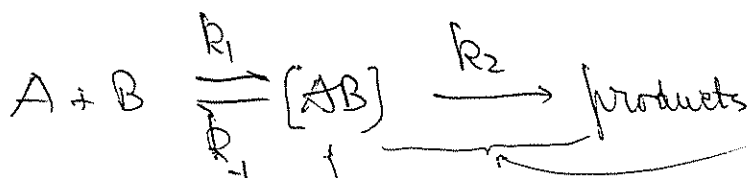


Another example of the importance of mass transport ... and of RDS...

Summary:



diffusion process $k_1 = k_d$

"cage" (encounter pair) ... in contrast to gas-phase rxns, the encounter frequency is lower, but the time spent together is longer!

"activation"

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[AB]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [A][B] \Rightarrow \text{RDS?}$$

* diffusion control: $k_2 \gg k_{-1} \Rightarrow \text{Rate} = k_d [A][B]$

* "activation" control: $k_2 \ll k_{-1} \Rightarrow \text{Rate} = k_2 k [A][B] \quad k = \frac{k_1}{k_{-1}}$

Estimation of k_d ?

- mass transport rate = $4\pi r^2 D_B \frac{dc_B}{dr}$, etc. \Rightarrow Rate of rxn = $4\pi (D_A + D_B) d_{AB} [A][B]$

$\therefore k_d = 4\pi R^* (D_A + D_B) \quad R^* = R_A + R_B$... critical distance (of approach)

- for $R_A \approx R_B \Rightarrow \left[k_d = \frac{8RT}{3\eta} \right]$ (and Stokes-Einstein eq. D vs. η)

indeed, of the order of $10^9 \frac{L}{mol \cdot s}$

- But, for $H^+ + OH^- = H_2O(l)$, $k_d \approx 1.4 \times 10^{11} \frac{L}{mol \cdot s}$ Why? \Rightarrow 1st neglect intermolecular/interaction forces (or?)

$$R_{H_3O^+} + R_{OH^-} = \frac{(1.4 \times 10^{11} \frac{L}{mol \cdot s}) \left(\frac{1 m^3}{10^3 L} \right)}{(4\pi) (6.022 \times 10^{23} \frac{1}{mol}) (9.31 \times 10^{-9} + 5.3 \times 10^{-9} \frac{m^2}{s})} \approx 1.3 \text{ nm}$$

Too large!?

$k_d = 4\pi (D_A + D_B) d_{AB} \left[\frac{z_A z_B e^2}{4\pi \epsilon_0 \epsilon d_{AB} RT} \right] \left[\frac{\exp\left(\frac{z_A z_B e^2}{4\pi \epsilon_0 \epsilon d_{AB} RT}\right) - 1}{z_A z_B} \right]$

electrostatic factor

0	1
-1	3.65
-2	7.08
1	0.106
2	0.006

Check!!

$\log k = \log k^0 + 2 z_A z_B A I^{0.5}$
 $I \uparrow, k \downarrow$ (shielding!)

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