Quiz 18.1 – Reaction Rate Theories

Name: Key

Collision Theory

Nitrogen monoxide can be produced by the reaction:

$$N_2 + O_2 \longrightarrow 2\,NO$$

Find the encounter rate (Z) for this reaction in the atmosphere ($p_{N_2} \approx 0.8atm$ and $p_{O_2} \approx 0.2\ atm$), then give an expression for the reaction rate.

$\sigma = 0.43\ nm^2$ $\sigma = 0.40\ nm^2$ @ 298 K

$\sigma_{N_2,O_2} = 0.415\ nm^2$

$\mu = \frac{m_1 m_2}{m_1 + m_2} = 14.44\ g/mol$

$[N_2] = \frac{0.8 atm}{0.08206 \frac{L\,atm}{mol\,K} \cdot 298\ K} = 0.0327\ M = 32.7 \frac{moles}{m^3}$

$[O_2] = 0.008\ M = 8 \frac{moles}{m^3}$

$$Z_{AB} = \sigma \left(\frac{8RT}{\pi\mu}\right)^{1/2} N_A^2 [A][B]$$

$$Z_{AB} = 0.415 \cdot 10^{-18}\ m^2 \left(\frac{8 \cdot 8.314\ J/mol\,K \cdot 298\ K}{\pi \cdot 0.01444\ kg/mol}\right)^{1/2} (6.022 \cdot 10^{23}\ mol^{-1})^2 \cdot 32.7 \frac{moles}{m^3} \cdot 8 \frac{moles}{m^3} = 2.56 \cdot 10^{34}\ m^{-3} s^{-1}$$

Diffusion-Controlled Reactions

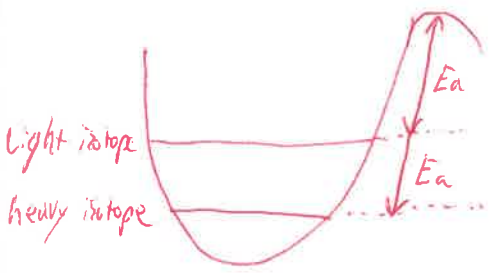
$$rate = \sigma \left(\frac{1000\ L}{1\ m^3}\right) v_{rel} N_A [O_2][N_2] = 1.624 \cdot 10^{11} \frac{1}{M\,s} [O_2][N_2]$$

The rate constant of diffusion controlled reactions depends only on the temperature and the solvent viscosity (if the reaction distance is the same as the Stokes radius of the reactants). Find the rate constant k_d in water at $298K$ for such reactions. (recall that for water at room temperature $\eta = 0.00089 \frac{kg}{m\,s}$)

$$k_d = \frac{8RT}{3\eta} = \frac{8 \cdot 8.314\ J/mol\,K \cdot 298\ K}{3 \cdot 0.00089\ \frac{kg}{M\,S}} \left(\frac{1\ m^3}{1000\ L}\right) = 7423 \frac{1}{M\,S}$$

Transition-State Theory

Describe the kinetic isotope effect in terms of transition-state theory



The heavier isotope has a lower vibrational zero-point energy in the activated complex. This leads to a greater E_a for complex dissociation and a lower reaction rate for heavier isotopes.