

Department of Chemistry, Indian Institute of Technology Madras

CY 101 Assignments (CHEMICAL KINETICS)

All Batches

ODD Semester (July-November 2007)

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{ $K_B=1.38 \times 10^{-23}$ J/K, $h=6.626 \times 10^{-34}$ Js, $1\text{eV}=1.602 \times 10^{-19}$ J, $1\text{cm}^{-1}=1.9864 \times 10^{-23}$ J}
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1. The linear plot of the integrated Michaelis-Menten equation exhibits a y-intercept of 1000. If $[E_0] = 1\text{M}$, calculate the turn over number (rate constant of dissociation of enzyme-substrate complex).

The integrated Michaelis-Menten equation is

$$\frac{[S_0]-[S]}{t} = k_3[E_0] - \frac{K_M \ln \frac{[S_0]}{[S]}}{t}$$

Intercept, $k_3[E_0] = 1000$. Given that $[E_0] = 1\text{M}$, ie; k_3 (turn over number) = 1000.

2. What is the unit of the rate constant of a zero order reaction? Derive the expression for the half life.

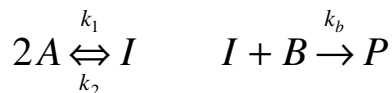


moles/sec.

$$-\frac{d[A]}{dt} = k \quad \text{Upon integration between limits, } [A] - [A_0] = -kt \quad \text{At } t_{1/2},$$

$$[A] = [A_0]/2. \text{ Hence } t_{1/2} = \frac{[A]_0}{2k}$$

3. Show that the following reaction is a third order reaction when pre-equilibrium assumption is valid.



Ans:

$$\frac{dP}{dt} = k_b[I][B]$$

$$\frac{d[I]}{dt} = k_1[A]^2 - k_2[I] - k_b[I][B] = 0$$

$$[I] = \frac{k_1[A]^2}{k_2 + k_b[B]}$$

$$\therefore \frac{dP}{dt} = k_b[I][B] = k_b \frac{k_1[A]^2[B]}{k_2 + k_b[B]}$$

Applying the condition for preequilibria

$$\frac{dP}{dt} = k_b[I][B] = k_b \frac{k_1[A]^2[B]}{k_2} = k_b K[A]^2[B]$$

4. Based on Lindemann theory, show that the overall rate constant for a unimolecular reaction $A \rightarrow P$, is given by

$$k_{uni} = \frac{k_{\infty}}{1 + \frac{k_{\infty}}{k_1[M]}}$$

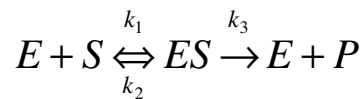
where k_{∞} is the overall rate constant at high pressure limit, k_1 is the rate constant of the formation of A^* and M is an inert gas.

Ans:

$$rate = k_2[A]^* = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2} = k_{uni}[A]$$

$$k_{uni} = \frac{k_1 k_2 [M]}{k_{-1}[M] + k_2} = \frac{\frac{k_1 k_2}{k_{-1}}}{1 + \frac{k_2}{k_{-1}[M]}} = \frac{k_{\infty}}{1 + \frac{k_1 k_2}{k_{-1}} \times \frac{1}{k_1[M]}} = \frac{k_{\infty}}{1 + \frac{k_{\infty}}{k_1[M]}}$$

5. Determine the unit of Michaelis-Menten constant in an enzyme catalyzed reaction



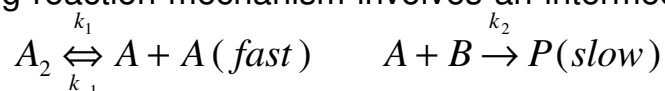
$$K_M = \frac{k_2 + k_3}{k_1} \text{ unit of } k_2 \text{ and } k_3 \text{ is } s^{-1}, \text{ and unit of } k_1 \text{ is } M^{-1}s^{-1}. \text{ Thus, unit of } K_M \text{ is } M.$$

6. A reaction follows the rate law. $\sqrt{A} - \sqrt{A_0} = -\frac{kt}{2}$. Find the order and units for k.

Substitute $n = 1/2$ which gives $\sqrt{A} - \sqrt{A_0} = -\frac{kt}{2}$

Units for k = mol ^{1/2} litre ^{-1/2} sec⁻¹

7. The following reaction mechanism involves an intermediate A. Deduce the rate law for the reaction.



Ans:

$$\frac{d[A]}{dt} = k_1[A_2] - k_{-1}[A]^2 - k_2[A][B]$$

$$[A]^2 = \frac{k_1[A_2] + k_2[A][B]}{k_{-1}}$$

Since k_2 is very low

$$[A] = \left(\frac{k_1[A_2]}{k_{-1}} \right)^{1/2}$$

$$\text{rate} = \frac{d[P]}{dt} = k_2[A][B] = k_2 \left(\frac{k_1[A_2]}{k_{-1}} \right)^{1/2} [B] = k_2 K^{1/2} [A_2]^{1/2} [B]$$

