國立台灣科技大學九十七學年度碩士班招生試題

系所組別： 化學工程系碩士班

科　　目： 化工熱力學與動力學

總分 100 分

Part I. 化工熱力學 (50 %)

1. A closed system changed from state "*a*" to state "*b*" via the path $a \rightarrow c \rightarrow b$, as shown in Fig. 1. It was found that 250 J of heat was transferred from surroundings to the system and 200 J of work was done by the system during the changing process.
   (a) Please calculate the amount of heat transfer (Q_a) as the system changes from state "*b*" to state "*a*" through the path $b \rightarrow d \rightarrow a$ as illustrated in Fig. 1. During this changing process, 100 J of work is done by surroudings. You are also asked to indicate that the heat is absorbed or evolved. (5 %)
   (b) As presented in Fig. 1, the system changes from state "*a*" to state "*b*" and then returns to state "*a*" via the path $a \rightarrow c \rightarrow b \rightarrow e \rightarrow a$. You are asked to calculate the amount of work interaction (W_b) between the system and surroundings, if 100 J of heat is evolved from the system to surroundings during this cyclic process. Is the work done by the system or surroundings? (5 %)

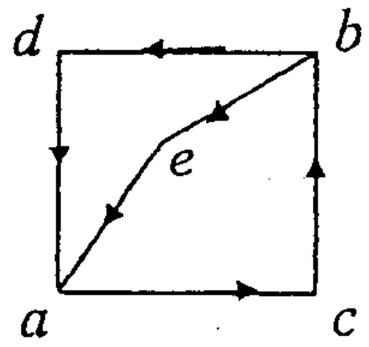

Fig. 1

2. Qualitatively plot a practical Rankine power cycle on a T-S diagram and indicate the constraint of each step. (5 %)

3. For water (1) + ethanol (2) system, its molar volume change of mixing ($\Delta_{mix}V$) at 300 K can be expressed by the following equation:

$$\Delta_{mix}\underline{V}\ \left(cm^3/mol\right) = -x_1x_2\left[5 + 0.5(x_1 - x_2)\right]$$

   where x_1 and x_2 are the mole fractions of water and ethanol, respectively. At 300 K, the density of pure water is 1.0 g/cm^3 and that of pure ethanol is 0.78 g/cm^3. Now, we try to prepare 100 cm^3 of water + ethanol solution with the molar ratio of water : ethanol = 1 : 1 at 300 K.
   (a) Calculate the density of this aqueous solution. (5 %)
   (b) How many grams of water and ethanol are needed, respectively, to prepare the solution? (5 %)
   (c) Calculate the partial molar volume of ethanol for this solution. (10 %)
   (d) Calculate the partial molar volume of ethanol at infinite dilution. (5 %)

4. Describe briefly the γ–ϕ method for vapor-liquid equilibrium (VLE) calculation. (10 %)

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Part II. 化工動力學 (50%)

5. Microelectronic devices are formed by first forming SiO_2 on a Si wafer by thermal oxidation and some procedures as illustrated in Fig. 2. The second procedure is followed by coating the SiO_2 with a photoresist. The pattern of the electronic circuit is then placed on the photoresist and the sample is irradiated with UV light. If the photoresist is a positive type, the sections that were irradiated with dissolve in the appropriate solvent, and those sections not irradiated will protect the SiO_2 from further treatment. The wafer is then exposed to strong acids, such as HF, which etch the exposed SiO_2. It is extremely important to know the kinetics of the reaction so that the proper depth of the channel can be achieved. The dissolution reaction is

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

(i) From the following initial rate data, determine the rate law. Also estimate the etching rate at 1 wt% of HF.

Etching rate (nm/min)	60	200	600	1000	1400
HF (wt %)	8	20	33	40	48

(ii) The etching rate may differ at various temperatures. This means that the reaction rate of a chemical reaction always follows Arrhenius behavior. Please give an example of reaction to show the transition state and the energy barrier of a reaction by using potential energy plot as a function of reaction coordinate. (15%)

