CYL110 2012-2013 Kinetics Tutorial 2

1. The decomposition of ozone $2O_3 \rightarrow 3\ O_2(g)$ occurs by the reaction mechanism

$$\begin{aligned} M(g) + O_3(g) &= O_2(g) + O(g) + M(g) \\ O(g) + O_3(g) &\rightarrow 2O_2(g) \end{aligned}$$

   where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but does not react. Use this mechanism to derive the rate law for $d[O_3]/dt$ assuming that O(g) can be treated by a steady state approximation(SSA)($-1/2 d[O_3]/dt = k_1 k_2 [O_3]^2[M]/(k_{-1}[O_2][M] + k_2[O_3])$)

2. Explain why in the previous problem either (a) $v_{-1} >> v_2$ and $v_{-1} >> v_1$ or (b) $v_2 >> v_{-1}$ and $v_2 >> v_1$ must be true for the SSA to apply. The rate law for the decomposition reaction is found to be $d[O_3]/dt = -k[O_3][M]$. Is this rate law consistent with the conditions given by either (a) or (b) or both? ((b))

3. The experimental rate constants for a reaction at various temperatures are tabulated below. Determine the Arrhenius parameters A and E_a. ($A = 7.39 \times 10^9$ dm^3 mol^{-1} s^{-1}; $E_a = 9.9$ kJ mol^{-1})

T	292	296	321	333	343	363
K/10^8dm^3 mol^{-1} s^{-1}	1.24	1.32	1.81	2.08	2.29	2.75

4. The rate of nitrogen elimination by an enzyme on a substrate was measured for a series of substrate concentrations [S]. Determine the Michaelis constant for the reaction.[$K_M = 0.01$ mol dm^{-3}]

10^2[S]/mol dm^{-3}	5.0	3.0	1.0	0.50	0.20
R/mm^3 min^{-1}	16.7	15.0	10.0	6.67	3.33

5. The turnover number is defined as the ratio of the number of moles of reactant that react per second to the number of moles of enzyme present. 8.0 μg of the enzyme carbonic anhydrase (molecular mass 30000 g mol^{-1}) catalyzes the hydration of 0.146 g of CO_2 in 30 seconds. Estimate the turnover number.

6. Suppose that a substance X decomposes into A and B in parallel paths with rate constants given by $k_A = 10^{15}$ s^{-1} exp(−126000/RT) and $k_B = 10^{13}$ s^{-1} exp(−83700/RT) where the activation energies are given in J mol^{-1}. (a) At what temperature will the two products be formed at the same rate? (b) At what temperature will A beformed 0.1 as fast as B? (c) State a generalization concerning the effect of temperature on the relative rates of reactions with different activation energies.

7. (a) Briefly explain the difference between order and molecularity of a reaction. (b) Using the Lindemann mechanism of unimolecular reactions discuss the steady state approximation and its validity in terms of the formation and consumption of A*.[F98]

8. A certain reaction is 20% complete in 15 min. at 313 K and in 3 min. at 333 K. Estimate its activation energy.[F98]

9. A proposed mechanism for the reaction of nitramide in water is

$$\begin{aligned} O_2NNH_2 &\rightleftharpoons O_2NNH^- + H^+ \\ O_2NNH^- &\rightarrow N_2O + OH^- \\ H^+ + OH^- &\rightarrow H_2O \end{aligned}$$

   The experimentally observed rate law for the reaction is $\frac{k_{obs}[O_2NNH_2]}{[H^+]}$. (a) What is the overall reaction? (b) What are the units of k_{obs}? (c) Under what conditions is this mechanism consistent with the rate law? (d) Express k_{obs} in terms of the rate constants of the elementary reactions. (e) With this mechanism as an example explain the concept of rate determining step.[F98]

10. An autocatalytic reaction is one where one of the products catalyses the reaction. Derive an integrated rate law for the autocatalytic reaction A → P given that $-d[A]/dt = k\,[A][P]$ and initial [A] = a, [P] = p.[F00]

