

1. For the reaction $A \rightarrow P$ with autocatalysis and with given initial amounts, find by explicit integration the amounts of A and P at a later time.

Ans. $A \rightarrow P \quad v = k[A][P]$
 $[A]_0 - x \quad x$

$$\frac{dx}{dt} = k([A]_0 - x)([P]_0 + x)$$

$$k \int_0^t dt = \int_0^x \frac{dx}{([A]_0 - x)([P]_0 + x)} \Rightarrow \text{write : } \frac{1}{([A]_0 - x)([P]_0 + x)} = \frac{1}{[A]_0 + [P]_0} \left[\frac{1}{[A]_0 - x} + \frac{1}{[P]_0 + x} \right]$$

$$\text{use : } \int \frac{dx}{x \pm a} = \ln(x \pm a)$$

$$\therefore kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}; \text{ or, } \ln \frac{[P]_0 + x}{b([A]_0 - x)} = ([A]_0 + [P]_0)kt = at, \text{ where } a = ([A]_0 + [P]_0)k \text{ and } b = \frac{[P]_0}{[A]_0}$$

$$\text{or, } \frac{[P]_0 + x}{[A]_0 - x} = be^{at}; \text{ adding 1 to both sides, } \frac{ak}{[A]_0 - x} = 1 + be^{at}, \text{ or, } [A]_0 - x = \frac{ak}{1 + be^{at}}, \text{ or, } x = [A]_0 - \frac{ak}{1 + be^{at}} = [P]_0 \cdot \frac{e^{at} - 1}{1 + be^{at}}$$

$$\therefore [A](t) = [A]_0 - x = [A]_0 - [P]_0 \frac{(e^{at} - 1)}{1 + be^{at}} = \frac{a}{k(1 + be^{at})} = [A]_0 \frac{[A]_0 + [P]_0}{[A]_0 + [P]_0 e^{([A]_0 + [P]_0)kt}}$$

$$\text{and } [P](t) = [P]_0 + x = [P]_0 + [P]_0 \frac{(e^{at} - 1)}{1 + be^{at}} = \frac{(b+1)[P]_0}{1 + be^{at}} e^{at} = [P]_0 \frac{[A]_0 + [P]_0}{[A]_0 e^{-([A]_0 + [P]_0)kt} + [P]_0}$$

$$\text{This is same as } [A]_0 + [P]_0 - [A](t) = \frac{a}{k} - \frac{a}{k(1 + be^{at})} = \frac{a}{k} \left[1 - \frac{1}{1 + be^{at}} \right] = \frac{abe^{at}}{k(1 + be^{at})}$$

2. The equilibrium constant for the autoprotolysis of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is 1.008×10^{-14} at 298 K. After a temperature-jump, the reaction returns to equilibrium with a relaxation time of 37 μs at 298 K and $pH \approx 7$. Given that the forward reaction is first-order and the reverse is second-order overall, calculate the rate constants for the forward and reverse reactions.

Ans. forward rate at final temp. $= k_1[H_2O]$; reverse rate $= k_2[H^+][OH^-]$

$$\text{net rate} = \frac{d[H_2O]}{dt} = -k_1[H_2O] + k_2[H^+][OH^-]$$

$$\text{write } [H_2O] = [H_2O]_{eq} + x, [H^+] = [H^+]_{eq} - x \text{ and } [OH^-] = [OH^-]_{eq} - x$$

$$\frac{dx}{dt} = - \left\{ k_1 + k_2 \left([H^+]_{eq} + [OH^-]_{eq} \right) \right\} x - \underbrace{k_1 [H_2O]_{eq} + k_2 [H^+]_{eq} [OH^-]_{eq}}_{=0} + \underbrace{k_2 x^2}_{\text{neglect}}$$

$$\therefore \frac{1}{\tau} = \frac{10^6}{37} = k_1 + k_2 \left([H^+]_{eq} + [OH^-]_{eq} \right) \text{ ————— (1); Also, } \frac{k_1}{k_2} = \frac{[H^+]_{eq} [OH^-]_{eq}}{[H_2O]_{eq}} = \frac{1.008 \times 10^{-14}}{[H_2O]_{eq}}$$

$$\text{usually, we take } [H^+]_{eq} = [OH^-]_{eq} = 10^{-7} \text{ mol dm}^{-3} \text{ taking } [H_2O]_{eq} \text{ absorbed in the equilibrium constant } 1.008 \times 10^{-14}$$

$$\text{However, here we are dealing with actual concentrations and } [H_2O]_{eq} = \frac{1000}{18} \text{ mol dm}^{-3}$$

$$\therefore \frac{k_1}{k_2} = \frac{1.008 \times 10^{-14}}{\frac{1000}{18}} = 1.8 \times 10^{-16} \text{ ————— (2)}$$

