1. (I) For an ideal gas at an initial state of p_1, T_1 and V_1.

   (1) What would be its pressure P_2 and temperature T_2 if the gas is allowed to expand freely against vacuum to a volume V_2? [4%]

   (2) What would be its pressure P_2 and temperature T_2 if the gas is allowed to expand adiabatically against a constant pressure p_o ($0 < p_o < p_1$) to V_2? [6%]

   (II) Starting with the definition of *internal pressure* $\pi_T \equiv (\partial U/\partial V)_T$ for real gases, show that

   (1) $C_p - C_V = \alpha (p + \pi_T)$ where *isobaric thermal expansion coefficient* $\alpha \equiv V^{-1} (\partial V/\partial T)_p$. [5%]

   (2) $\pi_T = T (\partial p/\partial T)_V - p$ and hence $C_p - C_V = \alpha^2 TV/\kappa_T$ where *isothermal compressibility* $\kappa_T \equiv -V^{-1}(\partial V/\partial p)_T$. [5%]

2. (I)(1) Please draw a schematic P-T (pressure-temperature) phase diagram of pure water at moderate pressures (1~50000 kPa). Mark all the phase regions, indicate the triple point and the critical point on the diagram, and briefly explain what the triple point and the critical point are. [4%]

   (2) The saturated vapor pressure of pure water at 300°C is 8592.7 kPa. Please draw a schematic f-P (fugacity-pressure) diagram of pure water with pressures ranging from 1-10000 kPa. [3%]

   (3) Please draw a schematic ϕ-P (fugacity coefficient-pressure) diagram of pure water with pressure ranging from 1-10000 kPa. [3%]

   (II)(1) Please draw a schematic T-X (temperature-composition) diagram at a constant pressure for the system ammonium thiocyanate-potassium thiocyanate, where the two constituents are completely miscible in both the solid and liquid states and their melting points are 147°C and 180°C, respectively. [3%]

   (2) What is the "Gibbs Phase Rule"? What is the degree of freedom in the two phase region of the diagram as mentioned in (1)? [4%]

   (3) Please draw a schematic binary T-X diagram at a constant pressure with a simple eutectic reaction. [3%]

3. (I)What is the Gibbs/Duhem equation? According to the Gibbs/Duhem equation, please show that in a two-component mixture, component 2 will obey the Lewis/Randall rule when Henry's law is valid for component 1. [10%]

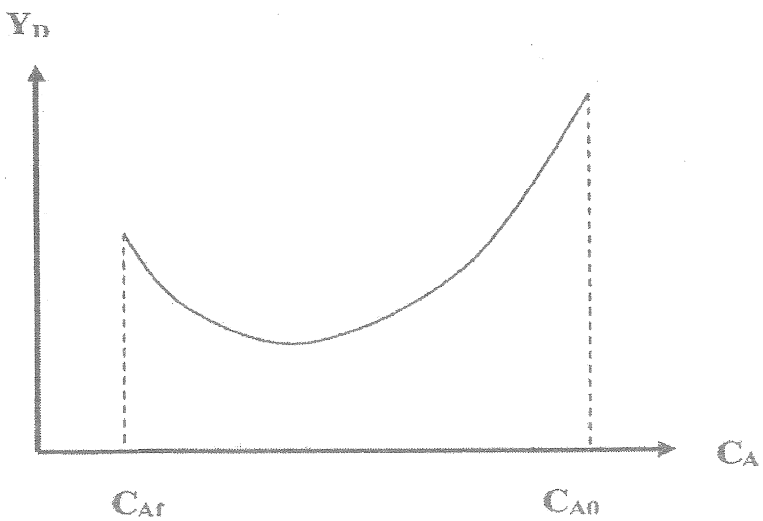
(II) A parallel reaction is expressed as following:

$$A \xrightarrow{k_D} D \qquad r_D = k_D C_A^{\alpha_1}$$

$$A \xrightarrow{k_U} U \qquad r_U = k_U C_A^{\alpha_2}$$

$$Y_D = \frac{r_D}{-r_A} = \frac{dC_D/dt}{-dC_A/dt}$$

D is the desire product. There are two reactors in series. One is a CSTR and the other is a PFR. If the relationship between the instantaneous yield, Y_D, and the concentration of reactant A (C_A) obeys the following equation: $Y_D = 0.1C_A^2 - 0.2C_A + 0.4$ when C_A is between 3 and 0.01 M (also see the attached figure) and the initial concentration of desired product (C_{D0}) is 0 M. Now, the initial concentration (C_{A0}) and exit concentration (C_{Af}) of A and C_{D0} are 3, 0.1 and 0 M, respectively. How to obtain the highest concentration of the desired product? What is the corresponding highest concentration of the desired product? [10%]



4. (I) Nitrogen and oxygen reacted in the cylinder of a car engine to form nitrous oxide:

$$N_2 + O_2 \leftrightarrows 2\,NO$$

The cylinder may be considered as a small batch reactor. The reaction may be considered to take place isothermally in the car cylinder at 2700 K in a constant-volume reactor (cylinder) of 0.4 dm^3 under a pressure of 20 atm. Assume that the reaction takes place rapidly with respect to the movement of the piston in the cylinder. Consider that the feed consists of 77% N_2, 15% O_2, and 8% other gases, which may be considered inerts. At this temperature the concentration equilibrium constant K_e is 0.01 (dimensionless). Calculate the equilibrium conversion of N_2. [10%]

(II)For the same reaction and conditions as in the previous problem (Problem 4(I)) and if a conversion of N_2 of 1.6% is reached in 151 μs, determine the forward reaction rate constant.

Note: You do not have to solve the resulting integral. The answer should be a number (with unit) multiplied by an integral. [10%]

5.(I)The elementary reversible gas-phase reaction $A \Leftrightarrow B$ is to be carried out adiabatically to achieve 45% conversion of A. Pure A is fed to the reactor at a rate of 10 mol/min at a pressure of 2.87 atm and a temperature of 77 °C. Shaft work is neglected. Calculate the temperature of the exit stream if a CSTR is used.

Additional data:

specific reaction rate at 0°C: 0.001 h^{-1} (first order)

activation energy: 10,000 cal/mol

heat of reaction at 27°C: -20,000 cal/mol A

equilibrium constant at 127°C: 25,000

Heat capacity of A=20 cal/mol·K

Heat capacity of B=30 cal/mol·K [10%]

(II)For the same reaction and conditions as in the previous problem (Problem 5(I)), calculate the reactor volume for a CSTR. [10%]