Lecture #4 of 12

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Thermal (Dark) Reactions

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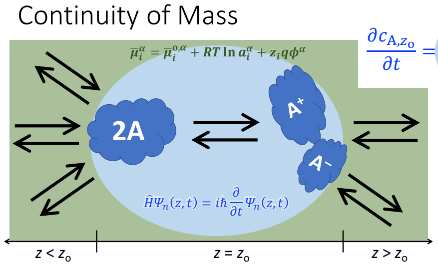
Continuity of Mass

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial \mathbf{N}_A}{\partial z}$$



Note: Adjusting just one variable is difficult… but people, like us, can try

"Jean Piaget, the Swiss psychologist who first studied object permanence in infants, argued that it is one of an infant's most important accomplishments, as, without this concept, objects would have no separate, permanent existence."
– Wiki, Object permanence

Transport for Photochemistry

So, what are ideal mass-transfer-related properties in photochemical systems?

$$\text{Flux}_{z,e} = \mathbf{N}_e = -\frac{\sigma_e}{F^2}\frac{d\bar{\boldsymbol{\mu}}_e}{dz}$$

(1) **Transport is fast** = flux is large…
… so that excited states can always interact with reactants to perform chemical reactions
… so that reactants are not depleted by chemical reactions

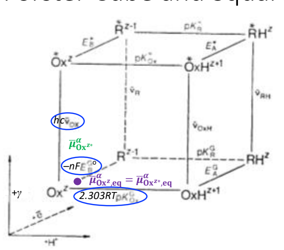
(2) **At least 2 non-equilibrium species transport to different locations** = "selective contacts"…
… which results in different observed rates for various chemical reactions at each location
… that are ideally oppositely charged, so that transport of only a few results in large ϕ, $\Delta\bar{\boldsymbol{\mu}}_i$

(2') **Reactivity by non-equilibrium species is selective** = desired reactions are fast…
… so that photon energy can be stored in chemical products, when $\Delta G > 0$ for the reaction
… so that photon energy can be used to speed up reactions with $\Delta G < 0$

$$\text{Flux}_{z,e} = -D_e\boldsymbol{n}_e\left(\frac{d\boldsymbol{\mu}_e^{\text{o}}}{k\boldsymbol{T}_e\,dz} + \frac{d(\ln\boldsymbol{\gamma}_e)}{dz} + \frac{d(\ln\boldsymbol{n}_e)}{dz} - \frac{d(\ln\boldsymbol{n}_e^{\text{o}})}{dz} - \frac{d(q\phi)}{k\boldsymbol{T}_e\,dz}\right) - \boldsymbol{D}_{\boldsymbol{n}_e,\boldsymbol{\gamma}_e,\boldsymbol{n}_e^{\text{o}},\boldsymbol{T}_e}\frac{d\boldsymbol{T}_e}{dz}$$

… okay… now let's try this again…

Förster Cube and Square Schemes



… all of these free energy terms are **standard-state** free energies (ΔG^{o})… but what is the actual free energy of the system (ΔG)?

… let's assume that $\Delta G = 0$ (equilibrium)… how could I indicate that on this slide, as a point(s), to depict the majority species present?

… now, how can one **push/pull** this system out of equilibrium?

… recall Le Châtelier's principle… and thus by addition of reactants or removal of products… such as mass or light!

… hopefully this made a little more sense this time around… and if not, let's keep on trying!

Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 11–28

Summary of Key Equations and Equilibrium

α is the phase

$$A \rightleftarrows B$$

$$\frac{\partial c_{\text{A},z_\text{o}}}{\partial t} = \sum_j R_{\text{A},j}$$

(Chemists should be yawning)

$$\bar{\boldsymbol{\mu}}_B^{\alpha} - \bar{\boldsymbol{\mu}}_A^{\alpha} = \boldsymbol{\Delta G^{\alpha}} = \boldsymbol{\Delta G^{\text{o},\alpha}} + \boldsymbol{RT\ln Q}\text{… where } Q = \frac{a_\text{B}^\alpha}{a_\text{A}^\alpha} = \frac{\gamma_\text{B}^\alpha\left(c_\text{B}^\alpha/c_\text{B}^{\text{o},\alpha}\right)}{\gamma_\text{A}^\alpha\left(c_\text{A}^\alpha/c_\text{A}^{\text{o},\alpha}\right)}$$

$R_{\text{A},f} = -\boldsymbol{k_f}a_\text{A}$ $\quad R_{\text{B},f} = +\boldsymbol{k_f}a_\text{A}$ $\quad \boldsymbol{k_j}$ (M/s)… a rate!

