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。

國立清華大學 108 學年度碩士班考試入學試題

系所班組別：化學工程學系碩士班

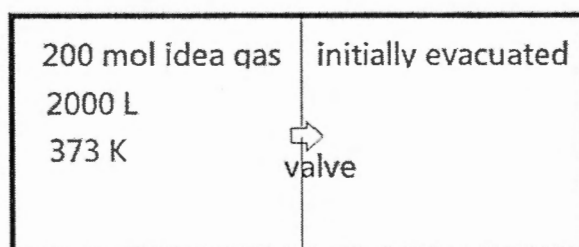考試科目（代碼）：化工熱力學及化學反應工程（0902）

Problem 1 (9%)

Please suggest some systems by yourself to explain the definition/physical meaning of the thermodynamic functions (not only the equation illustrating the relationships between the functions):

(a) internal energy (U);

(b) enthalpy (H);

(c) entropy (S);

Problem 2 (6%)

A process occurs toward the increase in entropy. It means that the maximum entropy change (ΔS) appears at the state of equilibrium in the following system. Please illustrate it.

A 4000 L tank is divided equally into two part with a valve connecting the two parts. One part is filled 200 mol of an idea gas at 373 K. The valve is open to allow the gas flow into the other part. The two parts have the same temperatures during the process. The tank is well insulated.

Problem 3 (10%)

For a pure substance, draw (a) a P(pressure)-V (volume) diagram, (b) a T(temperature)-S (entropy) diagram, and (c) an H(enthalpy)-S diagram showing solid region, liquid region, vapor region, critical point and triple-point line. (d) There are two sequences A-D-B and A-E-F-B on the P-T diagram. The A-D-B sequence is a sequence of reducing pressure at a constant temperature. The liquid phase vaporizes and there is an abrupt change in density when crossing the vaporization curve. The A-E-F-B sequence is a sequence that transition from liquid to gas is gradual and does not include an abrupt change in properties at constant T and P. Mark the A-D-B and the A-E-F-B sequences on the P-V diagram. (e) Mark the A-D-B and the A-E-F-B sequences on the T-S diagram.
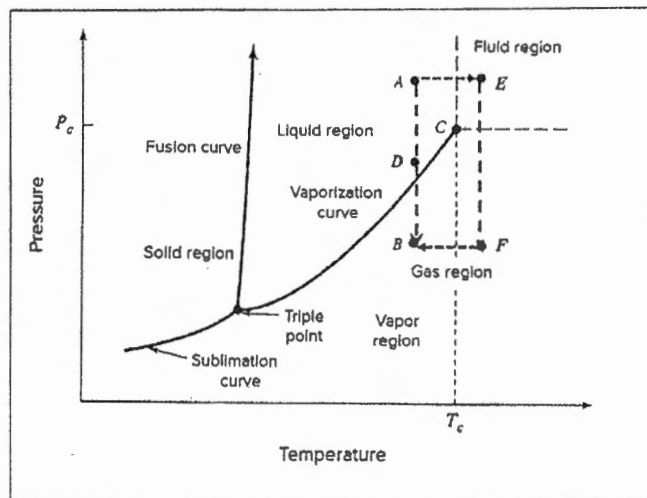
Problem 4 (10%)

(a) What is the mixing enthalpy of an ideal binary A-B solution? What is the mixing entropy of an ideal binary A-B solution? (b) What is the excess mixing enthalpy of an ideal binary A-B solution? What is the excess mixing entropy of an ideal binary A-B solution? (c) At a constant pressure P_1, the melting point of A is at 200°C and that of B is at 300°C. If both the liquid phase and the solid phases are ideal solution and there are no binary intermediate phases, draw the binary A-B phase diagram at P_1. Mark on the phase diagram the liquid phase region, the solid phase region, the liquid+solid two-phase region, the liquidus curve and the solidus curve. (d) What is the partial free energy of element A of the solid phase in the binary A-B system, $\overline{G_A^s}$, at P_1 and 150°C? The free energy of pure A is G_A^o and that of pure B is G_B^o. (e) Draw the G (Gibbs free energy)-X (composition) diagram of the A-B binary system at 250°C.

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Problem 5 (4%)

For a regular liquid mixture (*i.e.*, $\Delta \underline{H}_{mix} \neq 0$ and $\Delta \underline{V}_{mix} = 0$) of organic solution with 3 moles of A and 2 moles of B at 300 K and 10 bar. Please calculate the $\Delta \underline{S}_{mix}$ and $\Delta \underline{H}_{mix}$ of the mixture. Known that the excess Gibbs free energy of the mixture, $\underline{G}^{ex}$, is $RT\, x_A\, x_B$.　　Here, R=8.314 J/(mol K)

Problem 6 (6%)

Please calculate the final compositions of the mixture in the liquid and vapor phases if a vapor-liquid equilibrium is reached by decreasing the pressure to 0.5 bar for an ideal liquid mixture (*i.e.*, $\Delta \underline{H}_{mix} = 0$ and $\Delta \underline{V}_{mix} = 0$) of organic solution with 4 moles of A and 1 moles of B at 300 K and 1 bar.

Known that the temperature-dependent data of saturated pressure for A and B are $\ln P_A = 10.4 - (26800/RT)$ and $\ln P_B = 11.4 - (35200/RT)$ for P in bar and T in K, respectively. R = 8.314 J/(mol K).

Problem 7 (5%)

A distillation column has been designed to separate A and B components at 1 bar. The initial composition is 0.5 molar fraction of A and the final goal is to get the liquid mixture with 0.95 molar fraction of A. Known that the temperature-dependent data of saturated pressure for A and B are the same as above and the mixture is an ideal liquid mixture. Please estimate the dew point temperature at the first column (*i.e.*, the top column) of the distillation column.

