



25 %

1. Estimate the triple point temperature and pressure of benzene. The following data are available:

		Vapor Pressure			
T (°C)		-36.7	-19.6	-11.5	-2.6
P ^{vap} (Pa)		1.333	6.667	13.33	26.67
Melting point at atmospheric pressure = 5.49 °C					
Heat of fusion at 5.49 °C = 127 J/g					
Liquid volume at 5.49 °C = 0.901 x 10 ⁻³ m ³ /Kg					
Volume change on melting = 0.1317 x 10 ⁻³ m ³ /Kg					

25%

2. The heat of mixing data for the n-octanol + n-decane liquid mixture at atmospheric pressure is approximately fit by

$$\Delta H_{\text{mix}} = x_1 x_2 (A + B(x_1 - x_2)) \quad \text{J/mol}$$

where $A = -12974 + 51.505T$

and $B = 8782.8 - 34.129 T$

with T in K and x_1 being the n-octanol mole fraction.

- (a) Compute the difference between the partial molar and pure component enthalpies of n-octanol and n-decane at $x_1 = 0.5$ and $T = 300 \text{ K}$.
- (b) Compute the difference between the partial molar and pure component heat capacities of n-octanol and n-decane at $x_1 = 0.5$ and $T = 300 \text{ K}$.



10 %

3. (a) Give definition of Gibbs free energy G and Helmholtz free energy A , respectively?
 (b) What is the relationship between Gibbs free energy G and Helmholtz free energy A ?
 (c) What is the criterion for a spontaneous process at constant temperature & pressure and a process at constant temperature & volume, respectively?

20 %

4. One mole of an ideal gas, $C_p = (7/2)R$ and $C_v = (5/2)R$, expands from $P_1 = 10$ bar and $V_1 = 0.005$ m³ to $P_2 = 1$ bar by each of the following paths:
 (a) Constant volume.
 (b) Constant temperature.
 (c) Adiabatically.

Assuming mechanical reversibility, calculate W , Q , ΔU , and ΔH for each process.

20 %

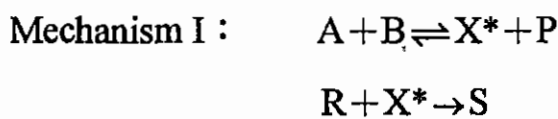
5. It is possible to cool liquid water below its freezing point of 273.15 K without the formation of ice if care is taken to prevent nucleation. A kilogram of subcooled liquid water at 263.15 K is contained in a well-insulated vessel. Nucleation is induced by the introduction of a speck of dust, and a spontaneous crystallization process ensues. Find the final state of the water, and calculate the entropy change of the water, the surroundings, and the total entropy change. $C_p = 4.185$ kJ/kg · K for liquid water and is assumed constant over the temperature range. Heat of fusion of ice is 334 kJ/kg.



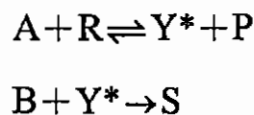
1. Reactants A, B, and R combine to give P and S with stoichiometry $A+B+R=P+S$. After the reaction has proceeded to a significant extent, the observed rate is

$$r_p = kC_A C_B C_R / C_P$$

The following two mechanisms involving formation of active intermediate have been proposed to explain the observed kinetics.

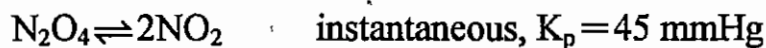
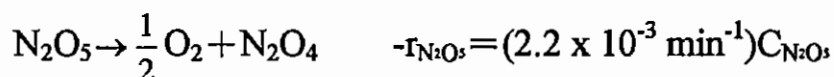


Mechanism II :



- (a) Are these mechanisms consistent with the kinetic data? (16%)
 (b) If both are consistent, how would you be able to choose between them? (4%)

2. Nitrogen pentoxide decomposes as follows :



Find the partial pressures of the contents of a constant-volume reactor after 7 hr if we start with pure N_2O_5 at atmospheric pressure. (20%)

3. At 600°K the rate of a bimolecular reaction is ten times the rate at 500°K. Find the activation energy of this reaction :

- (a) From Arrhenius' law. (5%)
 (b) From collision theory. (5%)



4. (a). The aqueous reaction $A + B \rightarrow$ products with known kinetics: $-r_A = kC_A C_B$ ($k = 500$ liter/mol.min) is to take place in an experimental plug flow reactor under the following conditions: volume of reactor = 0.1 liter, volumetric feed flow rate = 0.05 liter/min, and feed concentration $C_{A0} = C_{B0} = 0.01$ mol/liter.