$R_{\text{A},b} = +\boldsymbol{k_b}a_\text{B}$ $\quad R_{\text{B},b} = -\boldsymbol{k_b}a_\text{B}$ $\quad \boldsymbol{k_j'}$ (s^{-1})… an inverse time constant!

$$\bar{\boldsymbol{\mu}}_i^{\alpha} = \left(\frac{\partial \boldsymbol{G}^\alpha}{\partial \boldsymbol{n}_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad \frac{\partial c_{\text{A},z_\text{o}}^\alpha}{\partial t} = -\boldsymbol{k_f}a_\text{A}^\alpha + \boldsymbol{k_b}a_\text{B}^\alpha = -\boldsymbol{k_f'}c_\text{A}^\alpha + \boldsymbol{k_b'}c_\text{B}^\alpha = -\frac{\partial c_{\text{B},z_\text{o}}^\alpha}{\partial t}$$

Now, consider the reaction to be at equilibrium (3 ways)… $\boldsymbol{\Delta G^{\alpha} = 0} = \Delta G^{\text{o},\alpha} + RT\ln Q$

… and so, $\Delta G^{\text{o},\alpha} = -RT\ln K$, with $K = \frac{a_\text{B,eq}^\alpha}{a_\text{A,eq}^\alpha} = \frac{\gamma_\text{B}^\alpha\left(c_\text{B,eq}^\alpha/c_\text{B}^{\text{o},\alpha}\right)}{\gamma_\text{A}^\alpha\left(c_\text{A,eq}^\alpha/c_\text{A}^{\text{o},\alpha}\right)}$

And also, $\bar{\boldsymbol{\mu}}_\text{B}^\alpha - \bar{\boldsymbol{\mu}}_\text{A}^\alpha = \boldsymbol{0}$… and so, $\bar{\mu}_\text{A}^\alpha = \bar{\mu}_\text{B}^\alpha$… if that is even helpful

And also, $\frac{\partial c_{\text{A},z_\text{o}}^\alpha}{\partial t} = \boldsymbol{0} = -\frac{\partial c_{\text{B},z_\text{o}}^\alpha}{\partial t} = -\boldsymbol{k_f}a_\text{A,eq}^\alpha + \boldsymbol{k_b}a_\text{B,eq}^\alpha$… and so $\frac{\boldsymbol{k_f}}{\boldsymbol{k_b}} = \frac{a_\text{B,eq}^\alpha}{a_\text{A,eq}^\alpha} = \frac{\gamma_\text{B}^\alpha\left(c_\text{B,eq}^\alpha/c_\text{B}^{\text{o},\alpha}\right)}{\gamma_\text{A}^\alpha\left(c_\text{A,eq}^\alpha/c_\text{A}^{\text{o},\alpha}\right)} = K$

Today's Critical Guiding Question

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What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species… and uniquely for today, how does it allow us to quantitatively predict kinetic information… for real this time?

Thermal (Dark) Reactions

(UPDATED) 81

- **Activation energy, Eyring–Polanyi–Evans equation**
- **Marcus–Hush (electron-transfer) theory**
- **Transition-state character, Reorganization energies (outer and inner),** Linear free energy relationships
- Molecular orbital theory, Huang–Rhys factor
- Quantum mechanical tunneling, Superexchange
- Inner *versus* Outer sphere reactions, Robin–Day classification
- Self-exchange reactions, Marcus cross relations
- Charge transfer across electrified interfaces, Butler–Volmer equation, Rate-determining step, Fermi's golden rule, Marcus–Gerischer theory

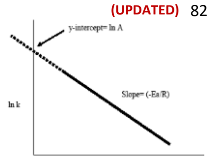
Activation Energy

(UPDATED) 82

Arrhenius (1889)
empirical rate constant equation

$A \rightleftarrows B$

$\boldsymbol{k_f} = Ae^{-\frac{E_a}{RT}}$ … **pre-exponential factor**, A, has units of s^{-1}



Eyring–Polanyi–Evans (1930s)

$A \rightleftarrows X^{\neq} \rightleftarrows B$

theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$\boldsymbol{k_f} = \kappa\nu K^{\neq} = \frac{\kappa k_B T}{h} K^{\neq}$ … with **transmission coefficient**, κ, and **vibrational frequency**, ν (s^{-1})

this N_A is the Avogadro constant → … and $R = N_A k_B$… and $\frac{\kappa k_B T}{h}$ has units of s^{-1}

$$\boldsymbol{k_f} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$ … and so A contains $\Delta S^{\neq}$

… what is the largest predicted pre-exponential factor at 25 °C? **$(161\ fs)^{-1} = (1.61 \times 10^{-13}\ s)^{-1}$**

83

Marcus–Hush Theory

$$\underbrace{D + A}_{A} \rightleftarrows \underbrace{D^+ + A^-}_{B}$$

... but how is this a first-order reaction (s^{-1})?... more on this later...

