

UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet VIII

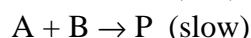
- 1 (a) (i) The rate of the reaction  $A + 2B \rightarrow 3C + D$  was reported as  $1.0 \text{ mol L}^{-1} \text{ s}^{-1}$ . State the rates of formation and consumption of the participants.
- (ii) The rate of formation of C in the reaction  $2A+B \rightarrow 2C+3D$  is  $1.0 \text{ mol L}^{-1} \text{ s}^{-1}$ . State the reaction rate, and the rates of formation or consumption of A, B, and D.
- (iii) The rate law for the reaction in (i) was found to be  $v = k[A][B]$ . What are the units of  $k$ ? Express the rate law in terms of the rates of formation and consumption of: (a) A, (b) C.
- (iv) The rate law for the reaction in (ii) was reported as  $d[C]/dt = k[A][B][C]$ . (a) Express the rate law in terms of the reaction rate. (b) What are the units for  $k$  in each case?
- (b) (i) At  $518^\circ\text{C}$ , the rate of decomposition of a sample of gaseous acetaldehyde (ethanal), initially at a pressure of 363 Torr, was  $1.07 \text{ Torr s}^{-1}$  when 5.0 per cent had reacted and  $0.76 \text{ Torr s}^{-1}$  when 20.0% had reacted. Determine the order of the reaction.
- (ii) Repeat the calculation if you were told that at the same temperature, the half-life for the this reaction initially at 363 Torr was 410 s whilst when the pressure was 169 Torr, the half-life was 880 s.
- (c) The rate constant for the first-order decomposition of  $\text{N}_2\text{O}_5$  in the reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  is  $k = 3.38 \times 10^{-5} \text{ s}^{-1}$  at  $25^\circ\text{C}$ . What is the half-life of  $\text{N}_2\text{O}_5$ ? What will be the pressure, initially 500 Torr, (a) 10s, (b) 10 min after initiation of the reaction?
- (d) A second-order reaction of the type  $A + B \rightarrow P$  was carried out in a solution that was initially  $0.050 \text{ mol L}^{-1}$  in A  $0.080 \text{ mol L}^{-1}$  in B. After 1.0 h the concentration of A had fallen to  $0.020 \text{ mol L}^{-1}$ . (a) Calculate the rate constant. (b) What is the half life of the reactants?
- (e) The second-order rate constant for the reaction:  
 $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{CH}_3\text{CH}_2\text{OH}(\text{aq})$   
is  $0.11 \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the concentration of ester after (a) 10s, (b) 10 min that the ethyl acetate is added to sodium hydroxide given that the initial concentrations are  $[\text{NaOH}] = 0.050 \text{ M}$  and  $[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.100 \text{ mol L}^{-1}$ ?
- (f) (i) A reaction  $2A \rightarrow P$  has a second-order rate law with  $k = 3.05 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ . Calculate

the time required for the concentration of A to change from  $0.260 \text{ mol L}^{-1}$  to  $0.011 \text{ mol L}^{-1}$ .

(ii) A reaction  $2A \rightarrow P$  has a third-order rate law with  $k = 3.05 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-2}$ . Calculate the time required for the concentration of A to change from  $0.077 \text{ mol L}^{-1}$  to  $0.021 \text{ mol L}^{-1}$ .

(g) The rate constant for the decomposition of two different substances are: (a)  $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $30^\circ\text{C}$  and  $1.38 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $50^\circ\text{C}$ , and (b)  $1.70 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $24^\circ\text{C}$  and  $2.01 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $37^\circ\text{C}$ . Evaluate the Arrhenius parameters for these reactions.

(h) The reaction mechanism



involves an intermediate A. Deduce the rate law for the reaction.

(g) Consider the following mechanism for renaturation of a double helix from its strands A and B:



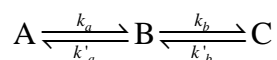
Derive the rate equation for the formation of the double helix and express the rate constant of the renaturation reaction in terms of the rate constants of the individual steps.