- (i). Show that the performance equation for this reaction is:

$$k \tau C_{A0} = X_A / (1 - X_A)$$

where X_A is the conversion of species A and τ is the space-time.

- (ii). What conversion of reactants can be expected? (8%)

- (b). Instead, when a mixed flow reactor is used,

- (i). For the same conversion as part (a), what size of mixed flow reactor is needed?

- (ii). What conversion can be expected in a mixed flow reactor equal in size to the plug flow reactor? (8%)

5. The desired liquid-phase reaction



is accompanied by the unwanted side reaction



- (a). In order to favor formation of R, the concentrations of the two reactants (C_A and C_B) should be both high, both low, or one high and the other low? Explain the reason. (5%)



(b). Equal volumetric flow rates of the A and B streams are fed to the reactor, and each stream has a concentration of 20 mol/liter of reactant. For 90% conversion of A, find the concentration of R in the product stream when the flow in the reactor flows: (i). plug flow and (ii). mixed flow. (12%)

6. At room temperature sucrose is hydrolyzed by the catalytic action of the enzyme sucrase as follows: sucrose $\xrightarrow{\text{sucrase}}$ products. The rate law for this enzyme-catalyzed reaction is:

$$-r_S = kC_{E0}C_S / (K_m + C_S) \quad (\text{Michaelis-Menten equation})$$

where $-r_S$ is the rate of disappearance of the substrate, C_S is the concentration of the substrate, C_{E0} is the total concentration of sucrase, and K_m is the Michaelis constant.

(a). If the reaction is carried out in a batch reactor, show that the concentration-time behavior is:

$$kC_{E0}t = K_m \ln(C_{S0}/C_S) + (C_{S0} - C_S)$$

where C_{S0} is the initial concentration of the substrate. (5%)

(b). Starting with a sucrose concentration $C_{S0} = 1.0$ mmol/liter and an enzyme concentration $C_{E0} = 0.01$ mmol/liter, the following kinetic data are obtained in a batch reactor:

C_S , mmol/liter	0.84	0.53	0.27	0.09	0.018
t, hr	1	3	5	7	9

Evaluate the rate constants: k and K_m . (12%)



1. (20%) Considering a fluid flow through a control volume as shown in Figure 1, if dA is a small area on the control surface, n is the unit normal vector of dA , v is the velocity vector of fluid flow, θ is the angle between the two vectors, ρ is the density of the fluid, V is the control volume, what are the physical meanings of each integration term expressed in equations [1] and [2]?

$$\oint \rho(v \cdot n) dA + \frac{\partial}{\partial t} \iiint \rho dV = 0 \quad [1]$$

$$\oint v \cdot \rho(v \cdot n) dA + \frac{\partial}{\partial t} \iiint \rho v dV \quad [2]$$

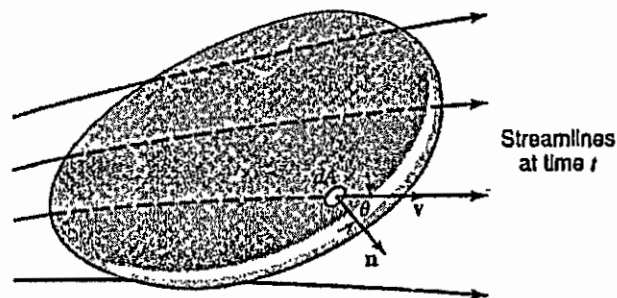


Figure 1. Fluid flow through a control volume.

2. (20%) In a gas absorption experiment a viscous fluid (viscosity = μ) flows upward through a small circular tube (outer radius = R) and then downward in laminar flow on the outside. If the film thickness ξ is very small. What is the mass flow rate of flow in the film?
3. (20%) A shell and tube heat exchanger is used to heat water (in the tube side) from 25°C to 40°C at a mass flow rate of 4 kg/sec . The fluid used for heating (shell side) is water (entering temperature of 90°C) with mass flow 2 kg/sec . A single shell pass is utilized. The overall heat transfer coefficient (based on inside tube area) is $1400 \text{ W/(m}^2\text{C)}$. Tubes are inside diameter of 1.88 cm and required an average water velocity of 0.38 m/sec . Available unit floor space limits the tube length to 2.5 m . The density and heat capacity of water are considered as constants. What is tubes per pass and tube length?
4. (20%) Consider the simple "rotating disk" process unit shown in Figure 2 for the treatment of phenol (species A) in waste water. The biofilm contains a microorganism rich in the enzyme peroxidase that oxidatively degrades phenol. The



