Lecture #4 of 12

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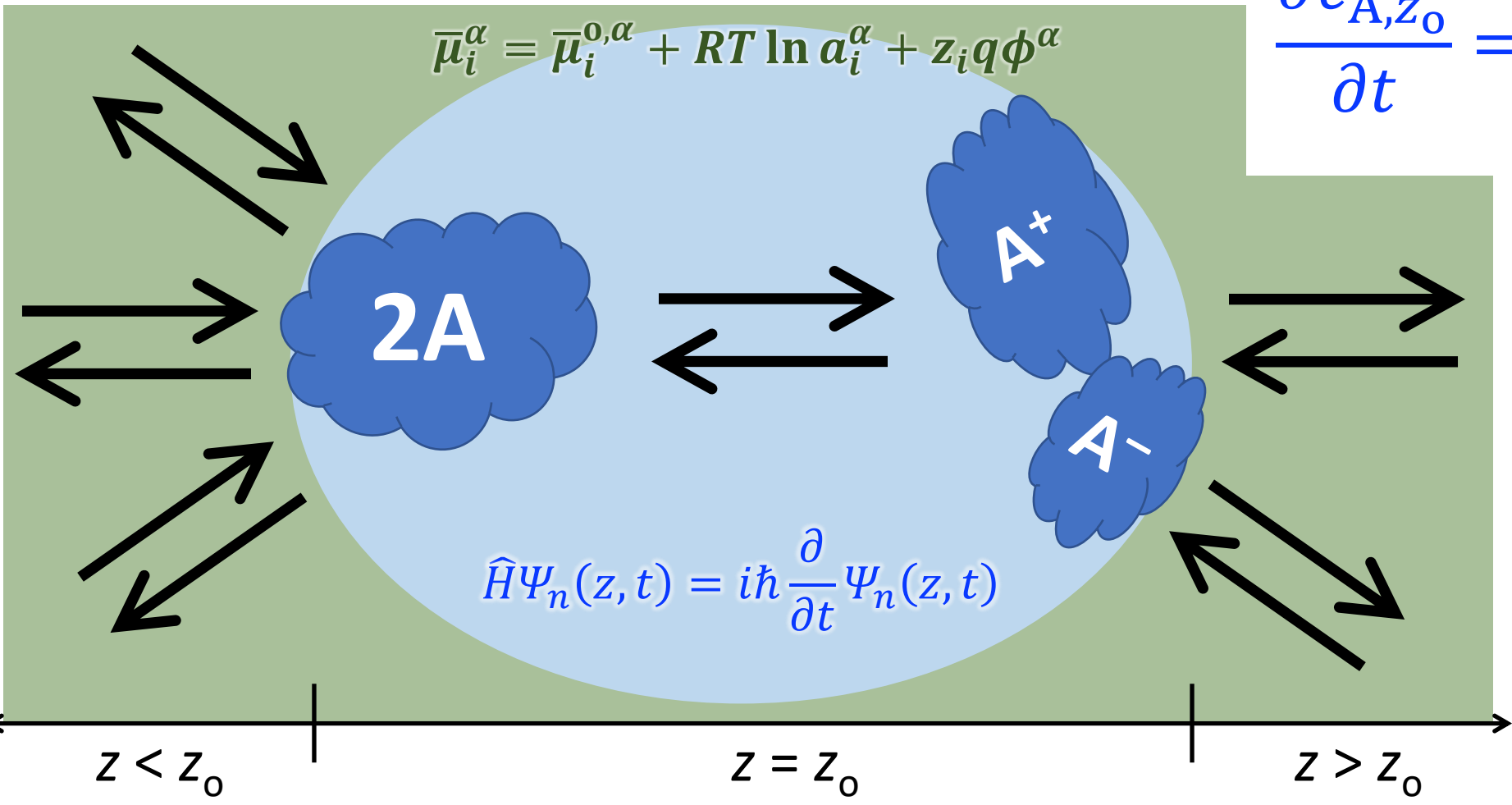
Thermal (Dark) Reactions

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Continuity of Mass

$$\overline{\mu}_i^\alpha = \overline{\mu}_i^{o,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$$

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

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

2A ⇌ **A$^+$** **A$^-$**

$$\hat{H}\Psi_n(z,t) = i\hbar \frac{\partial}{\partial t}\Psi_n(z,t)$$

$z < z_o$ $z = z_o$ $z > z_o$

"Jean Piaget, the Swiss psychologist who first studied <u>object permanence</u> 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?

