Problem 1 (10%) Describe Raout'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 $C_v = C_1 + C_2 T + C_3 T^2$ 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) → open-circle DNA (I) → linear DNA (P).
Let's suppose that the reaction takes place in two first-order steps, and the reverse reactions can be ignored.

$$A \rightarrow I \qquad r_1 = k_a C_A$$
$$I \rightarrow P \qquad r_2 = k_b C_I$$

(a) Show that a common feature of all first-order reactions is that the concentration of the reactant decays exponentially with time. (5%)
(b) 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%)
(c) 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%)
(d) 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.

$$E + S \rightarrow ES \qquad r_1 = k_1 C_E C_S$$
$$ES \rightarrow E + S \qquad r_2 = k_2 C_{ES}$$
$$E + I \rightarrow EI \qquad r_3 = k_3 C_E C_I$$
$$EI \rightarrow E + I \qquad r_4 = k_4 C_{EI}$$
$$ES \rightarrow E + P \qquad r_5 = k_5 C_{ES}$$

where E, S, I, and P represent the enzyme, substrate, inhibitor, and product, respectively. ES and EI are the intermediate complexes.
(a) 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%)
(b) 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 ≅ 0.43 and R ≅ 8.0 J·mol^{-1}·K^{-1} for quick calculation.) (7%)
(c) 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%)