concentration of species A in the bulk-fluid phase over the biofilm is constant if the fluid phase is well mixed. However, the concentration of A within the biofilm will decrease along the depth of the biofilm z as species A is degraded. There are no resistances to convective mass transfer across the fluid boundary layer between the bulk fluid and biofilm surface. Furthermore, phenol is equally soluble in both water and the biofilm, and the density difference between the biofilm and water can be neglected, so that the surface concentration of phenol in the aqueous phase equals the surface concentration of phenol in the gel phase just inside the biofilm, i.e., at $z = 0$, $C_{As} = C_{A0}$.

It is desired to treat 0.3 m^3 per hour of waste water containing $0.2 \text{ mol}\cdot\text{m}^{-3}$ of the toxic substance phenol. If the biofilm thickness is 2.0 mm , what is the required surface area of the biofilm necessary to achieve the desired outlet concentration of $0.05 \text{ mol}\cdot\text{m}^{-3}$? The rate of degradation of the toxic solute per unit volume of the biofilm is described by a kinetic rate equation of the form $R_A = -k_1 C_A$. The kinetic constant k_1 is $1.9 \times 10^{-2} \text{ sec}^{-1}$ and $D_{AB} = 2.0 \times 10^{-10} \text{ m}^2\cdot\text{sec}^{-1}$ at the process temperature of 25°C .

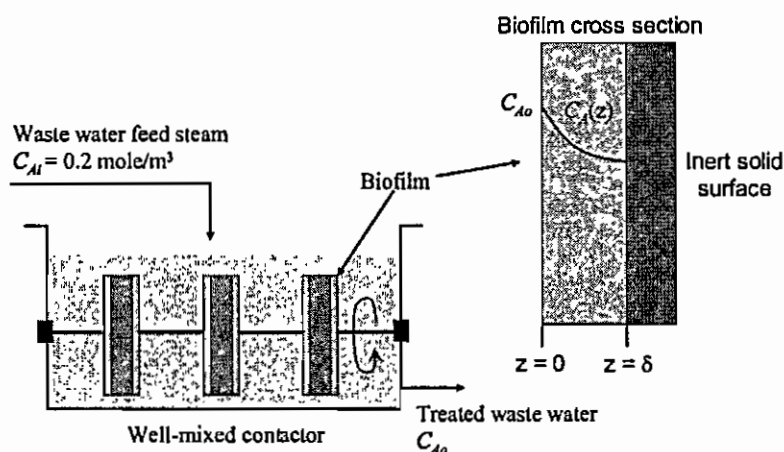


Figure 2. Biofilm for waste water treatment.

5. (20%) Considering a problem of drug dosage as shown in Figure 3, once inside the body, the capsule slowly releases the drug by a diffusion-limited process. A water-soluble drug (species A) is uniformly dissolved within the gel loaded in the spherical bead, and has an initial concentration C_{A0} . Consider a limiting case where the resistance to film mass transfer of the drug through the liquid boundary layer surrounding the capsule surface to the bulk surrounding fluid is negligible. Furthermore, assume that the drug is immediately consumed or swept away once it reaches the bulk solution. In this particular limiting case, C_{As} can be regarded as



zero, so at a long time the entire amount of drug initially loaded into the bead will be depleted. According to the situations as mentioned above, please derive a partial differential equation for the concentration profile of species A and give a set of boundary condition to obtain the concentration profile, $C_A(r, t)$. The radius of the bead is R and the diffusivity of the species A is D_{AB} . In addition, what is the center concentration (i.e., at $r = 0$) with time?

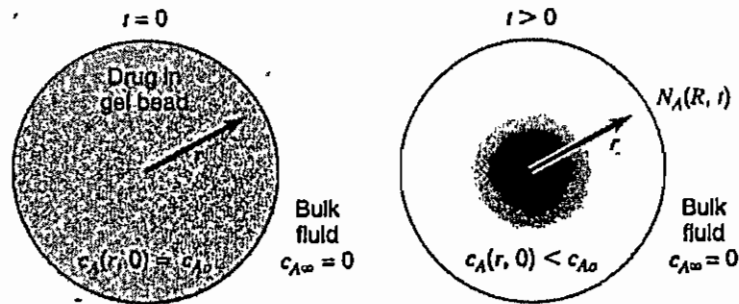


Figure 3. Drug release from a spherical gel bead.