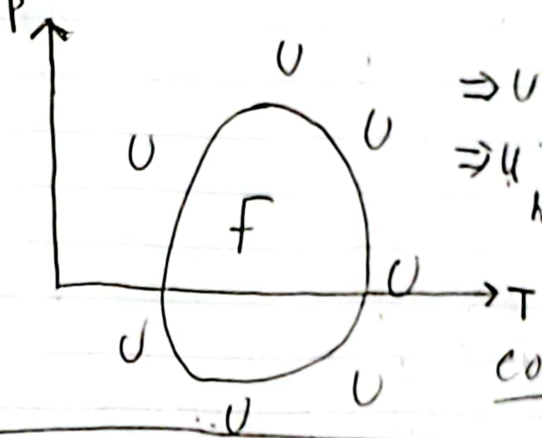
Lecture

Last time: Integrated flux j .. (steady-state)

$$J = \text{const.} = -D \cdot \frac{e^{\mu_0^{(0)}/RT} - e^{\mu_0^{(0)}/RT}}{\underbrace{\int_0^x dx' \, e^{\mu^{(0)}(x')/RT}}_{>0}} \quad \text{Le Châtlier}$$

ex: Le Châtlier : " J equalizes μ "

ex: protein folding phase diagram



⇒ U has smaller volume

⇒ U has higher entropy at higher T (than F)

cold denaturation

Today: Bayesian formulation of flux and transition state theory

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

Using $\mu_g = \mu^{(0)} + RT \ln c$ (ideal solution or gas), we can rewrite

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

two unitless factors

$\frac{1}{Z} = e^{F/RT}$

$\frac{1}{e^{-G/RT}}$ inverse of Boltzman factor

the two ratios of inverse Boltzman factors >0 and <1

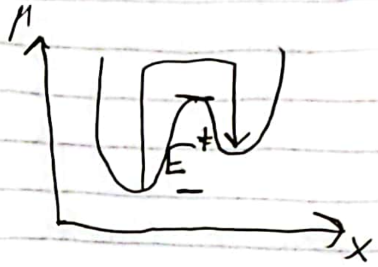
$$J = -\frac{D}{x} \left\{ \underbrace{c(x)\, P(0|x)}_{\text{Backward flux}} - \underbrace{c(0)\, P(x|0)}_{\text{Forward flux}} \right\}$$

$P(0|x)$: Probability a molecule ends up at $x=0$ if it started at x

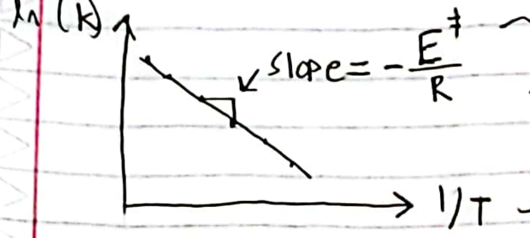
$P(x|0)$ = Probability a molecule ends up at x if it started at 0

e.g. Microscopic balance ; vehicle traffic ; economics

TST – transition state theory:

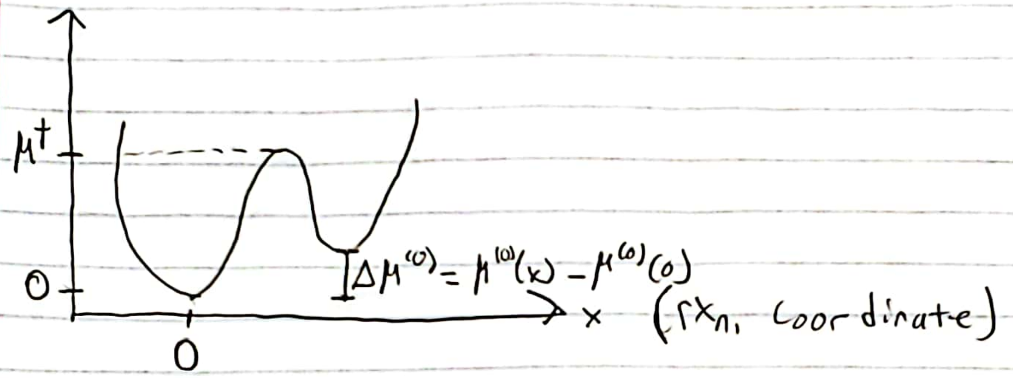


Svante Arrhenius:



$$k = A \cdot e^{-E^{\ddagger}/RT}$$

$\updownarrow \mu(x)$



Can we derive the Arrhenius eq. from stat mech., physico-chemical mechanics?

We'll derive the Arrhenius Law at const. T (μ) not at const. S (E).

$$v_{forward} = \frac{J_{forward}}{C(x)} = \frac{D}{x} \cdot \frac{e^{\mu^{(0)}(x \doteq 0)/RT}}{\frac{1}{x}\int_0^x dx' \, e^{\mu^{(0)}(x')/RT}}$$