國立清華大學 103 學年度碩士班考試入學試題

系所班組別：工程與系統科學系 甲組

考試科目（代碼）：材料熱力學 (2602)

　　*請在【答案卷、卡】作答

1. Referring to the First Law of Thermodynamics, we know that the work (w) done in an ideal gas system during a reversible isothermal process can be expressed as $w = RT \cdot \ln(V_2/V_1)$, where R is the gas constant (= 8.314 joules/degree-mole), T is the absolute temperature, and V_2 and V_1 are the volumes of the ideal gas at state 2 and state 1, respectively. Now, let us consider a particular case that one mole of an ideal gas at 25 °C and 1 atm undergoes the following reversibly conducted process:
   a. Isothermal expansion to 0.40 atm, followed by
   b. Isobaric expansion to 125 °C, followed by
   c. Isothermal compression to 1.00 atm, followed by
   d. Isobaric compression to 25°C

   The system then undergoes the following cyclic process:
   a. Isobaric expansion to 125 °C, followed by
   b. A decrease in pressure at constant volume to P atm, followed by
   c. An Isobaric compression at P atm to 24.50 liters, followed by
   d. An increase in pressure at constant volume to 1.00 atm

   Calculate the value of P which makes the work done on the gas in the first cycle equal to the work done by the gas in the second cycle. Note that 1 liter·atm = 101.3 joules. (20%)

2. One mole of an ideal gas is subjected to the following sequence of steps:
   a. Starting at 25 °C and 1 atm, the gas expands freely into a vacuum to four times of its original volume.
   b. The gas is then heated to 180 °C at constant volume.

   Assume that the molar heat capacity of the gas at constant volume, c_v, is 2.0R, the molar heat capacity of the gas at constant pressure, c_p, is 3.5R, and c_v and c_p are independent of temperature, where R is the gas constant. Calculate ΔU, ΔH, and ΔS (changes in molar internal energy, molar enthalpy, and molar entropy) in the gas in both <u>step a</u> and <u>step b</u>, respectively. (20%)

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3. The molar heats of formation and the molar entropies of formation of various vanadium oxide from vanadium metal and oxygen gas at 298 K are listed below. Based upon this information, calculate ΔG_{298}, ΔH_{298}, and ΔS_{298} (changes in molar free energy, molar enthalpy, and molar entropy) for the electrochemical reactions of $4VO_{(s)} + O_{2(g)} = 2V_2O_{3(s)}$ and $2V_2O_{3\,(s)} + O_{2(g)} = 4VO_{2(s)}$, respectively. (30% in total, 15% for each reaction)

Oxide	ΔH_{298} kJ/mole of oxide	ΔS_{298} Joules/degree · mole of oxide
VO	−431.8	−92.5
V_2O_3	−1219	−358
VO_2	−713.8	−184

4. When a quantity of supercooled liquid tin is adiabatically contained at 485 K, calculate the fraction of the tin which spontaneously freezes, given that
$\Delta H_{m,(\mathrm{Sn})} = 7070$ Joules at $T_m = 505$ K,
$c_{p,\mathrm{Sn}(l)} = 34.7 - 9.2\times10^{-3}T$ Joules/K, and
$c_{p,\mathrm{Sn}(s)} = 18.5 + 26\times10^{-3}T$ Joules/K. (10%)

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5. The phase diagram of copper and gold is given in the following figure. The excess molar Gibbs free energy of formation (G^{xs}) of the solid solutions is governed by the equation of

   $G^{xs} = -28280 X_{Au} X_{Cu}$ Joules.

   The standard vapor pressure of solid copper is given by

   $\ln P^{o}_{Cu}(atm) = -40920/T - 0.86 \ln T + 21.67$,

   and the saturated vapor pressure of solid gold is given by

   $\ln P^{o}_{Au}(atm) = -45650/T - 0.306 \ln T + 10.81$.

   Answer the following questions. (20%)

   a. Plot the Gibbs free energy of mixing curve at 600 °C. (8%)
   b. As random mixing is assumed, calculate the activity coefficients of Cu and Au when $X_{Cu} = 0.6$ at 600 °C. (6%)
   c. Calculate the partial pressures of Au and Cu exerted by the solid solution of $X_{Cu} = 0.6$ at 600 °C. (6%)