八十五學年度材料科學工程研究所(系)(所) 甲二 組碩士班研究生入學考試

科目 冶金熱力學 科號 1703 1802 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

1. Consider the equilibrium reaction of pure solid CaSi at 1000° K with Ca and Si dissolved in a solvent. Suppose that Ca initially has an activity of 0.5 in solution and CaSi is pure. Given that ΔG^0 for Ca(s) + Si(s) = CaSi(s) at 1000° K is -200 kJ/mol. and $p_{Ca}^0 = 15$ N/m^2, please find:

a) the activity of Si in equilibrium with Ca(a=0.5) and CaSi(s), (5 points)
b) the partial pressure of Ca(g) in equilibrium with the dissolved Ca (5 points)
c) the free energy of the reaction

Ca(a = 0.5) + Si(a = 0.4) = CaSi (a = 0.8) (10 points)

(where the notation "a" designates the activity, while "s" and "g" in the parentheses refer to solid state and gaseous state).

2. a) Explain the second law of thermodynamics, (5 points)
b) using the second law, construct a thermodynamic quantity that can be used to determine whether a reaction is spontaneous thermodynamically. (5 points)

3. An f.c.c. alloy of composition 40 % A and 60% B shows substantial short-range order. P_{AB}, the number of the A atom - B atom pairs, can be measured from x-ray scattering and was found to be 1.04 times the value for a random solution. Calculate P_{AA} and P_{BB} in a gram-atom of alloy. (10 points)

4. Prove that entropy is additive by showing that the entropy S_t of a system composed of two identical compartments and each of which has an entropy S_a is equal to $2S_a$. (5 points)

5. Given that dU = TdS -pdV, derive the Maxwell equation between pressure p and temperature T. (5 points)

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科目 冶金熱力學 科號 1703 1803 共 3 頁第 2 頁 *請在試卷【答案卷】內作答

6. (8%) From the e.m.f. measurements at 527°C, the following values of the activity coefficient of A, γ_A, in A-B solutions have been obtained as a function of the molar fraction of A, N_A

N_A:	0.2	0.3	0.4	0.5
γ_A:	2.153	1.817	1.544	1.352

If it can be shown that the A-B solution exhibits regular behavior, calculate the excess integral molar entropy of mixing.

7. (10%) The normal boiling point of A, T_A, is 907°C. Calculate the vapor pressure in mm Hg at 800°C. Assume that A follows Trouton's rule and the proportional constant between the molar heat of vaporization, ΔH_v, and the boiling point, T_A, is around 21.

8. (10%) The free energy of the reaction $A\text{-}B \rightarrow 2C$ can be represented in terms of the standard free energy ΔG°, temperature T, gas constant R and molar fraction N_A as

$$G = 2G^\circ_c + N_A(-\Delta G^\circ) + 2RT\left[N_A \ln\frac{N_A}{2} + (1-N_A)\ln(1-N_A)\right]$$

If $\Delta G^\circ = -3000 - 6T$ J/Mole,

evaluate the equilibrium concentration N_A when the temperature approaches infinity.

八十五學年度材料科學工程研究所(系)(所)第二組碩士班研究生入學考試

科目 冶金熱力學 科號 1703 1803 共 3 頁第 3 頁 *請在試卷【答案卷】內作答

9. (10%) Solid SiO_2 is reacted with Cl_2 gas in the presence of excess solid carbon to produce gaseous $SiCl_4$. The output stream contains unreacted Cl_2 and the product gases: CO, CO_2 and $SiCl_4$.

Assume that the solids do not form solutions. Apply the phase rule analysis to the system, and answer the following:

(1) components (list them)
(2) phases (list them)
(3) species (list them)
(4) independent chemical reactions (give balanced equation)
(5) degree of freedom (specify them)

10. (12%) Multiple choice (答錯一題倒扣二分)

(1)( )The change of enthalpy for supercooled pure liquid metal frozen isothermally and isobarically at a temperature 25°C below its equilibrium melting point. (a) negative (b) positive (c) zero (d) undetermined

(2)( )The change of entropy for problem 1. (a)negative (b) positive (c) zero (d) no way to determine

(3)( )The change of free energy for problem 1. (a)negative (b) positive (c) zero (d)undetermined

(4)( )The change of enthalpy for an endothermic chemical reaction occurred spontaneously within a constant temperature and pressure system. (a)negative (b) positive (c) zero (d)undetermined

(5)( ) The change of entropy for problem 4. (a)negative (b) positive (c) zero (d)undetermined

(6)( ) The change of free energy for problem 4. (a)negative (b) positive (c) zero (d)undetermined