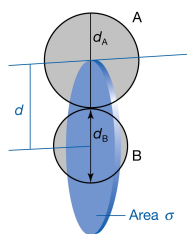
$$\text{Using Eqs. (1) and (2), find } k_2 = 1.4 \times 10^{11} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ and } k_1 = 2.4 \times 10^{-5} \text{s}^{-1}$$

3. How does the collision-theory explain the activation needed for a reaction? Describe the essential features of the harpoon mechanism.

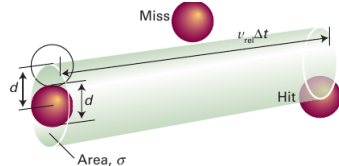
Ans. Collision theory starts with counting the number of collisions between reactant molecules. Assuming hard wall (marble balls) like interactions,

count 'hit' whenever centres of two molecules come within distance d of each other

$$d \text{ (collision diameter)} = \frac{1}{2} (d_A + d_B)$$



$$\text{collision frequency, } z = \frac{\text{\#collisions made by a molecule}}{\text{time interval of collisions}}$$



collision tube

if mean relative speed is \bar{v}_{rel} , cross-sectional area $\sigma = \pi d^2$, then in time Δt , length traveled $= \bar{v}_{\text{rel}} \Delta t$, volume $= \sigma \bar{v}_{\text{rel}} \Delta t$

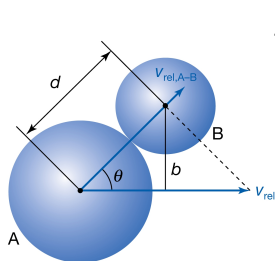
$$\text{\#stationary molecules with centres inside collision tube} = \frac{N}{V} \sigma \bar{v}_{\text{rel}} \Delta t \implies z = \frac{N}{V} \sigma \bar{v}_{\text{rel}}; \bar{v}_{\text{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}}; \mu = \frac{m}{2}$$

Total collision density, and $Z_{AB} = z \frac{N_B}{V} = \sigma \bar{v}_{\text{rel}} \left(\frac{N_A N_B}{V^2} \right)$ (a factor $\frac{1}{2}$ appears if A and B are the same)

Not all collisions will contribute to the reaction. Only when the energy is above a threshold, reaction occurs.

$$\text{energy requirement: } \sigma(\varepsilon) = 0 \quad \forall \varepsilon < \varepsilon_a; \therefore \frac{d[A]}{dt} = -\sigma(\varepsilon) v_{\text{rel}} N_A [A][B]; v_{\text{rel}} = \sqrt{\frac{2\varepsilon}{\mu}}$$

$$\text{for a wide range of approach energies, } \frac{d[A]}{dt} = - \left\{ \int_0^\infty \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon \right\} N_A [A][B] \implies k_2 = N_A \int_0^\infty \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon$$



$$v_{\text{rel, A-B}} = v \cos \theta = v_{\text{rel}} \sqrt{\frac{d^2 - b^2}{d^2}} \implies \varepsilon_{\text{A-B}} = \varepsilon \frac{d^2 - b^2}{d^2}$$

$$\forall b > b_{\text{max}}, \text{ reaction does not occur}$$

$$\varepsilon_a = \varepsilon \frac{d^2 - b_{\text{max}}^2}{d^2} \implies b_{\text{max}}^2 = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) d^2$$

$$\implies \forall \varepsilon > \varepsilon_a, \sigma(\varepsilon) = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) \sigma$$