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

(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, $\Delta\overline{\boldsymbol{\mu}}_i$
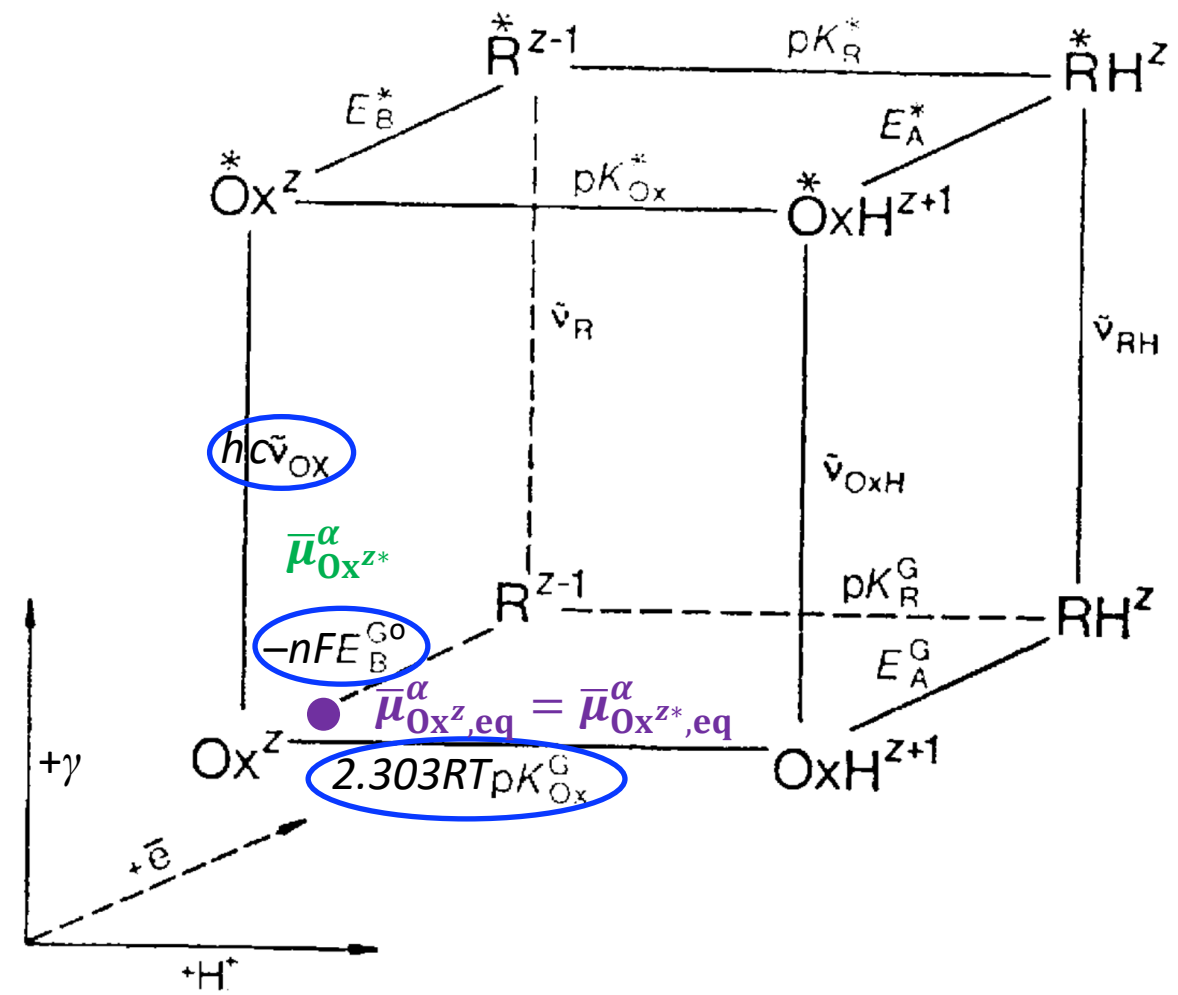
(2') **Reactivity by non-equilibrium species is selective** = desired reactions are fast…