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}k_BT}} \exp\left(-\frac{\Delta G_{AB}{}^{\neq}}{k_BT}\right)$$ ... $\frac{2\pi|H_{DA}|^2}{\hbar\sqrt{4\pi\lambda k_BT}}$ has units of s^{-1}

$$A \rightleftarrows X^{\neq} \rightleftarrows B$$

Eyring–Polanyi–Evans (1930s)
theoretical rate constant equation (from **transition-state theory / activated complex theory**)

$$k_f = \kappa\nu K^{\neq} = \frac{\kappa k_BT}{h}K^{\neq}$$ ... with **transmission coefficient**, κ, and **vibrational frequency**, ν (s^{-1})

... and $R = N_A k_B$... and $\frac{\kappa k_BT}{h}$ has units of s^{-1}

$$k_f = \frac{\kappa k_BT}{h}\exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \frac{\kappa k_BT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$ ... and so A contains $\Delta S^{\neq}$

... what is the largest predicted pre-exponential factor at 25 °C? **(161 fs)$^{-1}$ = (1.61 x 10^{-13} s)$^{-1}$**

84

Marcus–Hush Theory

$$\underbrace{D + A}_{A} \rightleftarrows \underbrace{D^+ + A^-}_{B}$$

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \underbrace{\frac{2\pi}{\hbar}|H_{DA}|^2}_{\text{quantum adiabatic electronic coupling}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}{}^{\neq}}{kT}\right)}_{\text{classical nuclear free-energy dependence}}$$

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

proportional to $\frac{d\bar{\mu}_A}{dz}$

proportional to $\exp\left((\lambda_{AB} + \Delta G_{AB}{}^{o})^2\right)$

... which term shall we discuss first?
... I don't know about you, but when given a choice between classical and quantum mechanical
... I go with classical... OK?

$$\Delta G_{AB}{}^{\neq} = \frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}}$$

... wait... there is a direct relation between thermodynamics ($\Delta G_{AB}{}^{o}$) and kinetics ($\Delta G_{AB}{}^{\neq}$)?
... this makes sense since $\frac{d\bar{\mu}_A}{dz}$ drives transport, which can be written as a chemical reaction
... but that key relationship is quadratic... meaning a parabola? Huh?!?!?!

85

Marcus–Hush Theory

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Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \underbrace{\frac{2\pi}{\hbar}|H_{DA}|^2}_{\text{quantum adiabatic electronic coupling}} \underbrace{\frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}{}^{\neq}}{kT}\right)}_{\text{classical nuclear free-energy dependence}}$$

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}kT}\right)$$ ... what kind of function is this?

$$\Delta G_{AB}{}^{\neq} = \frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}}$$

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2}\left(\frac{\Delta G_{AB}{}^{o} - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right)$$ ... does this help at all?

Marcus–Hush Theory

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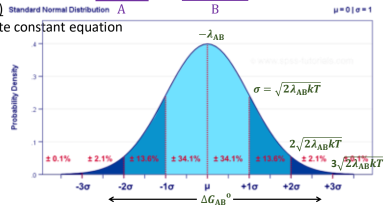
D + A ⇄ D⁺ + A⁻
A B

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

… wait… the classical component in Marcus electron-transfer theory is a **normal distribution** as a function of standard-state thermodynamic driving force ($\Delta G_{AB}{}^{o}$)?… **Yep!**



$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2}\left(\frac{\Delta G_{AB}{}^{o} - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right)$$

… does this help at all?

Marcus–Hush Theory

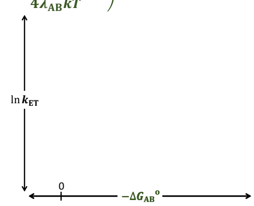
(UPDATED) 87

D + A ⇄ D⁺ + A⁻
A B

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}kT}\right)$$



?

Marcus–Hush Theory

(UPDATED) 88

D + A ⇄ D⁺ + A⁻
A B

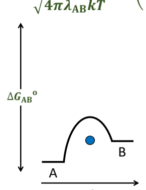
Marcus–Hush (1950s–1960s)

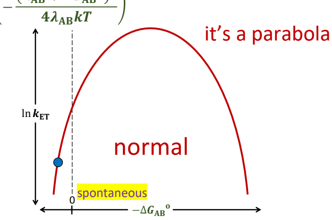
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}kT}\right)$$

How can a thermo-dynamically unfavorable reaction proceed?

