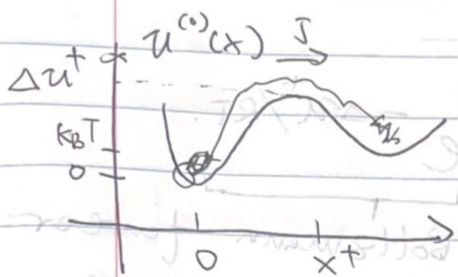
Last Time: integrated Flux.

① $J = -\frac{D}{X}\left(c(x) P(0|x) - c(0) P(x|0) \right)$

② TST

From Stat mech, $J = V \cdot C$



$$\Rightarrow V_{\text{forward}} = D \cdot \frac{e^{u^{(0)}(x=0)/RT}}{\int_0^x dx' e^{u^{(0)}(x')/RT}}$$

Today: Arrhenius equation:
We can simplify this formula in two ways when calculating flux J at x^{+}:

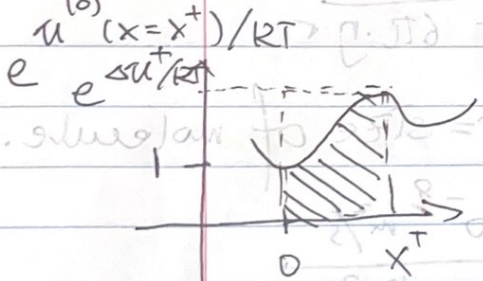
1) $e^{u(0)(x=0)/RT} = 1$.

2) $\int_0^x dx' e^{u^{(0)}(x=x^{+})/RT} \leq x^{+} \cdot e^{\Delta u^{+}/RT}$

$$= \frac{x^{+}}{\chi} e^{\Delta u^{+}/RT}$$

$\uparrow$

transition coefficient $\chi \geq 1$



$$\Rightarrow V_{\text{forward}} = D \cdot \approx \frac{1}{\frac{x^{+}}{\chi} e^{\Delta u^{+}/RT}}$$

$$= \frac{\chi D}{x^{+}} \cdot e^{-\Delta u^{+}/RT}.$$

Finally, to get the rate coefficient k ($\frac{1}{sec}$ =

$$k\left(\frac{\text{molecules}}{s}\right) = \frac{J_{forward}\ (m/s)}{(x^{\ddagger} - 0)\ (m)}$$

$$= \frac{J_{forward}}{x^{\ddagger}}$$

$$k_{TST}\ (s^{-1}) = \frac{\chi \cdot D}{(x^{\ddagger})^2}\ \underbrace{e^{-\Delta u^{\ddagger}/RT}}_{\text{Boltzmann factor}}$$

$\Delta u^{\ddagger} \equiv$ activation free energy

In-class exercise: the fastest a chemical rx can go?

$D \approx 10^{-9}\ m^2/s$ small organic molecule in solution.

$$D = uRT = \frac{RT}{\gamma} = \frac{RT}{6\pi \cdot \eta \cdot r}$$

η = viscosity r = size of molecule.

$x^{\ddagger} = 0.5\ Å$

$\chi = 1$

$$\frac{\chi D}{x^{\ddagger 2}} = \frac{1 \times 10^{-9}\ m^2/s}{(0.5 \cdot 10^{-10})^2}$$

$$\approx 4 \times 10^{11}\ s^{-1} \Rightarrow \tau \approx 2.5\ ps$$