(h) The equilibrium  $A \rightleftharpoons B$  is first-order in both directions. Derive an expression for the concentration of A as a function of time when the initial molar concentrations of A and B are  $[A]_0$  and  $[B]_0$ . What is the final composition of the system?

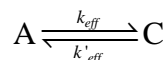
(i) Derive an integrated expression for a second-order rate law  $v = k[A][B]$  for a reaction of stoichiometry  $2A + 3B \rightarrow P$ .

(j) Derive the integrated form of a third-order rate law  $v = k[A]^2[B]$  in which the stoichiometry is  $2A + B \rightarrow P$  and the reactants are initially present in (a) their stoichiometric proportions, (b) with B present initially in twice the amount.

(k) (i) Set up the rate equations for the reaction mechanism:



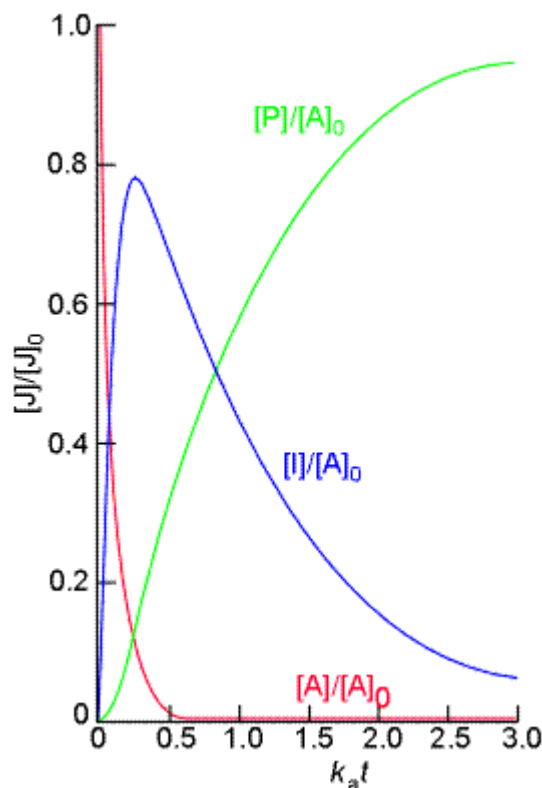
(ii) Show that the mechanism in (i) is equivalent to:



under special circumstances.

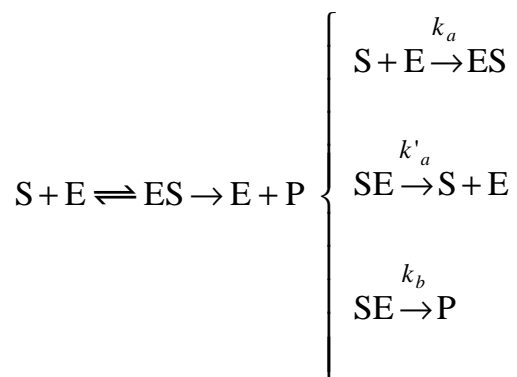
(l) Derive an equation for the steady-state rate of the sequence of reactions  $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons D$ , with  $[A]$  maintained at a fixed value and the product D removed as soon as it is formed.

- (m) For the consecutive reaction  $A \rightarrow I \rightarrow P$ , the figure below shows  $[I]$  plotted against time for  $k_a=10k_b$ .



For  $[A]_0 = 1.0 \text{ molL}^{-1}$  and  $k_a = 1.0 \text{ min}^{-1}$ , plot  $[I]$  against  $t$  for  $k_a/k_b = 5, 1$ , and  $0.5$ . For each case determine the time at which  $[I]$  reaches a maximum.

2. (a) (i) Prove that the rate of product P formation for an enzyme-catalyzed reaction proceeding through the Michaelis-Menten mechanism:



is given by:

$$\frac{d[P]}{dt} = k[E]_0$$

E and S represent the enzyme and substrate respectively,  $[E]_0$  is the initial concentration of the enzyme, and:

$$k = \frac{k_b[S]}{K_M + [S]}$$

where  $K_M$  is the Michaelis constant, given by:

$$K_M = \frac{k'_a + k_b}{k_a}$$

(ii) Show that if a reaction follows the Michaelis-Menten mechanism, then there is a linear relationship between  $1/k$  and  $1/[S]$  (x-axis) with a gradient of  $K_M/k_b$  and intercept of  $1/k_b$ . What do we call this plot?

