編號： 109　系所：化學工程學系乙組　　科目：物理化學

本試題是否可以使用計算機： ☑可使用 ， ☐不可使用 （請命題老師勾選）

$R=8.314\ J\ K^{-1}\ mol^{-1} = 8.314\times10^{-2}\ L\ bar\ K^{-1}\ mol^{-1} = 8.206\times10^{-2}\ L\ atm\ K^{-1}\ mol^{-1}$

1. For each of the following processes, state which of the quantities ΔU, ΔH, ΔS,ΔA, and ΔG are equal to zero: (15%)
   a. Isothermal reversible expansion of an ideal gas.
   b. Adiabatic reversible expansion of a nonideal gas.
   c. Vaporization of liquid water at 100 °C and 1 atm pressure.
   d. Reaction between H_2 and O_2 in a thermally insulated bomb.
   e. Reaction between H_2SO_4 and NaOH in dilute aqueous solution at constant temperature and pressure.

2. One mole of an ideal gas at T K expands isothermally from a pressure of P_1 bar to P_2 bar. What are w, q, ΔU, ΔH, ΔS, ΔA, and ΔG in the following cases? (a) The expansion is free. (b) The gas and its surroundings form an isolated system, and the expansion is free. (15%)

3. Liquid water can be superheated to 110 °C at 1.01325 bar. Calculate the changes in entropy, enthalpy, and Gibbs energy for the process of superheated water at 110 °C and 1.01325 bar changing to steam at the same temperature and pressure. The enthalpy of vaporization is 40.58 kJ mol^{-1} at 100 °C and 1.01325 bar. Given: $C_P(H_2O, l) = 75.3\ J\ K^{-1}\ mol^{-1}$ and $C_P(H_2O, g) = 33.6\ J\ K^{-1}\ mol^{-1}$. (15%)

4. (a) The dissociation pressures of $CaCO_3(s)$ versus temperature are shown as Fig. 1. Which phases are there in the regions I, II, and III, respectively ?
   (b) How many degrees of freedom are there when only $CaCO_3(s)$ and $CO_2(g)$ are present ?
   (c) Calculate the value of ΔG° at 1000K. (15%)

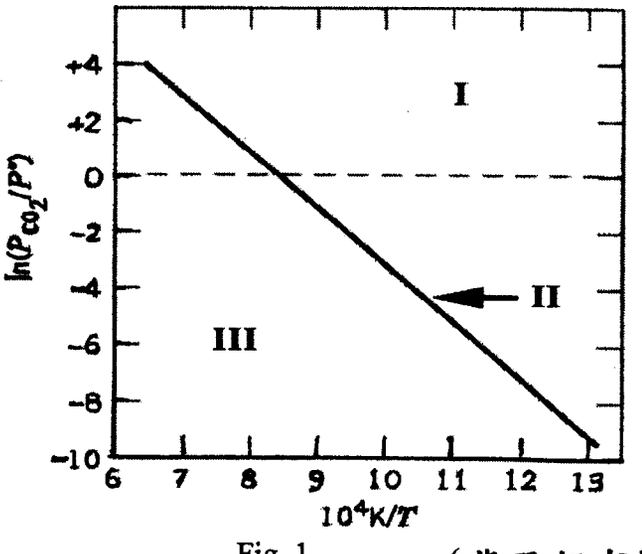

Fig. 1

（背面仍有題目，請繼續作答）

5. Benzene and toluene form very nearly ideal solutions. At 80°C, the vapor pressure of benzene is100.4 kPa, and that of toluene is 38.7 kPa. For a solution containing 4 mole of benzene and 6 mole of toluene, (a) calculate the partial pressures and the total vapor pressure of the solution at 80°C, and (b) calculate the mole fraction of benzene in the vapor at 80°C. (10%)

6. The following thermodynamic data apply to the complete oxidation of butane at 25°C. $C_4H_{10\,(g)} + 6.5\ O_{2\,(g)} \rightarrow 4\ CO_{2\,(g)} + 5\ H_2O_{(l)}$

$\Delta H^\circ = -2877\ kJ\ mol^{-1}$

$\Delta S^\circ = -432.7\ JK^{-1}mol^{-1}$

(a) When one mole of methane is oxidized completely in a Carnot engine that operates between 100 °C and 25 °C, what is the maximum work that could be produced ? (b) Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate the electromotive force and the maximum electrical work. (15%)

7. For the reaction $A + B \rightarrow D$ consider the following mechanism:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C \qquad (1)$$

$$C \xrightarrow{k_3} D \qquad (2)$$

(a) Derive the rate law using the steady state approximation to eliminate the concentration of *C*. (7%)

(b) Derive the rate law by assuming that the reaction (2) is the rate determining step, and express the pre-exponential factor *A* and activation energy *Ea* for the second-order rate constant rate in terms of A_1, A_2 and A_3 and Ea_1, Ea_2, and Ea_3 for the three steps. (8%)