Lecture 37

Monday, December 4, 2023 9:54 AM

Past concepts: $c(t) = c_0 e^{-kt}$ ← rate coefficient s^{-1} units

$J = v \cdot c$

$P(x|0)$ = prob of being @ x, given you started @ x = 0

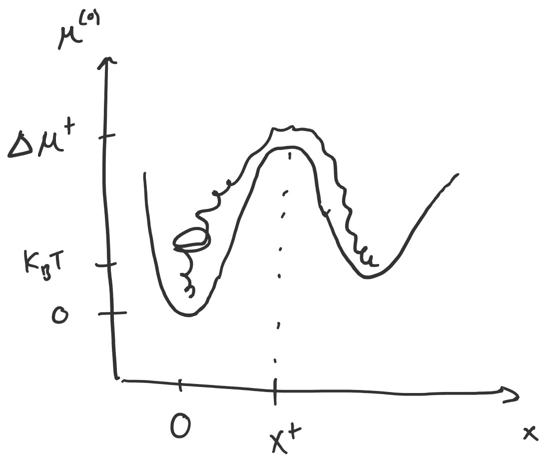
Last Time:

integrated flux

$$J = -\frac{D}{x}\left(\underbrace{c(x)\,P(0|x)}_{\text{backward}} - \underbrace{c(0)\,P(x|0)}_{\text{forward}}\right)$$

TST:

$$\mu^{(0)}(x) \longrightarrow v^{+} = \frac{J_{\text{forward}}(x^{+})}{c(0)} = +\frac{D}{x^{+}}\,P(x^{+}|0)$$

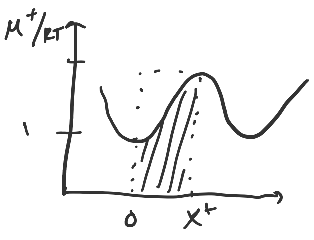


$$= +\frac{D}{x^{+}}\;\frac{e^{\mu^{(0)}(x=0)/RT}}{\frac{1}{x^{+}}\int_0^{x^{+}} dx'\, e^{\mu^{(0)}(x')/RT}}$$

Today: Arrhenius Eqn $k = a e^{-E^{\ddagger}/RT}$

We can simplify the formula for v^{+} in two ways

1) $\frac{1}{x^{+}}\int_0^{x^{+}} dx'\, e^{-\mu^{(0)}(x')/RT} \le e^{-\Delta\mu^{+}/RT}$



$= \frac{1}{\chi} e^{\Delta\mu^{+}/RT}$

$\chi \ge 1$

↑ transmission coefficient, use QM

2) $e^{\mu^{(0)}(x=0)/RT} = 1$

$$\Rightarrow v^{+}_{\text{forward}} = \frac{D}{x^{+}} \cdot \frac{1}{\frac{1}{\chi} e^{\Delta\mu^{+}/RT}} = \frac{\chi \cdot D}{x^{+}}\, e^{-\Delta\mu^{+}/RT}$$

Finally, the rate coefficient is

$$k(s^{-1}) = \frac{v^{+}_{\text{forward}}}{\text{distance}} = \frac{v^{+}_{\text{forward}}}{x^{+} - 0}$$

$$\Rightarrow k(s^{-1}) = \frac{\chi \cdot D}{(x^{+})^2}\, e^{-\frac{\Delta\mu^{+}}{RT}} \quad \text{Arrhenius}$$

In class exercise,

$$D \approx 10^{-9}\ \frac{m^2}{s} \quad \left(D = \frac{RT}{\gamma} = \frac{RT}{6\pi\eta \cdot R}\right)$$

↑ viscosity of solvent; ↖ diameter of molecule

$x^{+} \approx 0.5$ Å

$\chi \approx 1$

$$\Rightarrow \frac{\chi \cdot D}{(x^{+})^2} = \frac{1 \cdot 10^{-9}\ \frac{m^2}{s}}{(0.5 \times 10^{-10}\ m)^2} = 4 \times 10^{11}\ s^{-1}$$

$\tau = \frac{1}{k} = 2.5$ ps