P.S. Please list your equation and describe your approach for solution if you are unable to solve it.

## Problem 8 (25%)

Enzymes are important biocatalysts for many amazing reactions found in nature. Working at a perfume company, you recently identified a new enzyme (E) which is capable of making geraniol, a fragrance compound having the smell of roses. The simplified reaction is as follows:

$$X \rightleftharpoons \text{Geraniol}$$

In order to use this enzyme in the perfume-making process, you must first characterize its enzyme kinetics. After some experiments, you found that <u>this new enzyme follows the Michaelis-Menten kinetics behavior</u>, which can be represented by the schematics below (E = enzyme, S = substrate, ES = substrate-enzyme complex, P = product) and obeys the "initial rate" assumption, the "rate-limiting" assumption, and the "pseudo-steady state" assumption. You know in the Michaelis-Menten kinetics, the catalytic efficiency is determined by two enzymatic properties, the k_{cat} and the K_m.

$$E + S \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ES \overset{k_{cat}}{\longrightarrow} E + P$$
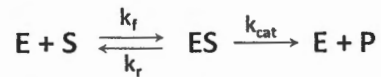
Please answer the following questions. ***DO NOT FORGET TO SHOW THE UNITS

(a) You conducted the enzyme kinetics assay using a total enzyme concentration of 10 μM. The experiments showed that the V_{max} of this enzyme for making geraniol is 100 mM/s while the K_m is 10 mM. Please roughly draw the nonlinear Michaelis-Menten curve for this enzymatic reaction. <u>Make sure you label the x-axis, y-axis, units, and the important numbers (V_{max} and K_m) on the figure</u>. *(6%)*

(b) Your boss would like to repeat the same experiment but using a total enzyme concentration of 20 μM, will the V_{max} change? <u>If yes</u>, please calculate the new number. *(7%)*

(c) Your boss would like to repeat the same experiment but using a total enzyme concentration of 2 μM, will the K_m change? <u>If yes</u>, please calculate the new number. *(7%)*

(d) Please briefly explain why enzymatic reactions have rate limits (rate cannot exceed maximum velocity) given a fixed concentration of total enzyme. *(5%)*
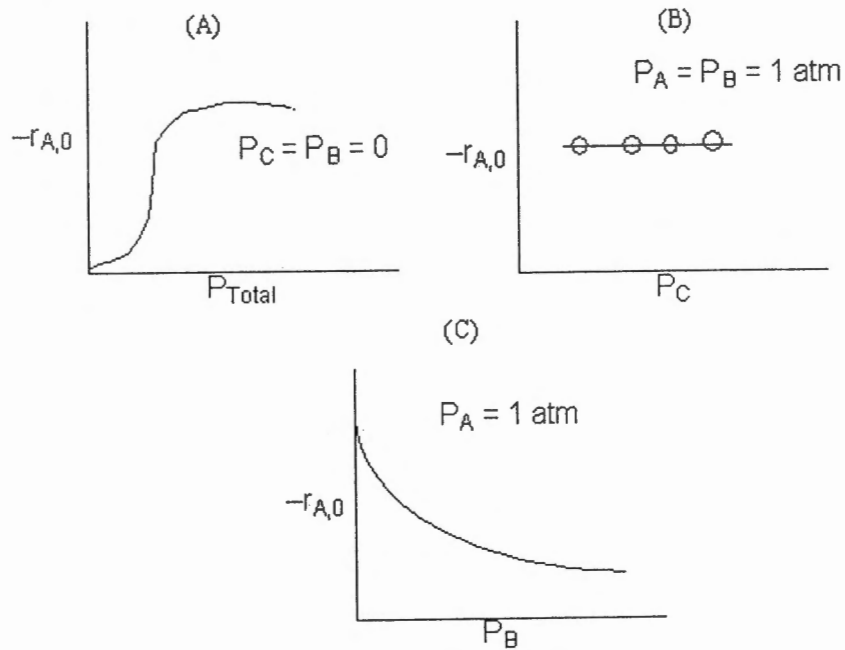
Problem 9 (10%)

The following experimental data were reported for the reaction A goes to B + C, the initial rate of the reaction is shown below:

Which rate law is consistent with above data? Explain your reason(s) or NO score will be given even your answer is correct!

(A)
$$-r_A = \frac{kP_A}{1 + K_A P_A + K_B P_B}$$

(B)
$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

(C)
$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_B P_B\right)^2}$$

(D)
$$-r_A = \frac{kP_A}{1 + K_A P_A + K_C P_C}$$

Problem 10 (15%)

Problem: What four things are wrong or may not be included with this solution?

Please explain and correct them!

The elementary gas phase reaction

$$A+2B \rightarrow C$$

is carried out in a packed bed reactor (PBR). Calculate the exit conversion from a PBR packed with 800 kg of catalyst. The feed is stoichiometric.

Additional Information:

$\alpha = 0.001$ kg^{-1} (pressure drop parameter)

$C_{A0} = 0.04$ mol/dm^3

$k = 3.0$ dm^6/mol^{2}s

$v_o = 20$ dm^2/s

Current solution

Mole balance: $\dfrac{dx}{dw} = \dfrac{-r_a'}{F_{A0}}$

Rate law: $-r_a' = k*C_A*C_B$

Stiochiometry: $C_A = C_{A0} \times (1-x) \times y$

$$C_B = C_{A0} \times (1-x) \times y$$

Pressure drop $\dfrac{P}{P_0} = y = (1-\alpha w)^{1/2}$

Parameter evaluations:

k=3

$C_{A0}=0.04$

$v_o=20$

$F_{A0}=C_{A0}*v_o$

$\alpha=0.001$

w(initial)=0

w(final)=800