Mass Action!





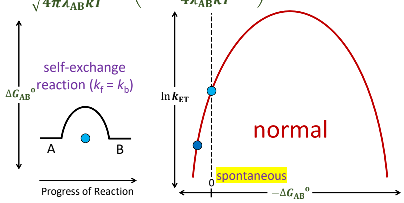
(UPDATED) 89

Marcus–Hush Theory

$\underset{\text{A}}{\underline{D + A}} \rightleftarrows \underset{\text{B}}{\underline{D^+ + A^-}}$

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}kT}\right)$$



(UPDATED) 90

Marcus–Hush Theory

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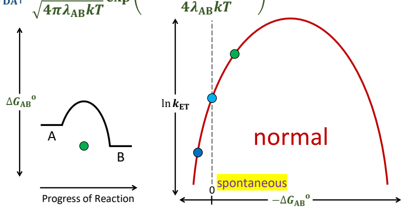

(UPDATED) 91

Marcus–Hush Theory

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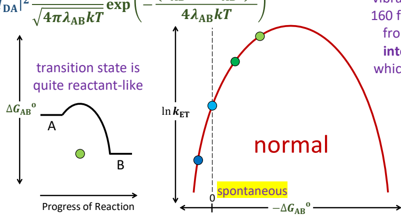
Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}{}^{o})^2}{4\lambda_{AB}kT}\right)$$



Note that a **transition state** only lasts on the order of a bond vibration ($h/k_BT \approx$ 160 fs) and differs from a proper **intermediate**, which lasts much longer

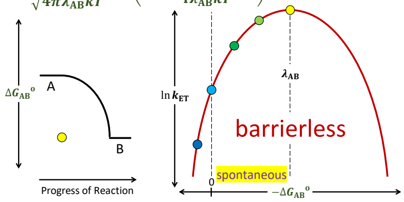
(UPDATED) 92

Marcus–Hush Theory

$D + A \rightleftarrows D^{+} + A^{-}$
A B

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB}+\Delta G_{AB}^{o})^2}{4\lambda_{AB}kT}\right)$$



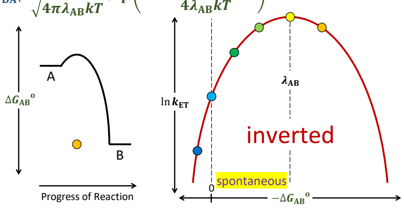
(UPDATED) 93

Marcus–Hush Theory

$D + A \rightleftarrows D^{+} + A^{-}$
A B

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB}+\Delta G_{AB}^{o})^2}{4\lambda_{AB}kT}\right)$$



(UPDATED) 94

Marcus–Hush Theory

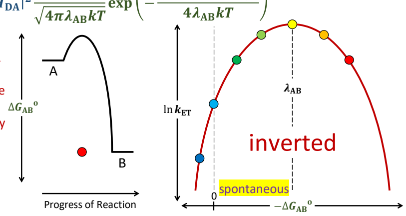
$D + A \rightleftarrows D^{+} + A^{-}$
A B

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB}+\Delta G_{AB}^{o})^2}{4\lambda_{AB}kT}\right)$$

... this looks odd...

... but what did we expect from a General Chemistry cartoon



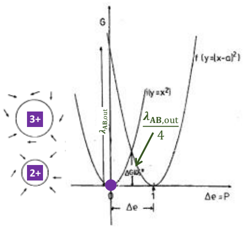
Outer Reorganization Energy

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^{\neq}}{kT}\right)$$

$$\Delta G_{AB}^{\neq} = \frac{(\lambda_{AB} + \Delta G_{AB}^{o})^2}{4\lambda_{AB}}$$

… but what causes this parabolic relationship?…
… what physical expression results in a quadratic dependence on **charge**?
… classical electrostatics… of the solvent!
… dielectric continuum model…
… $G_{out} \approx 1$ eV in water
… G_{out} decreases as permittivity decreases



$$\lambda_{out} = \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right)(\Delta e)^2$$

Outer + Inner Reorganization Energies

Marcus–Hush (1950s–1960s)
theoretical (semiclassical) rate constant equation

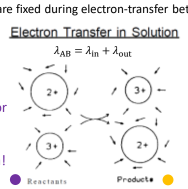
This theory came about by answering the following question: For an electron-transfer event, how does one satisfy the Franck–Condon principle and the conservation of energy?

