國立台灣科技大學九十八學年度碩士班招生試題

系所組別： 高分子工程系碩士班丙組

科　　目： 熱力學

熱力學；共七大題，總分 100 分；請於答案卷內依序作答

一、 The following equations have been proposed to present activity-coefficient data for a system at fixed T and P:

$$\ln \gamma_1 = x_2^2(0.5 + 2x_1)$$

$$\ln \gamma_2 = x_1^2(1.5 - 2x_2)$$

Do these equations satisfy the Gibbs/Duhem equation? Determine an expression for G^{xs}/RT for the system. (10 points)

二、 What is the "Phase equilibria condition"? Use the Fig. 1 to explain the relationship between the "thermodynamics" and "phase diagram". (20 points)

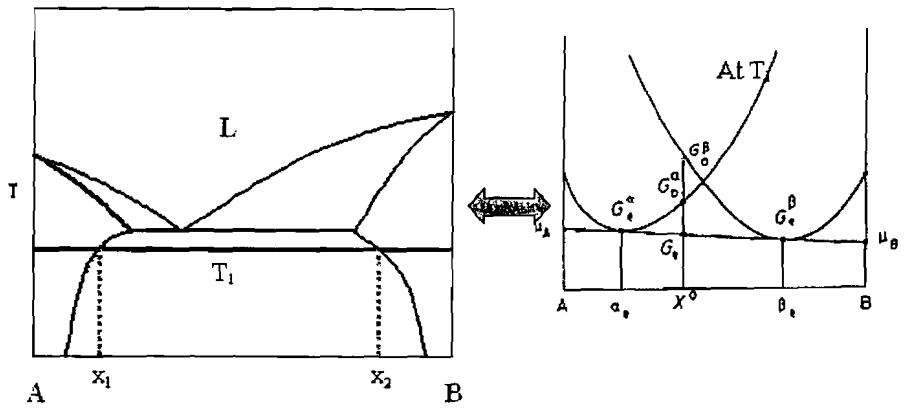

Fig. 1 The phase diagram of the A-B binary system.

三、 CaO and MgO form a simple eutectic system with limited ranges of solid solubility. The eutectic temperature is 2370 °C. Assuming that the solutes in the two solid solutions obey Henry's law with γ^{o}_{CaO} in MgO = 12.88 and γ^{o}_{MgO} in CaO = 6.23 at 2300 °C, calculate the solubility of CaO in MgO and the solubility of MgO in CaO at 2300 °C. (15 points)

四、 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

$$G^{XS} = \text{excess free energy (J)} = -28{,}280\, X_{Cu} \cdot X_{Au}$$

Calculate the activities of Cu and Au exerted by the solid solution at $X_{Cu} = 0.6$ at 600°C. (10 points)

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五、 (a) For non-ideal gases with an α value $\equiv (V_{ideal}-V)$ at constant temperature,

Derive $\ell n\left(\frac{f}{P}\right)=\int_{P=0}^{P=P}\frac{Z-1}{P}dP$, where Z≡ Compressibility factor. (10 points)

(b) Suppose that the attractive interactions between gas particles can be neglected, and find an expression for the fugacity of a van der Waals gas in terms of the pressure. Estimate its value for ammonia at 10.00 atm and 298 K. As a van der Waals gas, NH_3 has a b value of 0.0371 liters/mole. (5 points)

指數計算見對照表

x	exp(x)
0.010	1.01
0.100	1.11
1.000	2.72
2.000	7.39
3.000	20.1
4.000	54.6

自然對數計算見對照表

x	ln(x)
0.100	-2.30
0.200	-1.61
0.300	-1.20
0.400	-0.916
0.500	-0.693
0.600	-0.511
0.700	-0.357
0.800	-0.223
0.900	-0.105

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六、 (21 points) *Choose the best answer in each problem. 3 points each and no penalty on wrong guess. No procedure needed.* 單選不倒扣，答案寫於答案卷內

1. At a constant temperature, the total work of a reversible process equals to the change in (a) Gibbs free energy; (b) Helmholtz free energy; (c) internal energy; (d) enthalpy; (e) entropy.
2. In spontaneous processes at constant temperature and volume, systems move toward a state of minimum (a) entropy; (b) enthalpy; (c) internal energy; (d) Helmholtz free energy; (e) Gibbs free energy.
3. The ratio of the fugacity of a substance in any state to the fugacity in the standard state is known as the (a) compressibility factor; (b) isothermal coefficient of compression; (c) fugacity coefficient; (d) activity coefficient; (e) activity.
4. For an irreversible process, a net entropy change in the system and surroundings is (a) equal to zero; (b) greater than zero; (c) less than zero; (d) greater than or equal to zero; (e) less than or equal to zero.
5. The absolute entropy of matter is equal to Boltzmann constant times the logarithm of Q, where Q is related to temperature and (a) size of constituent particles; (b) mass of constituent particles; (c) kinetic energy of constituent particles; (d) energy levels (or distribution) of particles; (e) number of valence electrons of particles.
6. For an ideal solution, which one in the followings is zero? (a) molar entropy of mixing; (b) molar Gibbs free energy of mixing; (c) molar volume of mixing; (d) partial molar volume of each component; (e) chemical potential of each component.
7. Regular solution theory for non-ideal solutions containing simple molecules/atoms has been modified to deal with solutions consisting of long-chain molecules, yielding activities of all constituent components. This specific theory/result is called (a) Flory-Huggins equation; (b) van Laar equation; (c) Hildebrand equation; (d) Gibbs-Duhem equation; (e) Gibbs-Helmholtz equation.

七、(9 points) *Mathematical derivation and simple answers.*

We would like to determine the change in the freezing point of a solid material with increasing pressure.

(a) Starting with a phase-equilibrium criterion and fundamental thermodynamic relations from the first and second laws of thermodynamics, derive the interrelationship between freezing point and pressure. (4 points)

(b) The pressure effect on freezing point is completely opposite for ice and iron, respectively. Explain this difference of behavior based on results from part (a). (2 points)

(c) Draw the phase diagram (pressure versus temperature) for water. Label solid and liquid regions, as well as triple point. (2 points)

(d) Also specify the degree of freedom for the solid-liquid co-existence line. (1 points)