… 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 $\Delta G < 0$

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

Förster Cube and Square Schemes

... all of these free energy <u>terms</u> 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 <u>or light</u>!**
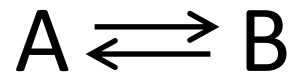
... hopefully this made a little more sense this time around... and if not, let's keep on trying!

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

$$A \rightleftharpoons B$$

$$\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = \Delta G^\alpha = \Delta G^{o,\alpha} + RT \ln Q \dots \text{ where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{\gamma_B^\alpha (c_B^\alpha / c_B^{0,\alpha})}{\gamma_A^\alpha (c_A^\alpha / c_A^{0,\alpha})}$$

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

$$R_{A,f} = -k_f a_A \qquad R_{B,f} = +k_f a_A \qquad k_j \text{ (M/s)... a rate!}$$

(Chemists should be yawning)

$$R_{A,b} = +k_b a_B \qquad R_{B,b} = -k_b a_B \qquad k_j' \text{ (s}^{-1}\text{)... an inverse time constant!}$$

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} \qquad \frac{\partial c_{A,z_o}^\alpha}{\partial t} = -k_f a_A^\alpha + k_b a_B^\alpha = -k_f' c_A^\alpha + k_b' c_B^\alpha = -\frac{\partial c_{B,z_o}^\alpha}{\partial t}$$

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

$$\dots \text{ and so, } \Delta G^{o,\alpha} = -RT \ln K, \text{ with } K = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha \left(c_{B,eq}^\alpha / c_B^{0,\alpha} \right)}{\gamma_A^\alpha \left(c_{A,eq}^\alpha / c_A^{0,\alpha} \right)}$$

And also, $\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha = 0 \dots$ and so, $\bar{\mu}_A^\alpha = \bar{\mu}_B^\alpha \dots$ if that is even helpful

And also, $\frac{\partial c_{A,z_o}^\alpha}{\partial t} = 0 = -\frac{\partial c_{B,z_o}^\alpha}{\partial t} = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha \dots$ and so $\frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha \left(c_{B,eq}^\alpha / c_B^{0,\alpha} \right)}{\gamma_A^\alpha \left(c_{A,eq}^\alpha / c_A^{0,\alpha} \right)} = K$

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?

Thermal (Dark) Reactions

- **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

<u>Arrhenius (1889)</u>

empirical rate constant equation

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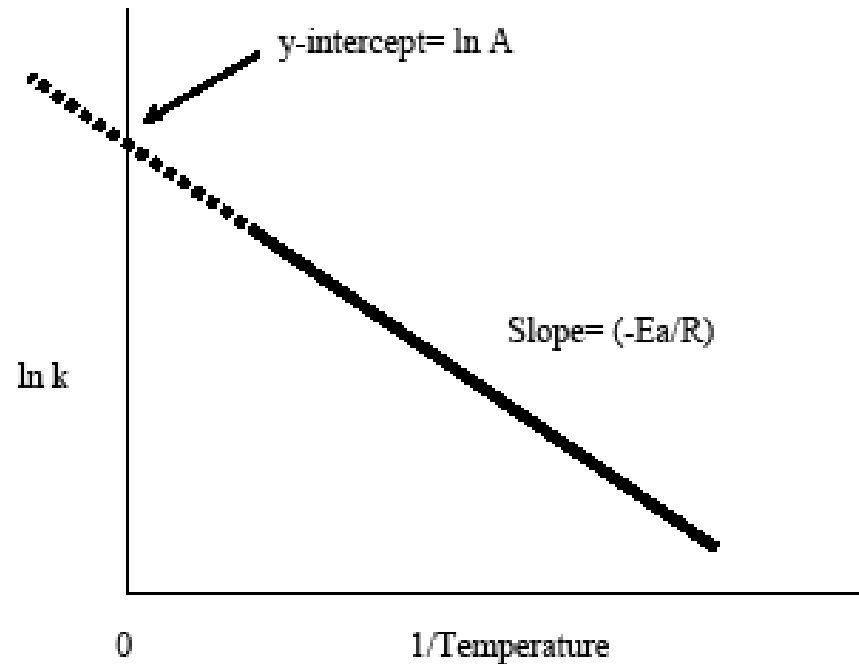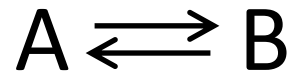
$$A \rightleftharpoons B$$

