

Problem 1 (10%) Describe Raoult's law and Henry's law as well as their applicability and limits.

Problem 2 (15%) A heat engine receives heat from a source at 1200 K at a rate of 500 kJ/s, and it rejects the waste heat to a medium at 450 K. The measured power output of the heat engine is 280 kW, and the environment temperature is 25°C. Determine (a) the reversible power, (b) the rate of irreversibility, and (c) the second-law efficiency of this heat engine.

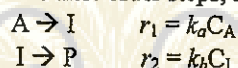
Problem 3 (15%) Derive a relation for the internal energy change as a gas that obeys the van der Waals equation of state. Assume that in the range of interest C_v varies according to the relation, where

$$C_v = C_1 + C_2 T + C_3 T^2 \text{ are constants.}$$

Problem 4 (10%) One enzyme catalyzed reaction in a biochemical cycle has an equilibrium constant that is 5 times the equilibrium constant of a second reaction. If the standard Gibbs energy of the former reaction is -200 kJ mol^{-1} , what is the standard reaction Gibbs energy of the second reaction?

Problem 5 (27%)

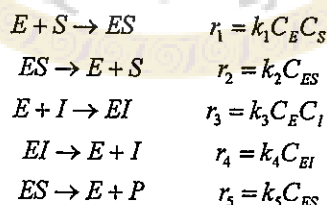
The restriction enzyme EcoRI catalyzes the cleavage of DNA at a specific sequence of nucleotides. The reaction sequence it brings about is: supercoiled DNA (A) \rightarrow open-circle DNA (I) \rightarrow linear DNA (P). Let's suppose that the reaction takes place in two first-order steps, and the reverse reactions can be ignored.



- Show that a common feature of all first-order reactions is that the concentration of the reactant decays exponentially with time. (5%)
- Derive $C_A(t)$, $C_I(t)$, and $C_P(t)$ (molar concentrations of A, I, and P at time t) using the steady-state approximation to the consecutive first-order mechanism. The initial concentration of A is C_{A0} . (12%)
- Briefly describe the difference between (i) the method of initial rates and (ii) the method of integrated rate laws for determination of k_a . (6%)
- Since the reaction is an enzymatic reaction, describe what main assumption is made from the aspect of Michaelis-Menten kinetics for the above discussion. (4%)

Problem 6 (23%)

The mechanism for an enzymatic reaction in the presence of a competitive inhibitor I can be described by the following reactions.



where E, S, I, and P represent the enzyme, substrate, inhibitor, and product, respectively. ES and EI are the intermediate complexes.

- Assume $r_1 \cong r_2$ and $r_3 \cong r_4$. Show that $1/r_5$ is linearly correlated to $1/C_S$. (8%)
- If the enzyme E reduces the activation energy for the conversion of S to P from 57 kJ mol^{-1} to 9 kJ mol^{-1} . This corresponds to an acceleration of the reaction by a factor of 10^N at 300 K. $N = ?$ (Set $\log e \cong 0.43$ and $R \cong 8.0 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ for quick calculation.) (7%)
- Derive the residence time (τ) for the above enzyme reaction carried out in a CSTR under the following operating conditions: the reactor volume is V ; the volumetric flow rate is F ; the substrate concentrations in the inlet and outlet streams are C_{S0} and C_S , respectively. (8%)