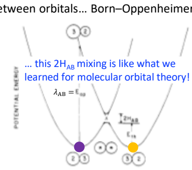
- Franck–Condon principle: Nuclei are fixed during electron-transfer between orbitals… Born–Oppenheimer approximation is relevant

$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2}\sum_l f_l\,(\Delta q_{e,l})^2$$

… this is for a harmonic oscillator
… with force constants, f_l…

… and yes, it's another parabola!





P. Chen & T. J. Meyer, *Chem. Rev.*, **1998**, *98*, 1439–1477

N. Sutin, *Acc. Chem. Res.*, **1982**, *15*, 275–282

Today's Critical Guiding Question

What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species… and uniquely for today, how does it allow us to quantitatively predict kinetic information… for real this time?

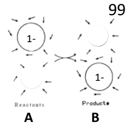
99

Transport as a Chemical Reaction

$$\frac{\partial c_{A,z_o}}{\partial t} = \sum_j R_{A,j} - \frac{\partial \mathbf{N}_A}{\partial z}$$

... in a reaction "volume" z_o...
... that encompasses z_1 and z_2

$$A^-_{z_1} \rightleftarrows A^-_{z_2}$$

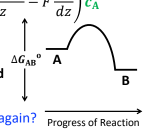


$\boldsymbol{R}_A = -k_f \boldsymbol{c}_{A_{z_1}} + k_b \boldsymbol{c}_{A_{z_2}} = (\boldsymbol{k}_b - \boldsymbol{k}_f)\boldsymbol{c}_{A_{z_1}} + \boldsymbol{k}_b \Delta \boldsymbol{c}_A$ ... where $\boldsymbol{c}_{A_{z_2}} = \boldsymbol{c}_{A_{z_1}} + \Delta \boldsymbol{c}_A$

$$\mathbf{N}_A = \left(-\frac{D_A}{RT}\frac{\partial \bar{\mu}_A}{\partial z}\right)c_A = -\frac{D_A}{RT}\left(\frac{RT}{c_A}\frac{dc_A}{dz} + \frac{d\mu_A^o}{dz} - RT\frac{d(\ln\gamma)}{dz} - RT\frac{d\left(\ln c_A^o\right)}{dz} - F\frac{d\phi}{dz}\right)c_A$$

$$= -D_A\frac{dc_A}{dz} + \frac{-D_A F\mathbf{E}'}{RT}c_A \approx -\frac{D_A}{l}\Delta c_A + \frac{-D_A F\mathbf{E}'}{RT}c_A$$

... where $\mathbf{E}'$ is an **effective force field**



$$-\frac{\partial \mathbf{N}_A}{\partial z} \approx \frac{D_A}{l^2}\Delta c_A + \frac{D_A F\mathbf{E}'}{RTl}c_A = \text{"}k_b\text{"}\Delta c_A + \text{"}(k_b - k_f)\text{"}c_A$$

(diffusion) *(drift)* ... what is D_A again?

... since the reaction volume is >1 Å^3 , l > 1 Å... and D(aq) < 10^{-4} cm^2/s... $k_{D(aq)}$ **< 10^{12} s^{-1} = (>1 ps)$^{-1}$**

100

Diffusion Coefficient

mean square displacement (variance)

$$\overline{\Delta^2} = ml^2 = \frac{t}{\tau}l^2 = 2Dt$$

$$\ldots D = \frac{l^2}{2\tau}$$

(Recall: D_z is has units of cm^2 s^{-1}... as zz)

... and why do we care?

m is just the number
τ is the step time

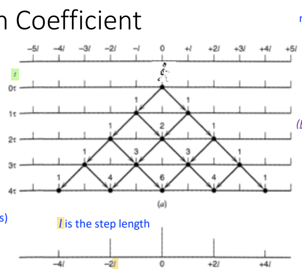


Figure 4.4.2 (*a*) Probability distribution for a one-dimensional random walk over zero to four time units. The number printed over each allowed arrival point is the number of paths to that point. (*b*) Bar graph showing distribution at $t = 4\tau$. At this time, probability of being at $x = 0$ is 6/16, at $x = \pm 2l$ is 4/16, and at $x = \pm 4l$ is 1/16.

l is the step length

root mean square (rms) displacement (standard deviation)

$\bar{\Delta} = \sqrt{(2d)Dt}$, **where *d* is the dimension**
... and the "2" is for positive and negative directions

Bard & Faulkner, Chapter 4, Figure 4.4.2, Page 147