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

<u>Eyring–Polanyi–Evans (1930s)</u>

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

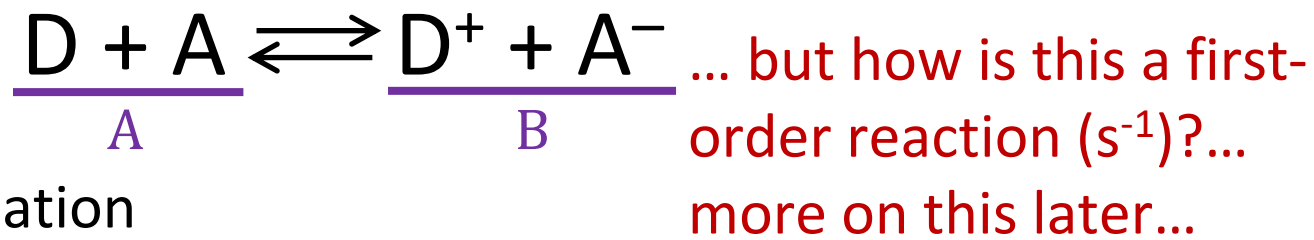$$k_f = \kappa \nu K^{\neq} = \frac{\kappa k_{\mathrm{B}} T}{h} K^{\neq}$$ ... with **transmission coefficient**, κ, and **vibrational frequency**, ν (s^{-1})

this N_A is the Avogadro constant $\longrightarrow$ ... and $R = N_A k_{\mathrm{B}}$ ... and $\frac{\kappa k_{\mathrm{B}} T}{h}$ has units of s^{-1}

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

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

ln k

y-intercept= ln A

Slope= (-Ea/R)

0   1/Temperature

Marcus–Hush Theory

$$D + A \underset{}{\overset{}{\rightleftharpoons}} D^+ + A^-$$
$$\underbrace{}_{A} \qquad \underbrace{}_{B}$$

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

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

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

... $\frac{2\pi|H_{\mathrm{DA}}|^2}{\hbar\sqrt{4\pi\lambda k_{\mathrm{B}}T}}$ has units of s^{-1}

$$A \underset{}{\overset{}{\rightleftharpoons}} X^{\neq} \underset{}{\overset{}{\rightleftharpoons}} B$$

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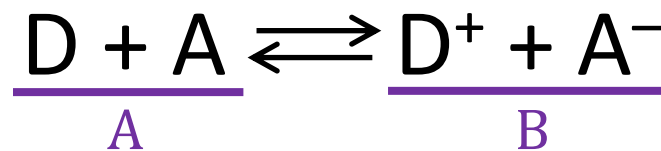theoretical rate constant equation (from **transition-state theory / activated complex theory**)

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

... and $R = N_A k_{\mathrm{B}}$... and $\frac{\kappa k_{\mathrm{B}}T}{h}$ has units of s^{-1}

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

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Marcus–Hush Theory

$$\text{D + A} \rightleftharpoons \text{D}^+ + \text{A}^-$$
$$\underbrace{\phantom{\text{D + A}}}_{A} \quad \underbrace{\phantom{\text{D}^+ + \text{A}^-}}_{B}$$

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

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

proportional to $\frac{d\bar{\mu}_{\mathrm{A}}}{dz}$

$$\frac{\partial c_{\mathrm{A},z_{\mathrm{o}}}}{\partial t} = \sum_j R_{\mathrm{A},j} - \frac{\partial \mathrm{N}_{\mathrm{A}}}{\partial z}$$

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

… which term shall we discuss first?

