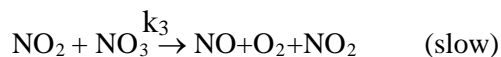
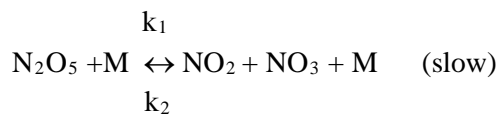


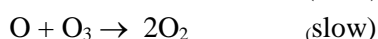
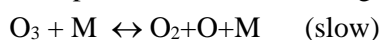
**PROBLEM SET 4**  
**(Mechanism of Chemical Reactions)**

1. The mechanism for the decomposition of  $N_2O_5$  is



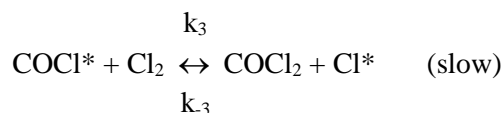
and the overall reaction is  $2N_2O_5 \rightarrow 4NO_2 + O_2$ . Find the rate expression.

2. The decomposition of ozone in the gas phase  $2O_3 \rightarrow 3O_2$  takes place through the following mechanism

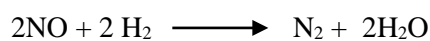


Derive the rate law.

3. Derive the rate expression for the reaction  $CO + Cl_2 \leftrightarrow COCl_2$  if the mechanism of the reaction is as follows:



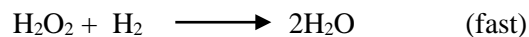
4. For the reaction



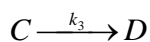
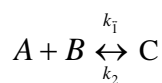
The rate expression for this reaction is given to be third order.

$$r_{N_2} = k [NO]^2 [H_2]$$

Show that the mechanism given below is consistent with this rate equation.

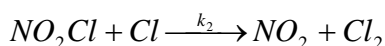
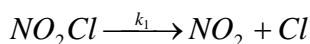


5. Consider the following mechanism:



- (a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.  
 (b) Assuming that  $k_3 \ll k_2$ , express the pre-exponential factor A and  $E_a$  for the apparent second order rate constant in terms  $A_1, A_2$  and  $A_3$  and  $E_{a1}, E_{a2}$  and  $E_{a3}$  for the three steps.

6. The reaction  $\text{NO}_2\text{Cl} = \text{NO}_2 + \frac{1}{2} \text{Cl}_2$  is first order and appears to follow the mechanism

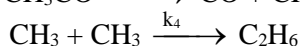
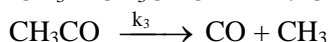
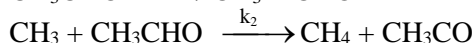
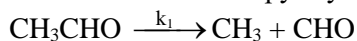


(a) Assuming a steady state for the chlorine atom concentration, show that the empirical first order rate constant can be identified with  $2k_1$

(b) The following data were obtained at 180 °C. In a single experiment the reaction is first order, and the empirical rate constant is represented by  $k$ . Show that the reaction is second order at these low gas pressures and calculate the second order rate constant.

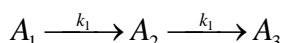
$c/10^{-8}\text{mol cm}^{-3}$	5	10	15	20
$k/10^{-4}\text{ s}^{-1}$	1,7	3,4	5,2	6,9

7. The mechanism of the pyrolysis of acetaldehyde at 520 °C and 0.2 bar is

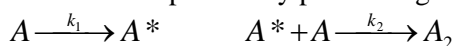


What is the rate law for the reaction of acetaldehyde, using the usual assumptions? (As a simplification further reactions of the radical CHO have been omitted and is the rate equation may be ignored.)

8. The equations for  $[\text{A}_2]$  and  $[\text{A}_3]$  in section 18.4 give an indeterminate result if  $k_1=k_2$ . Rederive the equations, giving  $[\text{A}_2]$  and  $[\text{A}_3]$  as functions of time for the special case that

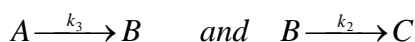


9. A dimerization  $2\text{A} \longrightarrow \text{A}_2$  is found to be first order with a half life of 666 s. This somewhat surprising result is explained by postulating the following mechanism



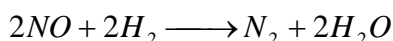
Where  $k_2 \gg k_1$  (a) What is the value for the rate constant  $k_1$ ? (b) if the initial concentration of A is 0.05 M, how much time is required to reach  $[\text{A}] = 0.0125 \text{ M}$ ?

10. Consider two consecutive first order nuclear decay reactions with the rate constants  $k_1$  and  $k_2$



If  $k_1=k_2=0.1340 \text{ year}^{-1}$ , draw  $[\text{B}]/[\text{A}]_0$  plot.

11. For the reaction



The overall rate expression is third order.

$$R_{\text{N}_2} = k[\text{NO}]^2[\text{H}_2]$$

Show that two mechanism below consistent with rate equation

