國立台灣科技大學九十九學年度碩士班招生試題

系所組別： 材料科學與工程學系碩士班丙組

科　　目： 熱力學

總分 100 分，共七大題。選擇題務必於答案卷內依序作答，在試題內作答者不予計分。

一、選擇題：30%- Choose the best answers in 12 questions. 2.5 points each, without any penalty on the wrong guess.單選題,無倒扣 (30%)

1. For a Cd(1)/Sn(2) mixture, Henrian (infinite- dilution) activity coefficient of Sn= $r_2^0 = r_2\ (x_2 \to 0)$ = exp(- 840/T + 1.58). The vapor pressure of Sn at 700℃= 1.2×10^{-10} atm. The Henry constant of Sn in Cd in atm=

   (a) exp(-840/700 + 1.58)　　(b) exp(-840/973 + 1.58)
   (c) 1.2×10^{-10} exp(-840/973 + 1.58)　　(d) 1.2×10^{-10} exp(-840/700 + 1.58)

2. Following the previous problem, but considering the finite-concentration activity activity coefficient. At 700℃ and the mole fraction of Sn= $x_2 = 0.2$, the activity coefficient of Sn=

   (a) exp[(-840/700 + 1.58) 0.2]　　(b) exp[(-840/973 + 1.58) 0.04]
   (c) exp[(-840/973 + 1.58) 0.8]　　(d) exp[(-840/973 + 1.58) 0.64]

3. Following the previous problem. The fugacity of Sn (atm) equals to activity coefficient timesY, where Y=
   (a) 1.2×10^{-10}　(b) $1.2\times10^{-10}(0.2)$　(c) $1.2\times10^{-10}(0.8)$　(d) $1.2\times10^{-10}(0.04)$

4. Following problem 3. The molar enthalpy of mixing of this solution at 700℃= ΔH^M (J/mol)= $b(8.314)x_1x_2$, where b =

   (a) exp(-840/973 + 1.58)　　(b) exp[-840 + 1.58(973)]
   (c) -840 + 1.58(700)　　(d) -840 + 1.58(973)

5. Given Clausius equation: dP/dT= $\Delta S/\Delta V$ = (entropy change)/ (molar volume change). The solid-liquid equilibrium (SLE) line in phase diagram (P vs. T) can be mathematically represented by P=
   (a) a lnT + c　(b) exp(a/T + c)　(c) a T + c　(d) a/ T + c (a, c = constant)

6. For SLE line in problem 5, the degree of freedom is (a) 2　(b) 1　(c) 0　(d) 3

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7. A battery is used to convert the energy. Given the first law of thermodynamics: dU= dQ- dW, thermodynamic relations dH= TdS+VdP, and dG= -SdT+VdP. At constant temperature and pressure, the maximum work done by the battery= (a) ΔG ，(b) $-\Delta G$ ，(c) ΔH ，(d) $-\Delta H$

8. Given the first law: dU= dQ- dW, and W_{rev} = reversible work. For any process, W (a) $\leq W_{rev}$ ，(b) $\geq W_{rev}$ ，(c) $> -W_{rev}$ ，(d) $< -W_{rev}$

9. It is known that, at constant temperature, ΔU (state 1 to 2)= a(1/V1- 1/V2) for a van der Waals gas, or $\Delta U(\text{state 1 to 2}) = \int_1^2 (T\alpha/K - P)dV$ for a liquid or solid. Which of the followings shown above is isothermal compressibility? (a) α (b) a (c)K (d)P

10. Given first law: $\Delta U = Q - W$, and second law : $TdS \geq dQ$. Also given relation dA= -PdV- SdT. For an irreversible process at constant temperature，the change of Helmholtz free energy of system (a) $< W$ ，(b) $\geq W$ ，(c)= $-W$ ，(d) $< -W$

11. The partial molar entropy and partial molar volume of a species in a mixture can be determined from X of the species as a function of temperature and pressure. X is (a)partial molar enthalpy, (b)partial molar internal energy, (c) molar excess Gibbs free energy, (d)chemical potential

12. The activity of solvent component in a non-ideal polymer solution can be determined by measuring (a)heat capacity of solution, (b)molar volume of solution, (c)osmotic pressure of solution, (d)absolute entropy of solution