… I don't know about you, but when given a choice between classical and quantum mechanical
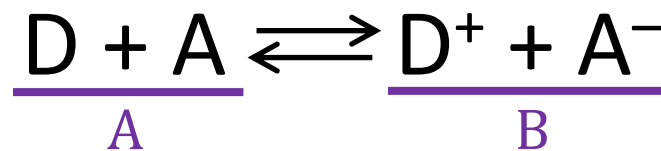
… I go with classical… OK?

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

… wait… there is a direct relation between thermodynamics ($\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$) and kinetics ($\Delta G_{\mathrm{AB}}{}^{\neq}$)?

… this makes sense since $\frac{d\bar{\mu}_{\mathrm{A}}}{dz}$ drives transport, which can be written as a chemical reaction

… but that key relationship is quadratic… meaning a parabola? Huh?!?!?!

Marcus–Hush Theory

$$D + A \underset{}{\overset{}{\rightleftharpoons}} D^+ + A^-$$

$$\underline{}_{A} \qquad \underline{}_{B}$$

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

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

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

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

Marcus–Hush Theory

$$D + A \underset{}{\overset{}{\rightleftharpoons}} D^+ + A^-$$

$$\underline{} \qquad \underline{}$$
$$A \qquad\qquad B$$

theoretical (semiclassical) rate constant equation
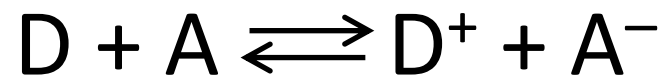
Standard Normal Distribution   μ = 0 | σ = 1

