國立高雄大學九十七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碩士班乙組 是否使用計算機:是

本科原始成績:100分

(備註:log()或e()內不用算出,只需化為最簡數字)

- 1. One hundred moles of hydrogen gas at 298K are reversibly and isothermally compressed from 20 to 10 liters. The van der Waals constants for hydrogen are a = 0.2461 liters² and b = 0.02668 1/mole, and in the range of pressure 1~1500 atm, the virial equation for hydrogen is $PV = RT(1+6.4? 10^{-4} P)$. Calculate the work that must be done on the system to effect the required change in volume and compare this with the values that would be calculated assuming that (a) hydrogen behaves as a van der Waal gas and (b) hydrogen behaves as an ideal gas. (18%)
- 2. The activity coefficient of Zn in liquid Zn-Cd alloys at 435°C can be represented as $\ln \gamma_{\rm Zn} = 0.875 \, X_{\rm Cd}^2 0.30 \, X_{\rm Cd}^3$

Derive the corresponding expression for the depedence of $\ln \gamma_{Cd}$ on composition and calculate the activity of cadmium in the alloy of $X_{Cd} = 0.6$ at 435° C. (12%)

3. Gold and silicon are mutually insoluble in the solid state and form a eutectic system with a eutectic temperature of 636 K and a eutectic composition of $X_{\rm Si} = 0.186$. Calculate the Gibbs free energy of the eutectic melt relative to (1) unmixed liquid Au and liquid Si, and (2) unmixed solid Au and solid Si. (Au $_{(S)} \rightarrow$ Au $_{(I)}$, $\Delta H_{\rm trans} = 12,600$ J, $T_{\rm trans} = 1338$ K;

Si
$$(S) \rightarrow Si_{(I)}, \Delta H_{trans} = 50,200 J, T_{trans} = 1658 K) (12\%)$$

4. By establishing the equilibrium

$$PCl_{5(g)} = PCl_{3(g)} + Cl_{2(g)}$$

at 500 K in a mixture of PCl₅ and PCl₃ a gas is obtained at 1 atm total pressure in which the partial pressure of Cl₂ is 0.1 atm. In what ratio were PCl₅ and PCl₃ mixed to obtain this equilibrium gas? $(PCl_{3(g)} + Cl_{2(g)} = PCl_{5(g)}, \Delta G^{\circ} = -95,600 - 7.94 T \ln T + 235.2 T J) (10\%)$

5. Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1600 K. Is the oxidation of Cr by water vapor exothermic or endothermic?

$$2Cr_{(S)} + 3/2 O_{2(g)} = Cr_2O_{3(S)}, \ \Delta G^{\circ} = -1,110,100 + 247.3 \ T J$$

 $H_{2(g)} + 1/2 O_{2(g)} = H_2O_{(g)}, \ \Delta G^{\circ} = -247,500 + 55.85 \ T J \ (12\%)$

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6. A CH₄—H₂ gas mixture at 1 atm total pressure, in which $p_{\rm H2} = 0.957$ atm, is equilibrated with an Fe-C alloy at 1000 K. Calculate the activity of C with respect to graphite in the alloy. What would the value of $p_{\rm H2}$ in the gas mixture (at $P_{\rm total} = 1$ atm) have to be in order to saturate the Fe with graphite at 900 K? (C $_{(gr)}+$ 2H_{2(g)} = CH_{4(g)}, $\Delta G^{\circ} = -91,040+110.7$ T J) (12%)

7. Below the triple point (-56.2°C) the vapor pressure of solid CO₂ is given as

$$\ln p \text{ (atm)} = -\frac{3116}{T} + 16.01$$

The molor latent heat of melting of CO₂ is 8330 joules. Calculate the vapor pressure exerted by liquid CO₂ at 25°C and explain why solid CO₂ is referred to as "dry ice." (12%)

8. A galvanic cell is set up with electrodes of solid aluminum and solid aluminum-zinc alloy and an electrolyte of molten AlCl₃-NaCl. When the mole fraction of Al in the alloy electrode is 0.38, the EMF of the cell is 7.43 milli-volts at 380°C, and the temperature coefficient of the EMF is 2.9? 0⁻⁵ volts/degree. Calculate (1) the activity of Al in the alloy, and (2) the partial molar Gibbs free energy of mixing of Al in the alloy. (12%)