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, ΔH^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
ΔH^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, γ_{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 γ_{CaO}^0 in MgO = 12.88 and γ_{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

$Ni_{(s)}$ |$NiO_{(s)}$ | $CaO\text{-}ZrO_2$ | $Cu_{(l)}$ containing dissolved oxygen

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

$\frac{1}{2}O_{2(g)} = [O]_{1\ wt\%\ in\ Cu}$, $\Delta G^o = -74{,}105 + 10.76T$ J

$2Ni + O_2 = 2NiO$, $\Delta G^o = -471{,}200 + 172T$ J

$2Cu_{(l)} + \frac{1}{2}O_2 = Cu_2O_{(s)}$, $\Delta G^o = -188{,}300 + 88.48T$ J

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

a. The activity of oxygen in the liquid copper cathode with respect to a standard state of oxygen gas at 1 atm pressure. (5%)
b. The activity of Cu_2O in the cathode metal with respect to copper-saturated pure solid Cu_2O. (5%)
c. The weight percentage of oxygen dissolved in the copper cathode. (5%)
d. The maximum solubility of oxygen in liquid copper at 1363 K. (5%)

6. Consider the metal Au in the initial state T = 298K, P = 1 atm.

a. 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%)
b. 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:
heat capacity $C_{p,Au(s)} = 23.7 + 5.19\times10^{-3}T$ J/K.mole
thermal expansion coefficient = 4.26×10^{-5} $(K)^{-1}$, isothermal compressibility = 5×10^{-5} $(atm)^{-1}$
density = 19.3 g/cm^{-3}, molecular weight: 197 g/mole, entropy at 298K = 47.36 J/K.mole
enthalpy of melting ΔH_m = 12800 J/mole

7. Please explain the following terms:

a. Chemical potential (4%), b. Fugacity (4%)
c. Spinodal curve (6%), d. Intensive properties (3%), e. Configuration entropy (3%)

ln298 = 5.697, ln3 = 1.099, ln7 = 1.946, ln10 = 2.303
$e^{-0.397} = 0.672$, $e^{-7.56} = 5.2\times10^{-4}$, $e^{-20.89} = 8.4\times10^{-10}$, $e^{-11.94} = 6.47\times10^{-6}$

背面尚有試題