P liquid solution is equilibrated at 1900K with solid CaO, solid  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  and a gas phase containing  $p_{\text{O}_2} = 10^{-10}$  atm, the activity of P in the iron, with respect to the 1 wt% in Fe standard state, is 20. Calculate  $\Delta G^\circ_{1900\text{K}}$  for the reaction  $\text{P}_{2(\text{g})} + 5/2 \text{O}_{2(\text{g})} = \text{P}_2\text{O}_{5(\text{g})}$ . (Given that  $\Delta G^\circ_{1900\text{K}} = -564,600\text{J}$  for  $3\text{CaO}_{(\text{s})} + \text{P}_2\text{O}_{5(\text{g})} = 3\text{CaO}\cdot\text{P}_2\text{O}_{5(\text{s})}$ , and  $\Delta G^\circ = -122,200 - 19.22T$  J for  $1/2 \text{P}_{2(\text{g})} = \text{P}_{(1\text{wt}\% \text{ in Fe})}$ ) (10 points)

4. The elements A and B, which are both solid at 1273K, from two stoichiometric compounds  $\text{A}_2\text{B}$  and  $\text{AB}_2$ , which are also both solid at 1273K. The system A-B does not contain any solid solutions. A has an immeasurably small vapor pressure at 1273K, and, for the change of state,  $\text{B}(\text{s})=\text{B}(\text{v})$

$$\Delta G^\circ = 187220 - 108.8T \text{ J}$$

the vapor pressure exerted by an equilibrated  $\text{AB}_2$ - $\text{A}_2\text{B}$  mixture is given by

$$\log p(\text{atm}) = -\frac{11242}{T} + 6.53$$

and the vapor pressure exerted by an equilibrated A- $\text{A}_2\text{B}$  mixture is given by

$$\log p(\text{atm}) = -\frac{12603}{T} + 6.9$$

from these data,

- (a) Plot the variation, with composition, of the vapor pressure of component B. (3 points)
- (b) Calculate the standard Gibbs free energies of formation of  $\text{A}_2\text{B}$  and  $\text{AB}_2$ . (4 points)
- (c) Calculate the standard Gibbs free energies of formation of  $\text{A}_2\text{B}$  and  $\text{AB}_2$ . (4 points)
- (d) Plot the integral Gibbs free energies, with composition, of component B. (3 points)

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5. For a reaction equilibrium in a gas mixture, please discuss the effects of pressure and temperature, separately, on the equilibrium constant (in terms of the pressures and the mole fractions, individually). (10 points)
6. At 700K, the activity of Ga in a liquid Ga-Cd solution of composition  $X_{\text{Ga}} = 0.5$  has the value 0.79. on the assumption that liquid solution of Ga and Cd exhibit regular solution behavior, estimate the energy of the Ga-Cd bond in the solution. The molar enthalpies of evaporation of liquid Ga and liquid Cd at their melting temperatures are, respectively, 270,000 and 100,000J. (At their melting temperature, the coordination numbers of liquid Cd and liquid Ga are, respectively, 8 and 11.) (10 points)
7. Using the virial equation ( $PV = RT(1 + 6.4 \times 10^{-4}P)$ ) of state for hydrogen at 298K, calculate
  - (a) the fugacity of hydrogen at 200 atm and 298K, (3 points)
  - (b) the pressure at which the fugacity is twice the pressure, (3 points)
  - (c) the change in the Gibbs free energy caused by a compression of one mole of hydrogen at 298K from 1 atm to 200 atm. (4 points)
8. Please set up the equilibrium between the following substances. in aqueous solution.
  - (a) Al and  $\text{AlO}_2^-$  (4 points)
  - (b) Al and  $\text{Al}_2\text{O}_3$  (4 points)
  - (c)  $\text{Al}^{3+}$  and  $\text{AlO}_2^-$  (2 points)
9. Please explain the following terms:
  - (a) the law of corresponding states (4 points)
  - (b) partial molar quantities (4 points)
  - (c) compressibility factor (2 points)

$$\ln 159 = 5.069, \quad \ln 2 = 0.693, \quad \ln 3 = 1.099, \quad \ln 5 = 1.609, \quad \ln 7 = 1.946, \quad \ln 10 = 2.303$$
$$e^{0.128} = 1.137, \quad e^{-8.56} = 1.9 \times 10^{-4}, \quad e^{-20.89} = 8.4 \times 10^{-10}, \quad e^{-11.94} = 6.47 \times 10^{-6}$$