國 立 清 華 大 學 命 題 紙

九十一學年度工程與系統科索(所) 甲 組碩士班研究生招生考試 科目 材料 熱力學 科號 3602 共二 頁第一頁 *請在試卷【答案卷】內作答

1. (15%)

A reversible heat engine, operating in a cycle, withdraws heat from a high-temperature reservoir (the temperature of which consequently decreases), performs work w; and rejects heat into a low-temperature reservoir (the temperature of which consequently increases). The two reservoirs are, initially, at the temperatures T_1 and T_2 and have constant heat capacities C_1 and C_2 respectively. Calculate the final temperature of the system and the maximum amount of work, which can be obtained from the engine.

2. (15%)

A quantity of supercooled liquid tin is adiabatically contained at 495 K.

Calculate the fraction of the tin which spontaneously freezes. Given

$$\triangle H_{m,(Sn)} = 7070$$
 (Joules) at $T_m = 505$ K
 $c_{p,Sn(l)} = 34.7 - 9.2 \times 10^{-3}$ T (Joule/K)
 $c_{p,Sn(s)} = 18.5 + 26 \times 10^{-3}$ T (Joule/K)

3. (15%)

Below the triple point (-56.2°C) the vapor pressure of solid CO₂ is given as $\ln p \text{ (atm)} = -3116 / T + 16.01$

The molar latent heat of melting 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".

4. (15%)

n moles of an ideal gas A and (1-n) moles of an ideal gas B, each at 1 atm pressure, are mixed at total constant pressure. What ratio of A to B in the mixture maximizes the decrease in the Gibbs free energy of the system? If the decrease in the Gibbs free energy is $\triangle G^M$, to what value must the pressure be increased in order to increase the Gibbs free energy of the gas mixture by $\frac{1}{2}\triangle G^M$?

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5. (10%)

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 $X_{Si} = 0.186$. 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.

Given
$$\triangle H_m = 50,200$$
 Joule and $T_m = 1685$ K for Si $\triangle H_m = 12,600$ Joule and $T_m = 1338$ K for Au.

6. (15%)

Three equations for the oxidation of Mg according to Mg + 1/2 $O_{2(g)} = MgO_{(g)}$ are

$$\Delta G^{\circ} = -604,000 - 5.36 \text{ T ln T} + 142.0 \text{ T}$$
 (Joule) (i)

$$\Delta G^{\circ} = -759,800 - 13.4 \text{ T ln T} + 317 \text{ T}$$
 (Joule) (ii)

$$\Delta G^{\circ} = -608,100 - 0.44 \text{ T ln T} + 112.8 \text{ T}$$
 (Joule) (iii)

One of these expressions is for the oxidation of solid Mg, one is for the oxidation of liquid Mg, and one is for the oxidation of gaseous Mg. Determine which equation is for which oxidation. (You have to provide your explanations). Also calculate the melting and normal boiling temperature of Mg.

7. (15%)

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 1000 K?

Given:
$$\Delta G^{\circ} = -91,040 + 110.7 \text{ T}$$
 (Joules) for reaction $C_{\text{(graphite)}} + 2H_{2(g)} = CH_{4(g)}$