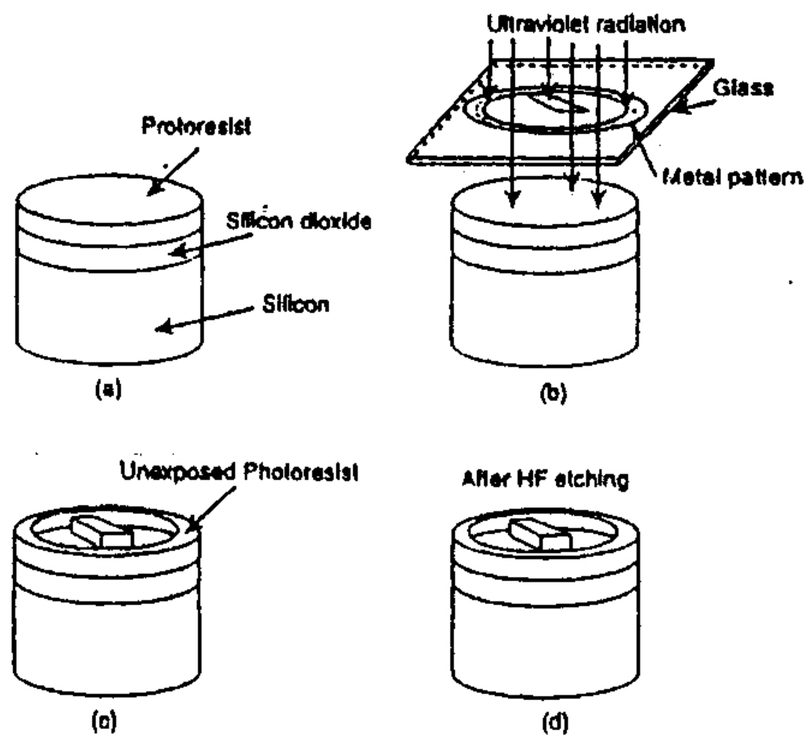

Fig. 2 Semiconductor etching

6. Chemical vapor deposition (CVD) is a technique to deposit thin films through chemical reactions of gaseous species on a solid substrate. In order to deposit $PbTiO_3$ films on Si wafers, a CVD reaction system was designed which used TEL and TTIP as the gaseous sources for Pb and Ti, respectively. Also O_2 was used as an oxidant. A surface reaction scheme concerning the deposition of $PbTiO_3$ is proposed as follows.

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$$TEL_{(g)} + \sigma \underset{k_1}{\overset{k_1}{\rightleftarrows}} TEL\cdot\sigma \qquad (1)$$

$$\frac{1}{2}O_{2(g)} + \sigma \underset{k_2}{\overset{k_2}{\rightleftarrows}} O\cdot\sigma \qquad (2)$$

$$TEL\cdot\sigma + 3O\cdot\sigma + TTIP_{(g)} \xrightarrow{k_3} PbTiO_{3(s)} + 4C_2H_{4(g)} + 4C_3H_{6(g)} + 4H_2O_{(g)} \qquad (3)$$

where σ designates a surface adsorption site, k and k' are the rate constants for adsorption and desorption, respectively, k_3 is the rate constant for $PbTiO_3$ deposition. The above reaction scheme considers an Eley-Rideal mechanism, i.e., a surface reaction among three species: two adsorbed species, TEL and dissociated oxygen, and one gaseous species TTIP, reacting to form $PbTiO_3$ films. Considering that reactions in eqs. (1) and (2) are reversible, please answer the following questions.

(i) According to the Langmuir treatment of adsorption, please write down the rate expression for each step including adsorption and desorption using denotations of θ (the fraction of surface adsorption site covered by the adsorbed molecules) and P (partial pressure for each species, e.g., P_{TEL} as the partial pressure of TEL, P_{O_2} as the partial pressure of oxygen)

(ii) Please express the conservation equation of surface site.

(iii) Please derive the adsorption isotherms for TEL ($\theta_{TEL\cdot\sigma}$) and dissociated oxygen ($\theta_{O\cdot\sigma}$).

(iv) Please show that the deposition rate is linearly proportional to TTIP partial pressure but nonlinear to TEL and O_2 partial pressures. (20%)

7. For a reactant A proceeding the following parallel reactions:

$$A \rightarrow D \text{ (desired)}$$
$$A \rightarrow U \text{ (undesired).}$$

The rate expressions for each reaction are $r_D = k_D C_A^{\alpha 1}$ and $r_U = k_U C_A^{\alpha 2}$, respectively. Please answer the following questions.

(i) What is the total consumption rate of A?

(ii) If the rate selectivity parameter is $S_{DU} = r_D / r_U$, show the relation between S_{DU} and the rate laws.

(iii) When $\alpha 1 - \alpha 2 > 0$, then what kind of reactor should be adopted in order to increase the growth rate of D? For the same purpose, is the concentration of reactant A should be increased or decreased? Why? (15%)