L38: review

- flux (at steady state) in integral form:

$$J_{0\to x} = -\underbrace{\frac{D}{x}}_{\text{permeability}} \frac{e^{\frac{\mu(x)}{RT}} - e^{\frac{\mu(0)}{RT}}}{\frac{1}{x}\int_0^x e^{\frac{\mu^o(x')}{RT}} dx'}$$

numerator is "the driving force" and the rest is analogous to friction

- flux in Bayesian form

$$J_{0\to x} = -\frac{D}{x} \frac{C(x)\, e^{\frac{\mu^o(x)}{RT}} - C(0)\, e^{\frac{\mu^o(0)}{RT}}}{\frac{1}{x}\int_0^x e^{\frac{\mu^o(x')}{RT}} dx'}$$

$$= -\frac{D}{x}\Big[\underbrace{C(x)\, P(0|x)}_{\text{backward flux}} - \underbrace{C(0)\, P(x|0)}_{\text{forward flux}}\Big]$$

$$P(0|x) = \frac{e^{\frac{\mu^o(x)}{RT}}}{\frac{1}{x}\int_0^x e^{\frac{\mu^o(x')}{RT}} dx'}$$

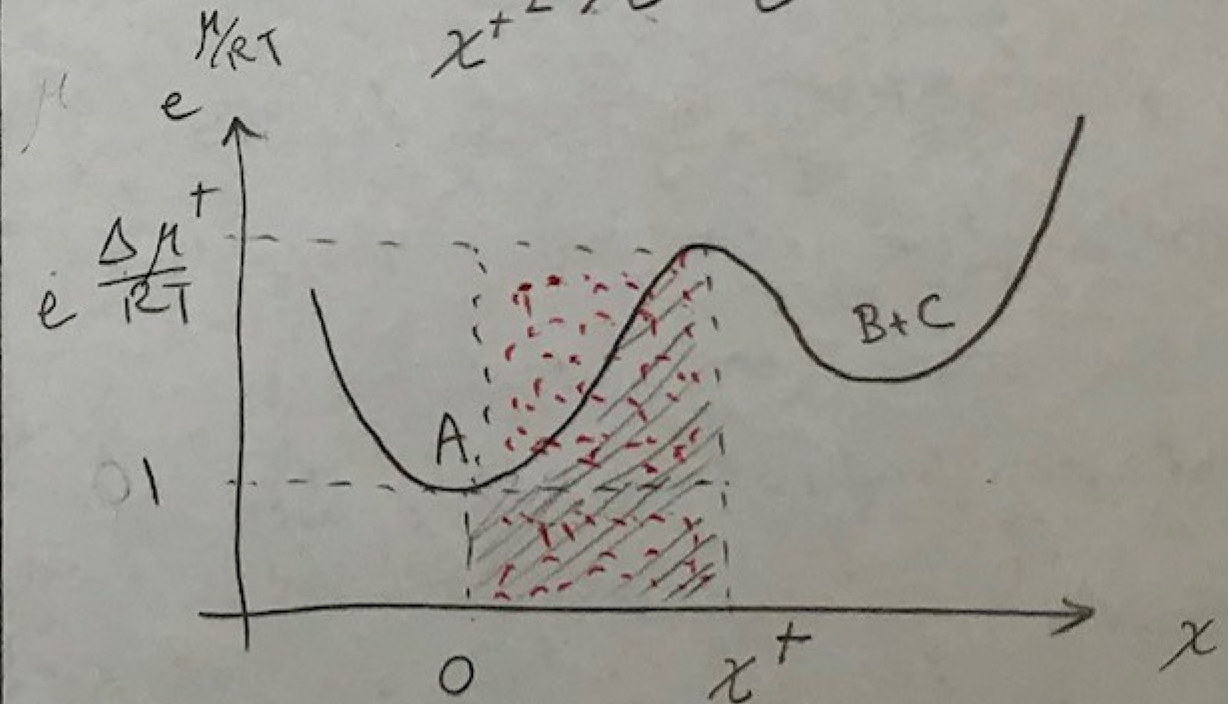
Probability is the probability of molecules appearing at 0 <u>starting from</u> x

- Transition state theory of a unimolecular reaction ($A \to B + C$)

$$\underset{s^{-1}}{k_F} = \frac{\overset{m/s}{v_F}}{\underset{m}{x^+}} = \frac{J_F / C(0)}{x^+} = \frac{D}{x^{+2}} \frac{e^{\mu^o(x=0)}}{\frac{1}{x^+}\int_0^{x^+} e^{\frac{\mu^o(x')}{RT}} dx'}$$

$\mu^o(x=0) \xrightarrow{} 0$; $\stackrel{!}{=}$

$$= \frac{D}{x^{+2}} \chi\, e^{-\Delta\mu^+/RT}$$



$$\underset{\text{transmission coefficient}}{\chi} = \frac{\int_0^{x^+} dx'\, e^{\frac{\mu^o(x')}{RT}}}{x^+\, e^{\frac{\Delta\mu^+}{RT}}}$$

numerator: area of the hashed region

denominator: area of the dotted red rectangle

Today: Three numerical examples of Transition State theory

#1: Find the prefactor $\left(\frac{D\chi}{x^{+2}}\right)$ of an ion diffusing in water. $D = 10^{-9}\ \frac{m^2}{s}$

$\chi = 1$. $x^+ = 0.5$ Å

Ans

$$\frac{D\chi}{x^{+2}} = \frac{10^{-9}}{(5\times10^{-11})^2} = 4\times10^{11}\ s^{-1}$$

Ions "attempt" to react with a frequency of 4×10^{11} times per second. If there is no barrier to reaction this value equals the reaction rate constant. Remember the assumption is that reaction happens at a steady state (flux does not change much)

#2: Find Prefactor and rate constant (k) of a reaction at 225°C using the following data:

$\chi = 0.5$; $D(25°C) = 10^{-9}\ \frac{m^2}{s}$; $x^+ = 0.5$ Å

viscosity decreases five-fold with increasing T by 100°C

Ans

First, let's find D (225°C).

$$D = \frac{RT}{6\pi r\eta} \Rightarrow \frac{D_2}{D_1} = \frac{\eta_1 T_2}{\eta_2 T_1}$$

for a sphere

$$\Longrightarrow \frac{D(225°C)}{D(25°C)} = 25\cdot\left(\frac{225+273}{25+273}\right) \approx 40$$

$$\Rightarrow D(225°C) = 4\times10^{-8}\ \frac{m^2}{s}$$

Now, we will calculate the prefactor and rate constant:

$$\frac{D\chi}{x^{+2}} = \frac{4\times10^{-8}\times0.5}{(5\times10^{-11})^2} = 8\times10^{13}\ s^{-1}.$$

$$k = \frac{D\chi}{x^{+2}}\, e^{-\Delta\mu^+/RT} = 8\times10^{13}\, e^{-\frac{100\,000}{8.314\times498}}$$

$$= 2.60\times10^{3}\ s^{-1}$$

Note that due to the activation barrier the actual reaction rate is much slower than the rate of collisions.