The speeds of the molecules can be assumed to have a Maxwell-Boltzmann distribution:

$$f(v) dv = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv = 2\pi \left(\frac{1}{\pi k_B T} \right)^{\frac{3}{2}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon = f(\varepsilon) d\varepsilon$$

$$\therefore \int_0^\infty \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon = 2\pi \left(\frac{1}{\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty \sigma(\varepsilon) \sqrt{\frac{2\varepsilon}{\mu}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$= \sqrt{\frac{8}{\pi \mu k_B T}} \left(\frac{1}{k_B T} \right) \underbrace{\int_0^\infty \varepsilon \sigma(\varepsilon) e^{-\frac{\varepsilon}{k_B T}} d\varepsilon}$$

$$\searrow \int_{\varepsilon_a}^\infty \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) \varepsilon e^{-\frac{\varepsilon}{k_B T}} d\varepsilon = (k_B T)^2 \sigma e^{-\frac{\varepsilon_a}{k_B T}}$$

$$\therefore k_2 = N_A \int_0^\infty \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon = N_A \sigma \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{\varepsilon_a}{k_B T}}$$

The last factor in the above expression is the activation energy needed for the reaction to occur.

The harpoon mechanism explains the anomaly of high steric factor for reactions like between alkali metal and halogen.

Distance of approach at which reaction occurs \gg distance needed for deflection of path of approaching molecules in non-reactive collision

Ex. $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$: an electron is used like a harpoon to hook up the Br_2 molecule. The ionized K^+ and Br_2^-

are electrostatically attracted to each other, thus explaining reactivity higher than that predicted by usual collision theory.

Harpoon: K atom

approaches Br₂

molecule,



when they are close enough an electron (harpoon) flips across from K to Br₂

In place of two neutral particles there are two ions

with Coulombic attraction between them : [line on the harpoon](#)

Under its influence ions move together

(line wound in), reaction takes place \Rightarrow KBr + Br

harpoon extends the cross-section for reactive encounter

Estimating steric factor, P , for harpoon mechanism:

net change in energy when transfer of charge occurs at separation R : $E = I - E_{ea} - \frac{e^2}{4\pi\epsilon_0 R}$

$$I > E_{ea} \Rightarrow E < 0 \text{ iff } R < R^* \text{ s.t. } \frac{e^2}{4\pi\epsilon_0 R^*} = I - E_{ea}$$

At $R = R^*$, harpoon shoots across from K to Br₂, $\therefore \sigma^* = \pi R^{*2} \Rightarrow P = \frac{\sigma^*}{\sigma} = \left[\frac{e^2}{4\pi\epsilon_0 d(I - E_{ea})} \right]^2$ where $d = R(K) + R(\text{Br}_2)$

$$I = 420 \text{ kJ.mol}^{-1}, E_{ea} = 250 \text{ kJ.mol}^{-1} \text{ and } d = 400 \text{ pm} \Rightarrow P = 4.2 \text{ (Exp. } P = 4.8)$$

4. An amino acid on the surface of an enzyme was labelled covalently with 1.5-I AEDANS and it is known that the active site contains a tryptophan residue. The fluorescence quantum yield of tryptophan decreased by 15% due to quenching by 1.5-IAEDANS.

What is the distance between the active site and the surface of the enzyme? (Förster parameter, $R_0 = 2.2 \text{ nm}$)

Ans. The efficiency of RET, $\eta_T = 1 - \frac{\phi_f}{\phi_{f,0}} = 0.15$

$$\text{FRET : } \eta_T = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6} \Rightarrow R = R_0 \left(\frac{1}{\eta_T} - 1 \right)^{\frac{1}{6}} = 2.9 \text{ nm}$$

5. For gas phase reactions other than unimolecular, show that the pre-exponential factor, $A = e^{-(\Delta n^\ddagger - 1) \frac{k_B T}{h}} e^{\frac{\Delta S^\ddagger}{R}}$ (ΔV^\ddagger = change in volume for activation, and Δn^\ddagger = change in number of moles on activation; you may get a factor of N_A depending on the units you choose).

$$\text{Ans. } k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}$$

Using Arrhenius equation: $k = A e^{-\frac{E_a}{RT}}$, we have $\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2}$

$$\text{using } k = \frac{k_B T}{h} K_c^\ddagger, \quad \frac{d(\ln k)}{dT} = \frac{1}{T} + \frac{d(\ln K_c^\ddagger)}{dT}$$

$$\frac{d(\ln K_c^\ddagger)}{dT} = \frac{\Delta U^\ddagger}{RT^2} \text{ (} U \text{ refers to internal energy, often written as simply } E \text{)}$$

$$\therefore E_a = RT + \Delta U^\ddagger; \Delta H^\ddagger = \Delta U^\ddagger + p(\Delta V^\ddagger) \text{ or } E_a = \Delta H^\ddagger + RT - p(\Delta V^\ddagger)$$