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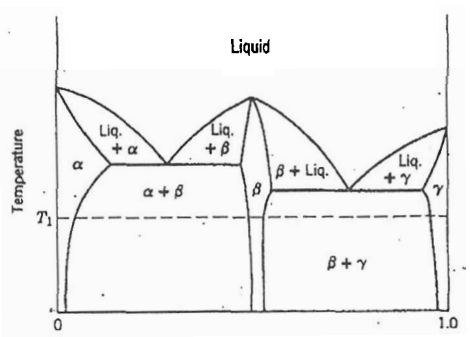
二、Metals A and B can form a complete solid solution. Metal A has a higher melting temperature. Derive the solidus ($X_{A(s)}$) and liquidus ($X_{A(L)}$) at different temperatures in terms of $\Delta G^{o}_{m(A)}$ and $\Delta G^{o}_{m(B)}$. (10%)

三、 Cu and Au form complete range of solid solution at 410~889°C, and at 600°C, the excess molar Gibbs free energy of formation of the solid solutions is given by G^{XS}= excess free energy (J)= -28,280 $X_{Cu} \times X_{Au}$. Calculate the activities of Cu and Au exerted by the solid solution at X_{Cu} = 0.4 at 600°C. (10%)

ln M	M	ln M	M
-1	0.36788	-4	0.018316
-1.2	0.30119	-4.2	0.014996
-1.4	0.2466	-4.4	0.012277
-1.6	0.2019	-4.6	0.010052
-1.8	0.1653	-4.8	0.00823
-2	0.13534	-5	0.006738
-2.2	0.1108	-5.2	0.005517
-2.4	0.090718	-5.4	0.004517
-2.6	0.074274	-5.6	0.003698
-2.8	0.06081	-5.8	0.003028
-3	0.049787	-6	0.002479
-3.2	0.040762	-6.2	0.002029
-3.4	0.033373	-6.4	0.001662
-3.6	0.027324	-6.6	0.00136
-3.8	0.022371	-6.8	0.001114
-4	0.018316	-7	0.000912

四、The known A-B phase diagram is plotted in below. At the temperature of T_1, show the ΔG_m (mixing free energy)-X_B and a_B (activity of B)-X_B plots. (10%)



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五、Calculate the vapor pressure of Mg exerted at 1400oC by the system in which reaction : 4 MgO (s) + Si (s) = 2 Mg (g) + MgSiO4 (s) is established. (10%)

You can find the lnX-X table from the Question 1.

Known: $2MgO + SiO2 = Mg2SiO4$ $\Delta Go1673 = -59{,}989$ J

$2MgO = 2\,Mg\,(g) + O2$ $\Delta Go1673 = 776{,}616$ J

$Si + O2 = SiO2$ $\Delta Go1673 = -613{,}153$ J

六、Use the phase diagram in Fig. 1 to plot the each phase relationship of the Gibbs free energy vs. temperature at various pressures (at P_1, P_2 and P_3). Meanwhile, the point O in Fig.1 is the triple point. It is also the invariant point. What is the physic meaning of point O?

(20 points)

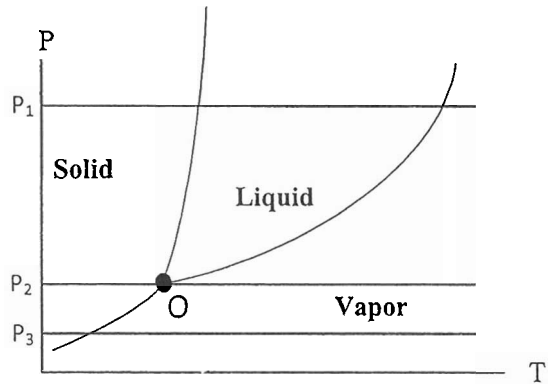

Fig.1 Phase diagram of the unary system.

七、The van der Waals equation is common used to describe the real gas behavior. For one mole of gas, it is written as

$$(P + a/V^2)(V - b) = RT$$

Where P is the measured pressure of the gas, a/V^2 is a correction term for the interactions which occur among the particles of the gas, V is the measured volume of the gas, and b is a correction term for the finite volume of the particles. Please show the "a" and "b" with critical properties of the gas in the van der Waals equation. Where T_{cr}, P_{cr} and V_{cr} are the critical temperature, pressure and volume of the gas. **(10 points)**