11. The chlorination of an organic molecule (M) to give P may proceed by the following mechanism: (i) $Cl_2 \rightarrow 2Cl$ (ii) $Cl + M \rightarrow R$ (iii) $R + Cl_2 \rightarrow P + Cl$ (iv) $Cl + Cl \rightarrow Cl_2$. (a) Setup the rate expressions for Cl, R, and P. (b) Apply the steady state approximation to the intermediate species and obtain the rate law. [F00]

12. A reaction A + B + C → D follows the mechanism (i) A + B ⇌ AB (ii) AB + C → D, in which the first step remains essentially in equilibrium. (a) Derive the expected rate law and express k_{obs} in terms of the rate constant of the elementary reactions. (b) If ΔH and E_a are the enthalpy change for the first step and the activation energy of the second step respectively, show that the dependence of k_{obs} on temperature is given by $k_{obs} = Ae^{-(E_a+\Delta H)/RT}$.[F01]

13. Ethyl acetate hydrolysis by aqueous NaOH follows the rate law $k_{obs}[CH_3COOC_2H_5][OH^-]$. The reaction occurs by the following mechanism

$$\begin{aligned} CH_3COOC_2H_5 + OH^- &\rightleftharpoons CH_3CO^-(OH)OC_2H_5 \\ CH_3CO^-(OH)OC_2H_5 &\rightarrow CH_3COOH + C_2H_5O^- \\ CH_3COOH + C_2H_5O^- &\rightarrow CH_3COO^- + C_2H_5OH \end{aligned}$$

Write the rates of formation of all the intermediate species? Under what conditions does this mechanism give the observed rate law? For these conditions, express k_{obs} in terms of the individual steps of the reaction mechanism.[F98]

14. The mechanism for the nitrogen pentoxide catalyzed decomposition of ozone is given below. Derive a rate law for the reaction by using the steady state approximation.[M02]

$$\begin{aligned} N_2O_5 &\xrightarrow{k_1} NO_2 + NO_3 \\ NO_2 + NO_3 &\xrightarrow{k_2} N_2O_5 \\ NO_2 + O_3 &\xrightarrow{k_3} NO_3 + O_2 \\ NO_3 + NO_3 &\xrightarrow{k_4} 2NO_2 + O_2 \end{aligned}$$

15. (a) Derive the rate law for the Michaelis-Menton mechanism for enzyme catalysis. (b) The enzyme carbonic anhydrase catalyzes the reaction $CO_2 + H_2O \rightarrow HCO_3^- + H^+$. When CO_2 is present in excess the Michaelis constant and turnover number are 1.2×10^{-2} M and 1×10^6 s^{-1}, while in the presence of excess HCO_3^- they are 2.6×10^{-2} M and and 4×10^5 s^{-1} respectively. Determine ALL the rate constants for the elementary steps in the reaction mechanism.[M02]

16. One suggested mechanism for the reaction

$$S_2O_8^{2-} + 3I^- \rightarrow 2SO_4^{21} + I_3^-$$

is:

$$S_2O_8^{2-} + I^- \rightleftharpoons SO_4I^- + SO_4^{2-} \text{ (rapid)}$$

$$I^- + SO_4I^- \xrightarrow{k_1} I_2 + SO_4^{2-} \text{ (slow)}$$

$$I^- + I_2 \xrightarrow{k_2} I_3^- \text{ (fast)}$$

while another is:

$$S_2O_8^{2-} + I^- \xrightarrow{k_1} S_2O_8I^{3-} \text{ (slow)}$$

$$S_2O_8I^{3-} \xrightarrow{k_2} I^+ + 2SO_4^{2-} \text{ (fast)}$$

$$I^- + I^+ \xrightarrow{k_3} I_2 \text{ (fast)}$$

$$I^- + I_2 \xrightarrow{k_4} I_3^- \text{ (fast)}$$

The reaction is first order both with respect to the persulfate and iodide ions. (i) Derive the rate laws for these two mechanisms (ii) Discuss whether the reaction could proceed according to either or both of these mechanisms.