Lecture 36

Last Time: Flux $J = v \cdot c = cU\left(-\frac{d\mu_g}{dx}\right)$

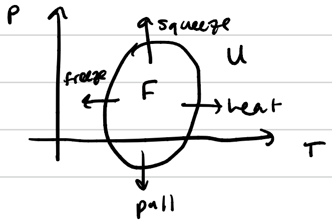
where $\begin{cases} \text{mechanical force} = -\frac{dE}{dx} \\ \text{molar force} = \frac{-d\mu_g}{dx} \end{cases}$

Integrate in steady state $\Rightarrow$

$$J = -D \frac{e^{\mu_g(x)/RT} - e^{\mu_g(0)/RT}}{\int_0^x dx' \, e^{\mu_g(x')/RT}}$$

ex: Le Chatelier: if $\Delta\mu_g = \mu_g(x) - \mu_g(0) \neq 0$
then flux restores equilibrium

ex: protein folding




Today: Bayesian formulation of flux & TST

Use $\mu_g = \mu^{(0)} + RT\ln(c)$ (ideal system)

$$\Rightarrow e^{\mu_g/RT} = e^{\mu^{(0)}/RT} e^{\ln c} = e^{\mu^{(0)}/RT} \cdot c$$

$$\Rightarrow J = -\frac{D}{x} \frac{c(x)\, e^{\mu^{(0)}(x)/RT} - c(0)\, e^{\mu^{(0)}(0)/RT}}{\frac{1}{x}\int_0^x dx' \, e^{\mu^{(0)}(x')/RT}}$$

$Z = e^{-F/RT}$ $\quad e^{+\mu/RT} \sim \frac{1}{Z} \sim P$

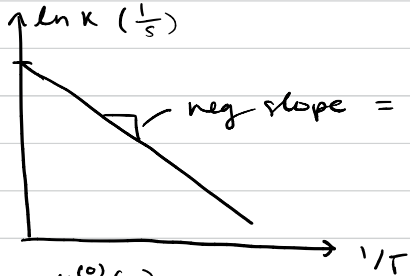
$$\Rightarrow J = \frac{-D}{x}\left\{ \underbrace{c(x)\, P(0|x)}_{\text{"backward flux" from } x \to 0} - \underbrace{c(0)\, P(x|0)}_{\text{"forward flux" from } 0 \to x} \right\}$$

$P(0|x)$ = prob. that a molecule ends up at 0 if it started at $x$

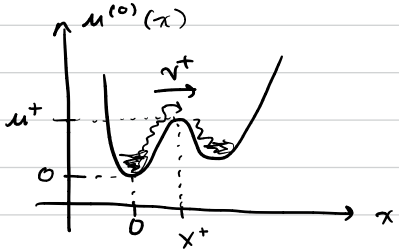
$P(x|0)$ = prob. that a molecule ends up at $x$ if it started at 0 eg. traffic, economics

TST – transition state theory

Arrhenius expt'l discovery =




neg slope = $-\frac{E^+}{R}$ $\Bigg\}$ $k = a\, e^{-E^+/RT}$




Can we derive Arrhenius's formula using the $-\frac{d\mu}{dx}$ driving force from a double well?

Notes: we will derive Arrhenius's law at constant T (not at constant E) $E \to G \sim \mu$

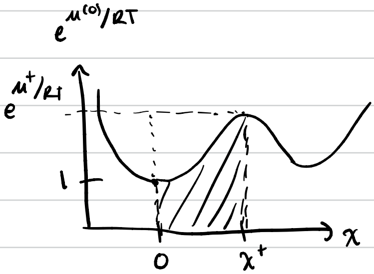
We will calculate the forward rate from the forward flux.

$$v^+_{forward}\left(\frac{m}{s}\right) = \frac{J_{forward}}{c(0)}$$

$$= \frac{D}{x^+}\, P(x\,|\,0)$$

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

Make a plot of $e^{\mu^{(0)}/RT}$ and see what the integral looks like:




integral < area of a box

$$\int_0^{x^+} dx' e^{\mu^{(0)}(x')/RT)} < x' \cdot e^{\mu^+/RT}$$

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

w/ $\chi \geq 1$

(Typically $\chi \approx 1.5$.)