For unimolecular reaction, since there is no change in number of molecules in going from reactants to products, $\Delta V^\ddagger = 0$

For gas phase reactions other than unimolecular, $p(\Delta V^\ddagger) = \Delta n^\ddagger RT$

$$\therefore E_a = \Delta H^\ddagger + RT - \Delta n^\ddagger RT = \Delta H^\ddagger + (1 - \Delta n^\ddagger) RT \Rightarrow A = e^{-(\Delta n^\ddagger - 1) \frac{k_B T}{h}} e^{\frac{\Delta S^\ddagger}{R}} \quad 6$$

6. (a) Explain briefly the variation of rate constant for Electron transfer between a donor and acceptor in homogeneous systems as different substituents are added to the acceptor.

Ans. If r , ΔE_R and $\kappa\nu$ are constant for a series of reactions,

$$\begin{aligned}\ln k_{et} &= \text{const} - \frac{\Delta^\ddagger G}{RT} = -\frac{(\Delta_r G^\ominus + \Delta E_R)^2}{4\Delta E_R RT} + \text{const} \\ &= -\frac{1}{4RT\Delta E_R} (\Delta_r G^\ominus)^2 - \frac{1}{2} \left(\frac{\Delta_r G^\ominus}{RT} \right) + \text{const}\end{aligned}$$

As different substituents are added to the acceptor, $\Delta_r G^\ominus$ and accordingly $\ln k_{et}$ varies.

The equation corresponds to an inverted parabola.

The inversion corresponds to a shift in the relative distance between the configuration

coordinates of the DA and D^+A^- complexes (a) $\Delta^\ddagger G > 0$; TS at $q_a^* > q_0^R$; as process becomes

more exergonic, $\Delta^\ddagger G$ decreases and k increases

(b) When $\Delta^\ddagger G = 0$; TS at $q_b^* = q_0^R$ rate constant for process reaches a maximum as there is no activation barrier to overcome

(c) As process becomes even more exergonic, $\Delta^\ddagger G$ becomes positive again; now the TS is at $q_c^* < q_0^R$;

k decreases steadily as the activation barrier for the process increases with decreasing $\Delta^\ddagger G$

(b) At 300 K, for an electron donor–acceptor pair, $k_{et} = 2.02 \times 10^5 \text{s}^{-1}$ for $\Delta_r G^\ominus = -0.665 \text{eV}$. When a substituent is added to the electron acceptor, the quantities change to $k_{et} = 3.33 \times 10^5 \text{s}^{-1}$ and $\Delta_r G^\ominus = -0.975 \text{eV}$. Assume that the distance between donor and acceptor is the same in both experiments and estimate the value of the reorganisation energy ($R = 8.63 \times 10^{-5} \text{eV/K}$).

Ans. From eq. in part (a)

$$\text{for the two sets, } \ln k_{et,1} + \frac{1}{4RT\Delta E_R} (\Delta_r G_1^\ominus)^2 + \frac{1}{2} \left(\frac{\Delta_r G_1^\ominus}{RT} \right) = \text{const} = \ln k_{et,2} + \frac{1}{4RT\Delta E_R} (\Delta_r G_2^\ominus)^2 + \frac{1}{2} \left(\frac{\Delta_r G_2^\ominus}{RT} \right)$$

$$\therefore \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4RT\Delta E_R} = \ln \frac{k_{et,2}}{k_{et,1}} + \frac{\Delta_r G_2^\ominus - \Delta_r G_1^\ominus}{2RT}$$

$$\text{and } \Delta E_R = \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4RT \cdot \ln \frac{k_{et,2}}{k_{et,1}} + 2(\Delta_r G_1^\ominus - \Delta_r G_2^\ominus)} = \frac{(0.665)^2 - (0.975)^2}{4 \times 8.63 \times 10^{-5} \times 300 \times \ln \frac{33.3}{2.02} - 2(0.975 - 0.665)} \approx 1.5 \text{eV}$$

7. An atom on a metal surface is hit 100 times a second by gas atoms above it. If the temperature is increased to twice its value, how many times will the surface atom hit in a second?

Ans. collision flux on a surface : $Z_W = \frac{p}{\sqrt{2\pi m k_B T}} \Rightarrow \# \text{ hits} \propto \frac{1}{\sqrt{T}}$ and the answer is $100 \times \sqrt{\frac{1}{2}} \approx 71$ times

