$R = 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $k = 1.381 \times 10^{-23}\,\mathrm{m^2\,kg\,s^{-2}\,K^{-1}}$, $1\,\mathrm{amu} = 1.661 \times 10^{-27}\,\mathrm{kg}$

Consider the reaction $2A \xrightarrow{k} P$ at constant temperature and volume. Let the concentration of A, [A], be given in terms of a measurable property Z by $Z = B\exp(b[A]t)$ where B and b are constants depending only on temperature and t denotes the time.

1. *(4 points)* Express the rate of the reaction in terms of rate of variation of Z.
2. *(4 points)* If the reaction is second order, obtain an expression for the specific rate constant k in terms of known quantities.

The steps of a proposed mechanism for the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ is given below in arbitrary order. For your information, the bond dissociation energies of H_2, HBr, HCl, Br_2, and Cl_2 are $432\,\mathrm{kJ\,mol^{-1}}$, $363\,\mathrm{kJ\,mol^{-1}}$, $428\,\mathrm{kJ\,mol^{-1}}$, $190\,\mathrm{kJ\,mol^{-1}}$, and $239\,\mathrm{kJ\,mol^{-1}}$, respectively.

$$Cl^{\cdot} + Cl^{\cdot} + M \xrightarrow{k_1} Cl_2 + M \qquad (1)$$

$$Cl^{\cdot} + H_2 \xrightarrow{k_2} H^{\cdot} + HCl \qquad (2)$$

$$Cl_2 + M \xrightarrow{k_3} Cl^{\cdot} + Cl^{\cdot} + M \qquad (3)$$

$$H^{\cdot} + Cl_2 \xrightarrow{k_4} Cl^{\cdot} + HCl \qquad (4)$$

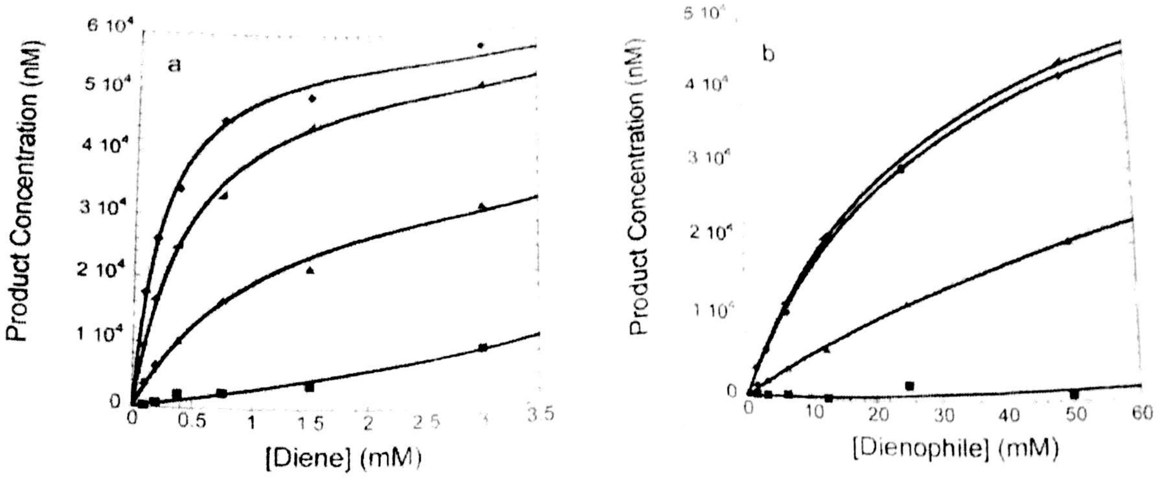
3. *(4 points)* Identify the initiation, propagation, and termination steps in this mechanism. In what way is this mechanism different from that of the $H_2 + Br_2$ reaction discussed in class?
4. *(3 points)* The steady state approximation (SSA) is not applicable in this case. With the help of a figure for a model case, illustrate why the SSA might not be applicable here.
5. *(3 points)* Under identical conditions do you expect this reaction to be faster or slower than the $H_2 + Br_2$ reaction? Why?
6. *(4 points)* SSA is applicable when this reaction is conducted in the presence of around 1% O_2 or greater. Under these conditions the following termination steps dominate:

$$H^{\cdot} + O_2 + M \xrightarrow{k_5} {}^{\cdot}HO_2 + M \qquad (5)$$

$$Cl^{\cdot} + O_2 + M \xrightarrow{k_6} {}^{\cdot}ClO_2 + M \qquad (6)$$

Set up, but DO NOT SOLVE, the steady state approximation for all the relevant species when H_2 and Cl_2 react in the presence of O_2.

In a recent paper Baker and coworkers computationally designed four enzymes to catalyze the reaction of a diene with a dienophile, the Diels-Alder reaction. The product concentration in 3.0 hour when the enzyme concentration is 10 µmol is given below. In the figure on the left the dienophile concentration is fixed at 50 mmol, while on the right the diene concentration is fixed at 3 mmol. The different curves in the figure give the data for the four enzymes, denoted by different symbols.



7. *(2 points)* Identify (with the symbol) the most efficient enzyme in the figure on the left. Justify your answer.

8. *(3 points)* List the steps involved to determine the kinetic parameters from data of the type given in the figure.

For the elementary reaction $CH_3 + H_2 \longrightarrow CH_4 + H$ at $T = 300\,K$, the measured Arrhenius pre-exponential factor is $6.7 \times 10^{12}\,cm^3\,mol^{-1}\,s^{-1}$ and activation energy is $40.7\,kJ\,mol^{-1}$.

9. *(4 points)* Calculate the steric or orientation factor, P, according to collision theory for this reaction at $T = 300\,K$. The cross sectional areas are $4.0 \times 10^{-19}\,m^2$ for CH_3 and $2.7 \times 10^{-19}\,m^2$ for H_2. The average velocity is $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$.

10. *(4 points)* What are the activation enthalpy and entropy for this reaction?

11. *(5 points)* Consider a surface-catalyzed bimolecular reaction between molecules A and B that has a rate law of the form $v = k_{obs}\theta_A\theta_B$ where θ_A is the fraction of surface sites occupied by reactant A and θ_B is the fraction of surface sites occupied by reactant B. A mechanism consistent with this reaction is as follows:

$$A(g) + S(s) \underset{k_d^A}{\overset{k_a^A}{\rightleftharpoons}} A{-}S(s) \quad \text{fast equilibrium} \tag{7}$$

$$B(g) + S(s) \underset{k_d^B}{\overset{k_a^B}{\rightleftharpoons}} B{-}S(s) \quad \text{fast equilibrium} \tag{8}$$

$$A{-}S(s) + B{-}S(s) \xrightarrow{k_3} \text{products} \tag{9}$$

Take K_A and K_B to be the equilibrium constants for equations 7 and 8, respectively. Derive an expression for θ_A in terms of p_A, p_B, K_A, and K_B.