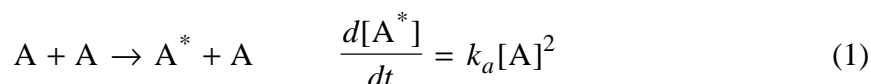
(iii) Obtain an expression the rate of formation of product and find its limiting behaviour for large and small concentrations of substrate for the Michaelis-Menten mechanism.

(iv) The enzyme-catalysed conversion of a substrate at  $25^\circ\text{C}$  has a Michaelis constant of  $0.035 \text{ mol L}^{-1}$ . The rate of the reaction is  $1.15 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  when the substrate concentration is  $0.110 \text{ mol L}^{-1}$ . What is the maximum velocity of this enzymolysis?

(v) The enzyme-catalysed conversion of a substrate at  $25^\circ\text{C}$  has a Michaelis constant of  $0.042 \text{ mol L}^{-1}$ . The rate of the reaction is  $2.45 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  when the substrate concentration is  $0.890 \text{ mol L}^{-1}$ . What is the maximum velocity of this enzymolysis?

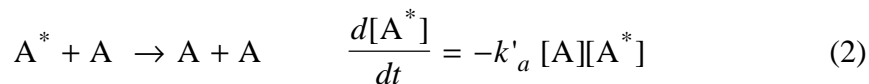
(vi) Many enzyme-catalysed reactions are consistent with a modified version of the Michaelis-Menten mechanism in which the second step (i.e.  $\text{ES} \rightarrow \text{E} + \text{P}$ ) is also reversible. For this mechanism obtain an expression the rate of formation of product and find its limiting behaviour for large and small concentrations of substrate.

- (b) Reactions such as the isomerisation of cyclopropane (reactant, A) to propene (product, P) proceeds according to the Lindemann-Hinshelwood (LH) mechanism can. According to this mechanism, the reaction takes off by having a molecule A getting energetically through a collision with another A molecule:

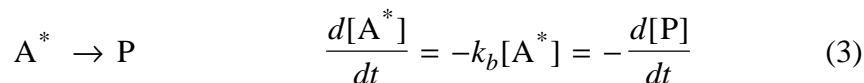


The energized molecule  $\text{A}^*$  might loose its excess energy either by:

- (1) Collision with another A molecule (forming no products), i.e.:



- (2) Shaking itself apart forming the **product** (the **unimolecular** step), i.e.:



Show that under different sets of conditions, the rate of product formation can be either first order in  $[\text{A}]$  or second order in  $[\text{A}]$ , or more specifically that:

$$\frac{d[P]}{dt} = k_{obs}[A] \quad \text{where} \quad \begin{cases} k_{obs} = \frac{k_a k_b}{k'_a} & \text{high [A]} \\ k_{obs} = k_a [A] & \text{low [A]} \end{cases}$$

Show also how this 'switch' in the rate can be demonstrated by a plot  $\log k_{obs}$  vs.  $\log [A]$ .

(ii) The effective rate constant for a gaseous reaction which has a Lindemann-Hinshelwood mechanism is  $2.50 \times 10^{-4} \text{ s}^{-1}$  at 1.30 kPa and  $2.10 \times 10^{-5} \text{ s}^{-1}$  at 12 Pa. Calculate the rate constant for the activation step in the mechanism.

(iii) Cyclopropane isomerizes into propene when heated to  $500^\circ\text{C}$  in the gas phase. The extent of conversion for various initial pressures has been followed by gas chromatography by allowing the reaction to proceed for a time with various initial pressures:

$p_o$ /Torr	200	200	400	400	600	600
$t$ /s	100	200	100	200	100	200
$p$ /Torr	186	173	373	347	559	520

where  $p_o$  is the initial pressure and  $p$  is the final pressure of cyclopropane. What are the order and rate constant for the reaction under these conditions?