

Department of Chemistry, Indian Institute of Technology Madras

CY 1001 Assignment II (Physical Chemistry)

September 2010

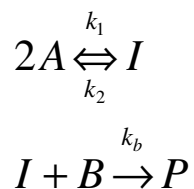
Batches a, b, c, d and e

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

Unit=moles/s

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

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



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

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

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

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

Applying the condition for preequilibria

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

3. The half-life of radium is 1600 years. How much disintegration per second would be undergone by 1 g of radium?

The half life in seconds will be

$$1600 \times 325.25 \times 24 \times 60 \times 60 = 5.049 \times 10^{10} \text{ s}$$

$$k = \frac{0.693}{t_{1/2}} = 1.37 \times 10^{-11} \text{ s}^{-1}$$

the number of nuclei present in 1 g of radium is

$$\frac{6.023 \times 10^{23} \text{ mol}^{-1}}{226 \text{ g/mol}} = 2.666 \times 10^{21} \text{ g}^{-1}$$

the number of disintegration, is therefore;

$$1.37 \times 10^{-11} \text{ s}^{-1} \times 2.67 \times 10^{21} \text{ g}^{-1} = 3.66 \times 10^{10} \text{ g}^{-1} \text{ s}^{-1}$$

4. 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

According to collision theory,

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

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

5. N_2O_5 gas decomposes according to the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. 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 $\frac{d[\text{N}_2\text{O}_5]}{dt}$, $\frac{d[\text{NO}_2]}{dt}$, $\frac{d[\text{O}_2]}{dt}$?

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = 1.5 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}, \quad \frac{d[\text{O}_2]}{dt} = 0.75 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}, \quad \frac{d[\text{N}_2]}{dt} = 3 \times 10^{-4} \text{ molL}^{-1} \text{ s}^{-1}.$$

6. 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?

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

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

7. What is the kinetic energy of the photoelectron ejected from an electronic energy level whose orbital energy is -13 eV ? Assume that the photoionization used HeI radiation of 21.2 eV .

$$\text{IP} = 13 \text{ eV}$$

$$\text{KE} = 21.2 - 13 = 8.2 \text{ eV}$$

8. Freundlich adsorption isotherm is $x/m = y = kP^n$ or $\ln y = \ln k + n \ln P$. Suggesting a straight line relation between $\ln y$ and $\ln P$. When will Langmuir adsorption become this?

$$\text{Rate of desorption} = k_d \theta$$

$$\text{Rate of adsorption} = k_a (1-\theta)P$$

$$\text{At equilibrium, } k_d \theta = k_a (1-\theta)P$$

$$\theta = KP/[1 + KP]$$

$$K = k_a/k_d$$

When $KP \ll 1$, or when P is small,

$$\theta = KP \text{ or proportional to } P$$

When $KP \gg 1$

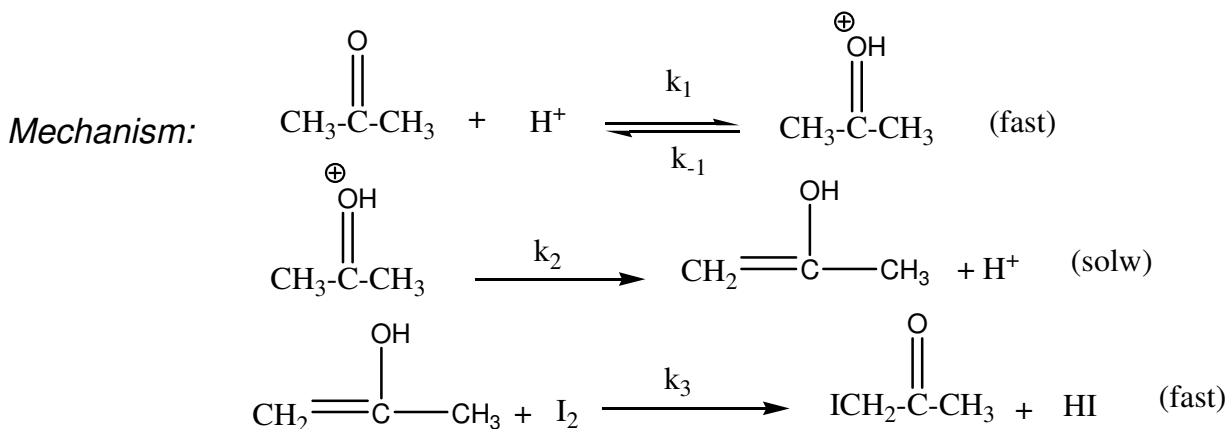
$$\theta = 1 \text{ or reaches a maximum value}$$

For all pressures in between, which is the physical reality, θ is proportional to P^n , n is a value between 0 and 1. So, Langmuir adsorption isotherm will become Freundlich kind in the intermediate pressures.

9. Write down the expression for the $t_{1/2}$ of an n^{th} order reaction.

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

10. 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?

$$\begin{aligned} -\frac{d[I_2]}{dt} &= k_3 [H_2C = C(OH) - CH_3] I_2 \\ \Rightarrow [H_2C = C(OH) - CH_3] &= \frac{k_2 [CH_3 - C = (^+OH) - CH_3]}{k_3 [I_2]} \\ &= \frac{k_2 (k_1/k_{-1}) [CH_3COCH_3][H^+]}{k_3 [I_2]} \end{aligned}$$

Substitute in rate expression

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

11. 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.

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

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

From TST

$$k = \frac{k_B T}{h} \left(\frac{RT}{P^0} \right) K_P \quad \text{substitute } K \text{ by } e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \text{ take } \ln k \text{ and differentiate wrt } T$$

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

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

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

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

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

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

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

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

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

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