8. Calculate the bimolecular rate constant at 298 K for the reaction of two different small radicals with a reduced mass of 4.98×10^{-26} kg and a collision diameter of 500 pm

Ans: $2.17 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

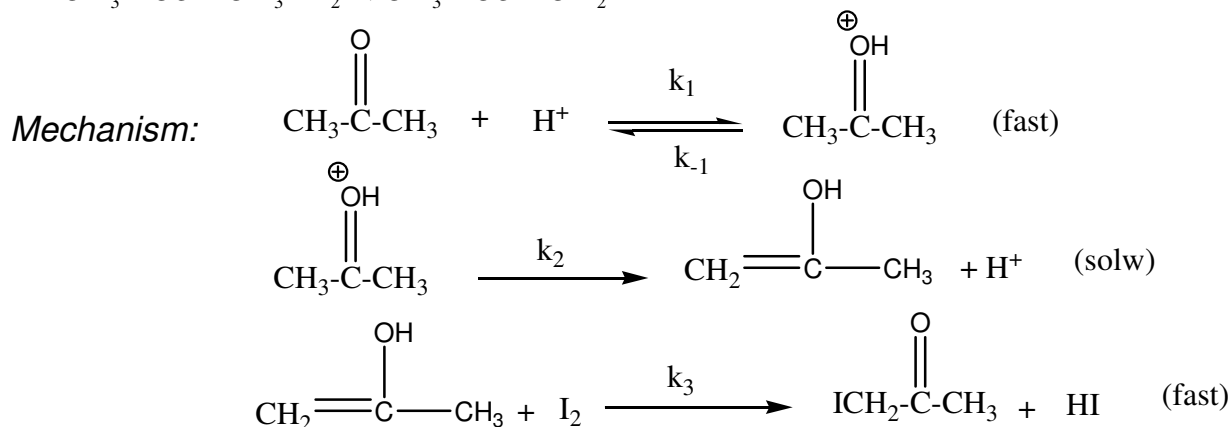
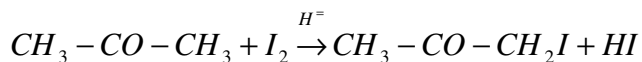
$$k = N_A \pi d_{12}^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2}$$

N_A is Avogadro number, d is the collision

diameter, μ is the reduced mass.

Substitute the given values.

9. The mechanism for the iodination reaction of acetone is given below:



Based on this mechanism, derive the rate law representing the system. What is the rate order of iodine in this reaction?

$$-\frac{d[I_2]}{dt} = k_3 [H_2C = C(OH) - CH_3] I_2$$

$$\Rightarrow [H_2C = C(OH) - CH_3] = \frac{k_2 [CH_3 - C = (\oplus OH) - CH_3]}{k_3 [I_2]}$$

$$= \frac{k_2 (k_1/k_{-1}) [CH_3COCH_3][H^+]}{[I_2]}$$

Substitute in rate expression

$$-\frac{d[I_2]}{dt} = k_2 \frac{k_1}{k_{-1}} [Acetone][H^+]$$

10. N_2O_5 gas decomposes according to the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate of reaction at 328 K is found to be $0.75 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$. What are the values of $\frac{d[N_2O_5]}{dt}$, $\frac{d[NO_2]}{dt}$, $\frac{d[O_2]}{dt}$?

Ans: $1.5 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}$; $0.75 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}$; $3 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}$



$$\frac{d[N_2O_5]}{dt} = 1.5 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}, \quad \frac{d[O_2]}{dt} = 0.75 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}, \quad \frac{d[NO_2]}{dt} = 3 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1}.$$

11. For a first order consecutive reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ write down the rate expressions and obtain concentrations [A], [B] and [C] at time t in terms of $[A]_0$, k_1 and k_2 . Obtain the same for B and C under steady state conditions. If $[A]_0 = 100 \text{ M}$, $k_1 = 0.04 \text{ min}^{-1}$, $k_2 = 0.006 \text{ min}^{-1}$, Calculate the concentrations of A, B and C at 5 min.

