

國立高雄大學 101 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. Solid A-B alloys are regular in their thermodynamic behavior. The molar enthalpies of formation of some specific A-B alloys,  $\Delta H^M$ , at 500°C are listed as a function of composition of the component A,  $X_A$ , as follows. (10%)

$X_A$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\Delta H^M$ , (J/mole)	-355	-655	-910	-1120	-1230	-1240	-1130	-860	-460

- a. Calculate the integral molar Gibbs free energy change due to the mixing of components A and B at  $X_A = 0.3$ .
- b. What is the activity of component A at  $X_A = 0.3$ ?
2. Tin obeys Henry's law in dilute liquid solutions of Sn and Cd and the Henrian activity coefficient of Sn,  $\gamma_{Sn}^0$ , varies with temperature as

$$\ln \gamma_{Sn}^0 = -840/T + 1.58$$

Calculate the change in temperature when 1 mole of liquid Sn and 99 moles of liquid Cd are mixed in an adiabatic enclosure. The molar constant pressure heat capacity of the alloy formed is 29.5 J/K. (10%)

3. A real gas is described by Van der Waals equation  $\left[ p + \frac{a}{v^2} \right] (v-b) = RT$ , where  $p$  is pressure,  $v$  is molar volume,  $T$  is temperature,  $R$  is the gas constant, and both  $a$  and  $b$  are positive constants. Does the volume affect the internal free energy and the heat capacity at a fixed temperature? Please debate your answers in quantitative derivations. (20%)
4. CaO and MgO form a simple eutectic system with limited ranges of solid solubility. The eutectic temperature is 2643 K. Assuming that the solutes in the two solid solutions obey Henry's law with  $\gamma_{CaO}^0$  in MgO = 12.88 and  $\gamma_{MgO}^0$  in CaO = 6.23 at 2573 K, calculate the solubility of CaO in MgO and the solubility of MgO in CaO at 2573 K. (10%)

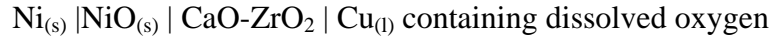
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5. By measuring the EMF's of cells of the type



It has been established that  $e_o^o$  in liquid copper at 1363K is -0.16 and that the standard Gibbs free energy change for



If the EMF of such a cell is 0.222 volts at 1363K, calculate,

- The activity of oxygen in the liquid copper cathode with respect to a standard state of oxygen gas at 1 atm pressure. (5%)
- The activity of  $\text{Cu}_2\text{O}$  in the cathode metal with respect to copper-saturated pure solid  $\text{Cu}_2\text{O}$ . (5%)
- The weight percentage of oxygen dissolved in the copper cathode. (5%)
- The maximum solubility of oxygen in liquid copper at 1363 K. (5%)

6. Consider the metal Au in the initial state  $T = 298\text{K}$ ,  $P = 1 \text{ atm}$ .

- What pressure (in atm) would you have to apply to Au at 298K in order to decrease its molar entropy by 1 J/K? (5%)
- By how much (in K) would you have to change the temperature of Au at constant pressure in order to decrease its molar entropy a J/K? (5%)

Given data:

$$\text{heat capacity } C_{p,Au(s)} = 23.7 + 5.19 \times 10^{-3} T \text{ J/K.mole}$$

$$\text{thermal expansion coefficient} = 4.26 \times 10^{-5} (\text{K})^{-1}, \text{ isothermal compressibility} = 5 \times 10^{-5} (\text{atm})^{-1}$$

$$\text{density} = 19.3 \text{ g/cm}^3, \text{ molecular weight: } 197 \text{ g/mole}, \text{ entropy at } 298\text{K} = 47.36 \text{ J/K.mole}$$

$$\text{enthalpy of melting } \Delta H_m = 12800 \text{ J/mole}$$

7. Please explain the following terms:

- Chemical potential (4%),
- Fugacity (4%)
- Spinodal curve (6%),
- Intensive properties (3%),
- Configuration entropy (3%)

$$\ln 298 = 5.697,$$

$$\ln 3 = 1.099,$$

$$\ln 7 = 1.946,$$

$$\ln 10 = 2.303$$

$$e^{-0.397} = 0.672,$$

$$e^{-7.56} = 5.2 \times 10^{-4},$$

$$e^{-20.89} = 8.4 \times 10^{-10},$$

$$e^{-11.94} = 6.47 \times 10^{-6}$$