注意：考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。

—作答注意事項—

1. 請核對答案卷（卡）上之准考證號、科目名稱是否正確。

2. 作答中如有發現試題印刷不清，得舉手請監試人員處理，但不得要求解釋題意。

3. 考生限在答案卷上標記「▌由此開始作答」區內作答，且不可書寫姓名、准考證號或與作答無關之其他文字或符號。

4. 答案卷用盡不得要求加頁。

5. 答案卷可用任何書寫工具作答，惟為方便閱卷辨識，請儘量使用藍色或黑色書寫；答案卡限用 2B 鉛筆畫記；如畫記不清（含未依範例畫記）致光學閱讀機無法辨識答案者，其後果一律由考生自行負責。

6. 其他應考規則、違規處理及扣分方式，請自行詳閱准考證明上「**國立清華大學試場規則及違規處理辦法**」，無法因本試題封面作答注意事項中未列明而稱未知悉。

Problem 1 (4%)

1. The well-known van der Waals equation (in which p is the pressure, V the molar volume, T the absolute temperature, R the gas constant, while positive constants a and b correspond to corrections for intermolecular interaction and excluded volume effects, respectively) serves a simple model to account for minor nonideality in gases under moderate pressures. Which of the following is the *correct* form of the van der Waals equation?
   (A) $(p + a/V)(V + b) = RT$
   (B) $(p - a/V)(V - b) = RT$
   (C) $(p + a/V)(V - b) = RT$
   (D) $(p - a/V)(V + b) = RT$
   (E) None of the above

Problem 2 (16%)
Each sub-question is 8% in score.

2. The Joule-Thomson coefficient is defined as $\mu_{JT} \equiv (\partial T/\partial p)_H$ (where T is the absolute temperature, p the pressure, and H the enthalpy) of a fluid going through a throttling process. Which of the following is *incorrect*?
   (A) For an ideal gas, $\mu_{JT} = 0$.
   (B) For a real gas, we have $\mu_{JT} = 0$ at an inversion temperature T_I, above which $\mu_{JT} < 0$ and below which $\mu_{JT} > 0$
   (C) For a liquid, we generally have $\mu_{JT} > 0$
   (D) All of the above
   (E) None of the above

3. Regarding values of *molar* heat capacity under constant pressure (c_p) for He, Ar, H_2, N_2, O_2, CO, NH_3, and CH_4 gases at ambient conditions, which of the following is *incorrect*?
   (A) $c_p(\text{He}) \approx c_p(\text{Ar})$
   (B) $c_p(N_2) \approx c_p(\text{CO})$
   (C) $c_p(O_2) \approx c_p(H_2)$
   (D) $c_p(NH_3) \approx c_p(CH_4)$
   (E) None of the above

Problem 3 (10%)

The vaporization points of **A** and **B** at 1 atm are at 200°C and 230°C, respectively. The **A-B** temperature-composition phase diagram at 1 atm has an azeotrope at 150°C and 45at%**B**.

(a) Draw a schematic **A-B** temperature-composition phase diagram at 1 atm with temperature range from 100°C to 250°C. *(2%)*

(b) Draw the Gibbs free energy curves of the vapor phase and liquid phase at 140°C, 180°C, 210°C and 240°C. The curves of vapor phase and liquid phase should be in one figure for each temperature, so there are totally 4 figures in answering this question. *(2%)*

(c) Assuming **A** and **B** are both ideal gases, is the **A-B** liquid phase mixture an ideal solution? Why or why not? *(2%)*

(d) If there is a liquid miscibility gap with a critical point at 95°C and 55at%**B**, draw a schematic **A-B** temperature-composition phase diagram at 1 atm with temperature range from 50°C to 250°C. *(2%)*

(e) Draw the Gibbs free energy curve of the liquid phase at 80°C. *(2%)*

Problem 4 (10%)

A is reacted in the liquid phase with **B** at atmospheric pressure to produce **C** and **D** according to the reaction: $A_{(l)} + B_{(l)} \rightarrow C_{(l)} + D_{(l)}$. For **A**, **B**, **C**, and **D**, the standard Gibbs energy of formation at 25°C (298.15 K), $\Delta G^o_{f,298.15}$, are -389900 J, -174780 J, -332200 J and -237129 J, respectively. There is one mole of each of **A** and **B** initially, and the liquid phase is an ideal solution.

(a) What is the value of standard Gibbs free energy of reaction at 25°C, ΔG^0_{298}? *(2%)*

(b) What is the equilibrium constant K at 298.15 K? *(2%)*

(c) What is the mole fraction of **C** in the reacting mixture in equilibrium at 25°C? *(2%)*

(d) Draw a schematic $G^t - \varepsilon$ diagram showing the relationships between total Gibbs free energy, G^t, and the reaction coordinate, ε. The variable, ε, called the reaction coordinate, characterizes the extent of degree to which a reaction has taken place. *(2%)*

(e) What are compositions of each component in the reacting mixture when the mixture has the lowest Gibbs free energy at 25℃? *(2%)*

Problem 5 (10%)

A 2 liter constant-volume reactor is evacuated and then filled with 0.1 gmol of methane, after which the temperature is raised to 1000 °C. At this temperature, the equilibrium pressure is measured to be 7.02 atm. Assuming methane dissociates according to the reactor,

$CH_4(g)=C(s)+2H_2(g)$
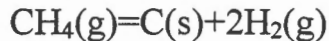
and that ideal gas and solution behavior prevail:

(a) What is the final number of moles of gas in the reactor? R=0.082 atm·L/gmol·K. *(2%)*