Refer text book for the first part

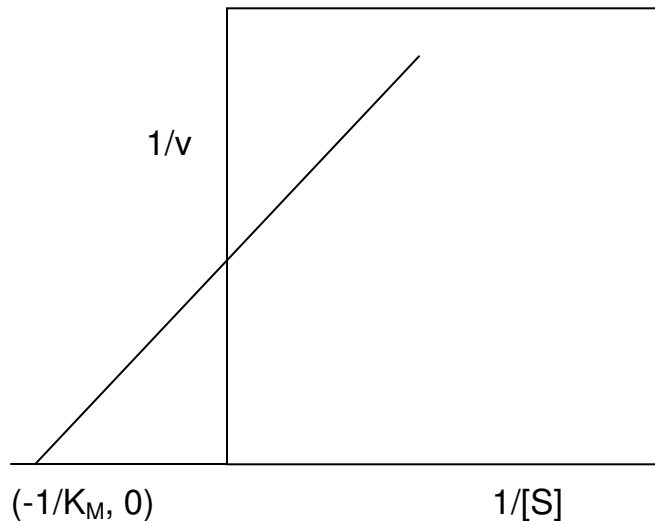
$$[A] = 81.87, [B] = 17.85, [C] = 0.278$$

12. A first order reaction has activation energy of $104,600 \text{ J mol}^{-1}$ and a pre-exponential factor $A = 5 \times 10^{13} \text{ s}^{-1}$, at what temperature will the reaction have a half-life of 30 days?

$$\frac{\ln 2}{t_{1/2}} = A \exp^{-E_a/RT}$$

$$\therefore T = 269.5 \text{ K}$$

13. Draw a Lineweaver-Burk plot for enzyme catalysis and indicate the point $(-1/K_M, 0)$



14. The Arrhenius parameters for the thermal decomposition of NOCl represented by, $2\text{NOCl (g)} \rightarrow 2\text{NO (g)} + \text{Cl}_2 \text{(g)}$ are $A = 1.00 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ and $E_a = 104 \text{ kJ mol}^{-1}$. Calculate the Entropy ($\Delta^\ddagger S$), Enthalpy ($\Delta^\ddagger H$), and Free energy of activation ($\Delta^\ddagger G$) for the reaction at 300K.

Ans: -12.7 J/Kmol, 99.0 kJ/mol and 103.0 kJ/mol respectively.

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow E_a = RT^2 \frac{d \ln k}{dT} \quad (1)$$

From TST

$$k = \frac{k_B T}{h} \left(\frac{RT}{P^\ddagger} \right) K_P \quad \text{substitute } K \text{ by } e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} \text{ take } \ln k \text{ and differentiate wrt } T$$

$$\Rightarrow \frac{d \ln k}{dT} = \frac{2}{T} + \frac{\Delta H^\ddagger}{RT^2} \quad (2) \text{ comparing (1) and (2)}$$

$$\Rightarrow E_a = \Delta H^\ddagger + 2RT$$

$$\Delta H^\ddagger = E_a - 2RT = 104 \text{ kJ mol}^{-1} - 2(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})$$

$$\Rightarrow \Delta H^\ddagger = 99.0 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = R \ln \left(\frac{A h c}{e^2 k_B T} \right)$$

$$\Rightarrow \Delta S^\ddagger = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{(1.00 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ Js})(1 \text{ M})}{e^2 (1.38 \times 10^{-23} \text{ JK}^{-1})(300 \text{ K})} \right)$$

$$\Rightarrow \Delta S^\ddagger = -12.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$\Rightarrow \Delta G^\ddagger = 99.0 \text{ kJ mol}^{-1} - (300 \text{ K}) \times (-12.7 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Rightarrow \Delta G^\ddagger = 102.8 \text{ kJ mol}^{-1}$$

15. Show that the ratio $t_{1/2}/t_{3/4}$, where $t_{1/2}$ is the half-life and $t_{3/4}$ is the time for the concentration of reactant to decrease to $3/4$ of its initial value, can be written as a function of the order of the reactions.

For zero order reaction

$$[A] - [A_0] = -kt$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$t_{3/4} = \frac{[A]_0}{4k}$$

$$\frac{t_{1/2}}{t_{3/4}} = 2$$

For first order reaction

$$\ln \frac{[A]_0}{[A]} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{3/4} = \frac{\ln 4/3}{k}$$

$$\frac{t_{1/2}}{t_{3/4}} \sim \frac{0.7}{0.28} = 2.5$$

For second order reaction

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$t_{3/4} = \frac{1}{3k[A]_0}$$

$$\frac{t_{1/2}}{t_{3/4}} = 3$$

The ratio gives an indication of the order of the reaction as it changes from 2 to 2.5 to 3 and so on. You can try it for higher order reactions also.