

Lecture 36 Review:

Integrated flux J

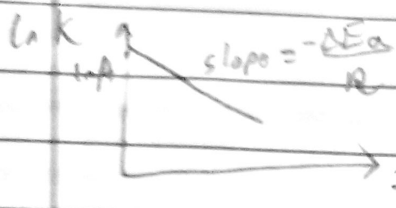
$$J = -D \frac{d}{dx} \left(\frac{N_A c_A e^{-\mu_A(x)/RT}}{N_A c_A e^{-\mu_B(x)/RT}} \right)$$

$J < 0$ if $\mu_B(x) > \mu_B(0) \rightarrow$ flux restores equilibrium (Le Chatelier's Principle)

$$J = -\frac{D}{x} \left(\underbrace{([A] P(0|x))}_{\text{backward rxn}} - \underbrace{([B] P(x|0))}_{\text{forward rxn}} \right) \quad (\text{Principle of microscopic reversibility})$$

Lecture 37: Activated rate theory:

rate constant: $k \left(\frac{\text{units}}{s} \right) = A e^{-\Delta E_a / RT}$

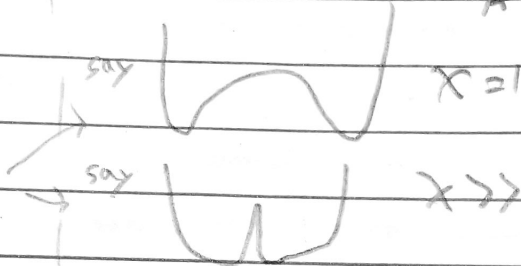
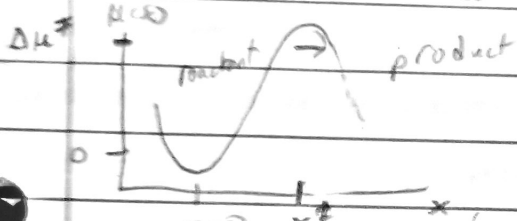


We can calculate $x \geq 1$ if we know the function $\mu(x)$ from quantum mechanics.

$$V_F \left(\frac{m}{s} \right) = \frac{x D}{x^\ddagger} e^{-\Delta \mu^\ddagger / RT}$$

$$k_f = \frac{V_F \left(\frac{m}{s} \right)}{x^\ddagger (m)} \rightarrow k_f \left(\frac{1}{s} \right) = \frac{x D}{(x^\ddagger)^2} e^{-\frac{\Delta \mu^\ddagger}{RT}}$$

The chemical potential $\mu = \frac{\partial E}{\partial N}$, not the energy, is what drives the reaction.



Typically, x ranges from 1 to 2 for chemical rxns.

in-class exercise:

ion in H_2O , $D = 10^{-9} m^2/s$, reaction distance $\approx 0.5 \text{ \AA}$

assume $x=1 \rightarrow A = \frac{1 \cdot 10^{-9} m^2/s}{(5 \times 10^{-11} m/s)^2} = 4 \times 10^{11} s^{-1}$

$\tau = \frac{1}{k} = 2.5 \text{ ps}$
(units) \uparrow barrier free

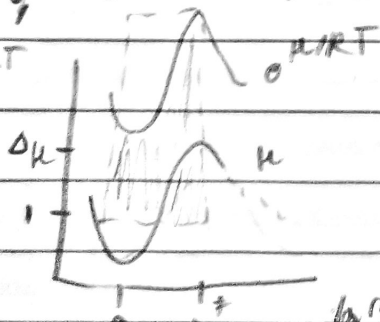
$$J_F(x^\ddagger) = D \frac{([B]_0 e^{\mu_B(0)/RT})}{\int_0^{x^\ddagger} dx e^{\mu(x)/RT}}$$

(flux at peak determines rate; rate limited step)

$$V_F = \frac{J_F}{[B]} = D \frac{e^{\mu_B(0)/RT}}{\int_0^{x^\ddagger} e^{\mu(x)/RT} dx}$$

Can set $\mu_B(0) = 0$, so $e^{\mu_B(0)/RT} = 1$

Can plot $e^{\mu/RT}$



$$\int_0^{x^\ddagger} dx e^{\mu(x)/RT} < x^\ddagger e^{\Delta \mu / RT} \quad (\text{area under curve} = 5 \text{ is less than the box})$$

$$= \frac{x^\ddagger}{x} e^{\Delta \mu / RT} \quad \text{for } x > 1$$