(b) What is the conversion for the 0.1 gmol of methane (In other words, how many moles react?) *(2%)*

(c) Calculate K_a for the reaction at 1000 °C utilizing standard states that correspond to the states of matter given in the above equation for the reaction. *(3%)*

(d) An alternative experiment is performed in which a hydrogen line connected to the vessel is left open. Initially the reactor contains some methane. The temperature is the same, but the pressure is now 5 atm. The hydrogen concentration is measured to be 0.58 mole fraction. The vessel size is unknown. Will any carbon be present? Justify your action quantitatively. *(3%)*

Problem 6 (10%)

The figure below shows the residence time distribution function from pulse inputs to two different packed bed reactors of equal volume with equal flow rates. Answer the following questions with succinct explanations:

(a) Which reactor is more like a PFR and which is more like a CSTR? (You must explain why to receive credit.) *(2%)*

(b) Consider the reaction A → P to be conducted in reactor 1 or 2. If the rate of reaction is first-order in the concentration of A, which reactor will achieve a higher conversion, all other things being equal? What if the reaction were zeroth-order? In both cases, please explain why? *(2%)*

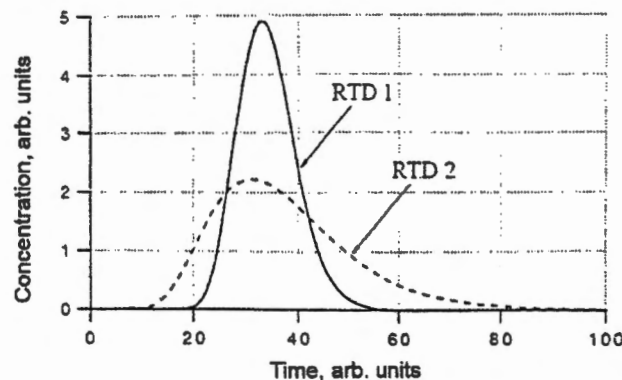(c) Consider the following reactions to be carried out in reactor 1 or 2.

$$A \rightarrow B \quad r_1 = k_1 C_A \quad\quad (1)$$
$$B \rightarrow C \quad r_2 = k_2 C_B \quad\quad (2)$$

Where C_A and C_B are the concentrations of A and B. Which reactor will maximize the yield of B? Why? *(3%)*

(d) Consider the following reactions to be carried out in reactor 1 or 2.

$$A \rightarrow B \quad r1 = k_1 C_A \quad\quad (3)$$
$$A \rightarrow C \quad r2 = k_2 C_A^2 \quad\quad (4)$$
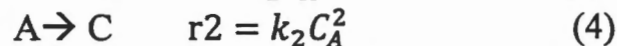
Which reactor will maximize the selectivity of B over C? Why? *(3%)*

Problem 7 (10%)

The formation of diphenyl ($C_{12}H_{10}$) is to be carried out at 760°C. The feed is to be pure benzene (C_6H_6) in the gas phase at a total pressure of 5 atm and 760°C. The specific reaction rate is 1800 ft^3/(lbmol*s) and the concentration equilibrium constant is 0.3.

(The gas constant $R = \frac{1.987\ Btu}{lb\ mole*{}^oR} = \frac{0.73 ft^3*atm}{lb\ mole*{}^oR} = \frac{8.314 kPa*dm^3}{mole*K}$ and $^oR = 1.8*K$)

(a) What is the equilibrium conversion? *(5%)*

(b) Calculate the reactor volume necessary to achieve 98% of the equilibrium conversion of benzene in a CSTR (with a benzene feed of 10 lbmol/min). *(5%)*

Problem 8 (10%)

Nitrogen oxide is one of the pollutants in automobile exhaust and can react with oxygen (in the air) to form nitrogen dioxide according to

$$2NO+O_2 \rightarrow 2NO_2$$
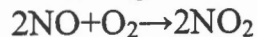
At 298 K the specific reaction rate is

$$k=14.8*10^3\ L^2/(mol^2*s)$$

or in parts per million

$$k=1.4*10^{-9}\ ppm^{-2}/min$$

(a) What is the half-life of 3000 ppm NO (a typical precontrol auto exhaust value) in air? *(5%)*

(b) What is the half-life of 1 ppm NO (a typical polluted atmosphere value)? *(5%)*

Problem 9 (10%)

An isomerization reaction, $A \xleftrightarrow{k} B$, is to be carried out adiabatically in the liquid phase at 360 K with k = 31.1 h^{-1}. Calculate the CSTR volume necessary to process 163 mol/h at 40% conversion of a mixture containing 90 mol% A and 10 mol% C which is considered as an inert. The feed enters at 330 K.

Additional information:

Heat of reaction, ΔH°_R = -6900 J/mol·A, activation energy, E_a = 65.7 kJ/mol, Concentration equilibrium constant, K_C = 3.03 at 60°C; $C_{A,0}$ = 9.3 mol/dm^3; heat capacity, $C_{P,A} = C_{P,B}$ = 141 J/mol·K, $C_{P,C}$ = 161 J/mol·K

Problem 10 (10%)

The first-order irreversible isomerization ($r_A' = k'aC_A$), A → B, is being carried out isothermally in a batch reactor on a catalyst that is decaying as a result of aging. If the catalyst decay mechanism is under the separable kinetics of catalyst activity decay and the decay law is second order with respect to the present activity ($r_d = k_d a^2$). Please show that the conversion of A (X_A) in this batch reactor as a function of time can be expressed as follow:

$$X_A = 1 - \frac{1}{(1 + k_d t)^{k'/k_d}}$$