… 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!**

$$-\lambda_{AB}$$

$$\sigma = \sqrt{2\lambda_{AB}kT}$$

$$2\sqrt{2\lambda_{AB}kT}$$

$$3\sqrt{2\lambda_{AB}kT}$$

± 0.1%   ± 2.1%   ± 13.6%   ± 34.1%   ± 34.1%   ± 13.6%   ± 2.1%   ± 0.1%

-3σ   -2σ   -1σ   μ   +1σ   +2σ   +3σ

$$\longleftarrow \Delta G_{AB}{}^o \longrightarrow$$

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

Marcus–Hush Theory

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

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

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

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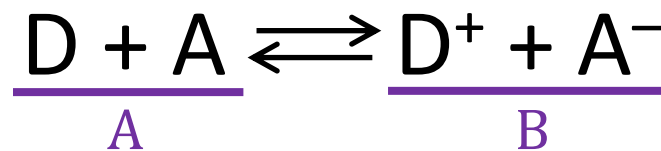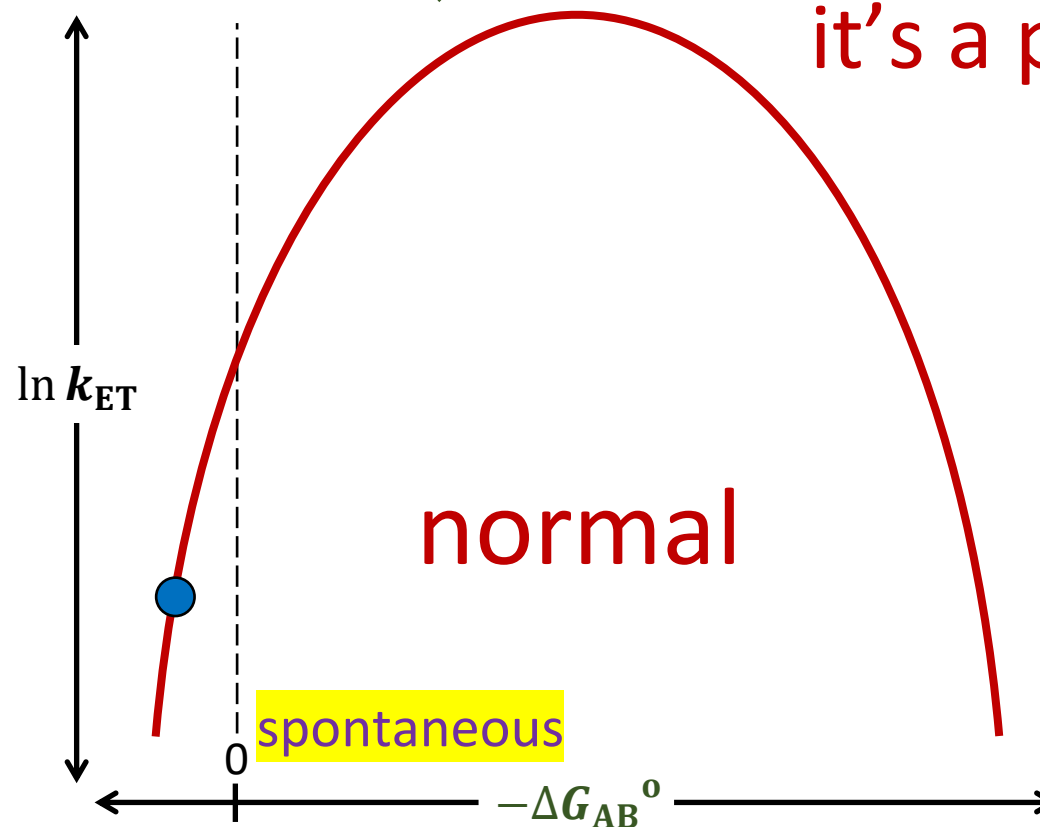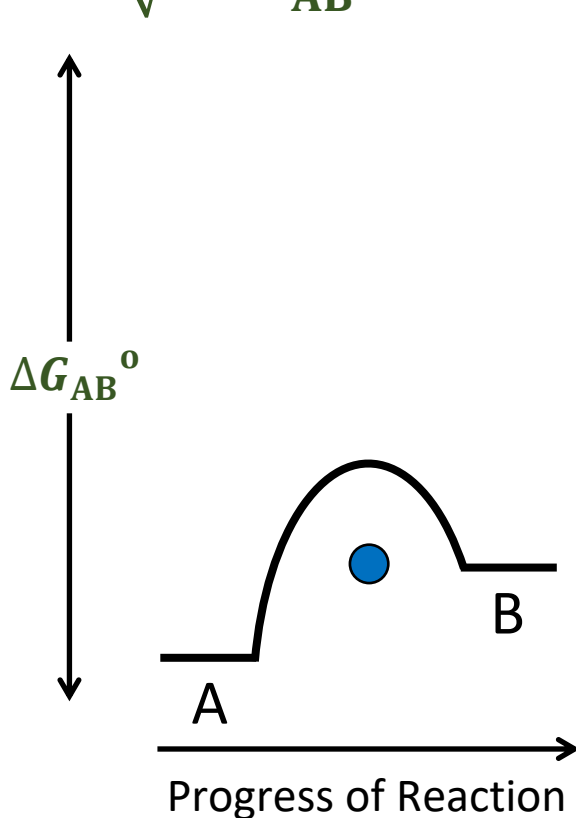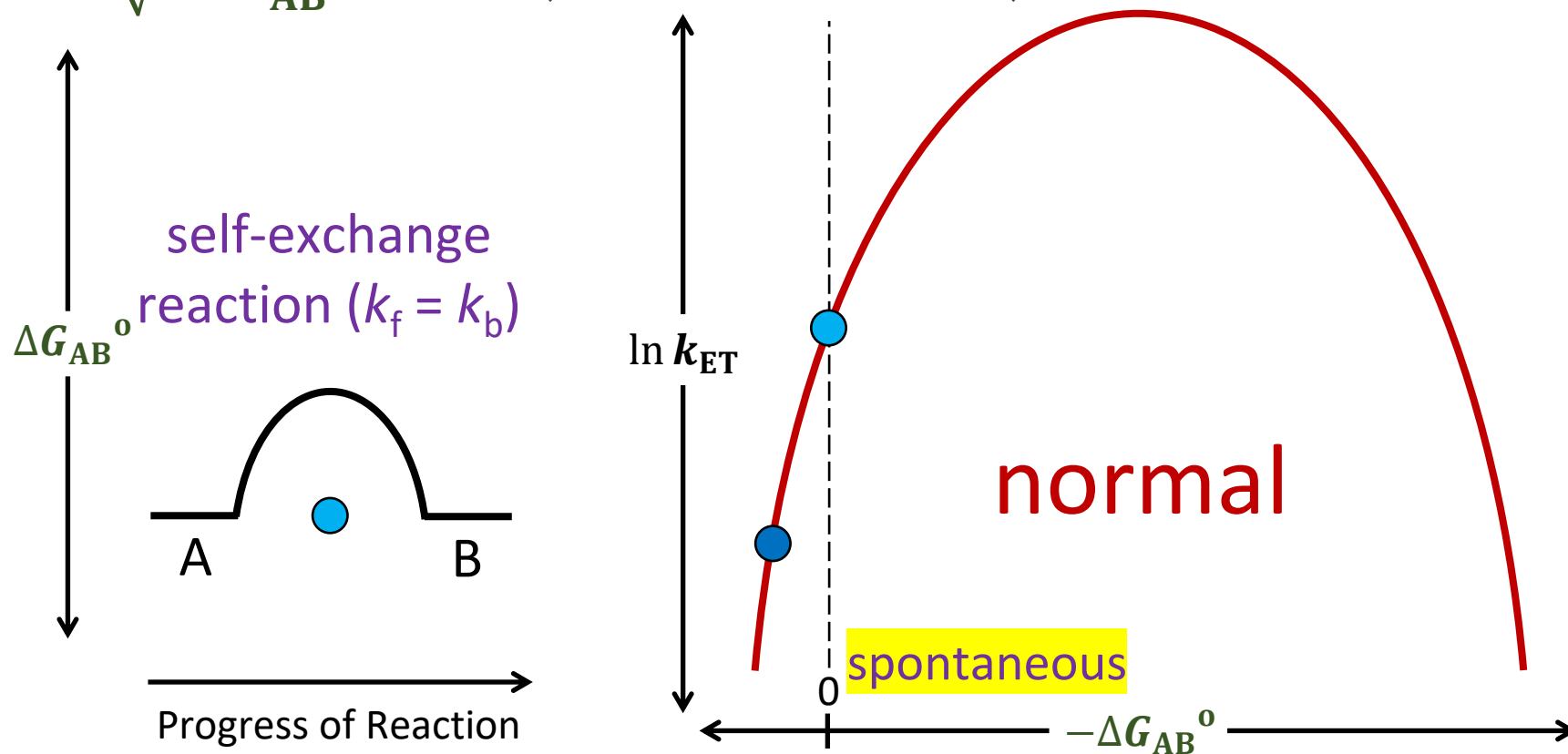
$\ln k_{\text{ET}}$

0

$-\Delta G_{\text{AB}}{}^{\text{o}}$

?

Marcus–Hush Theory

$$\underset{A}{\underline{D + A}} \rightleftharpoons \underset{B}{\underline{D^+ + A^-}}$$
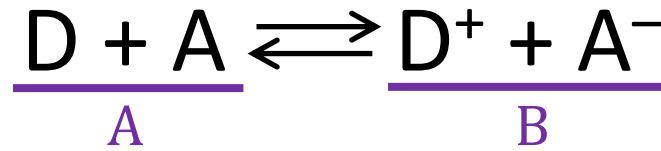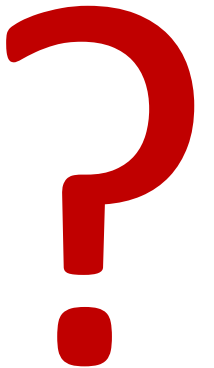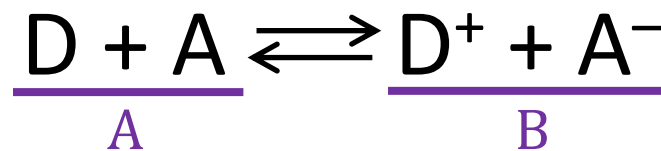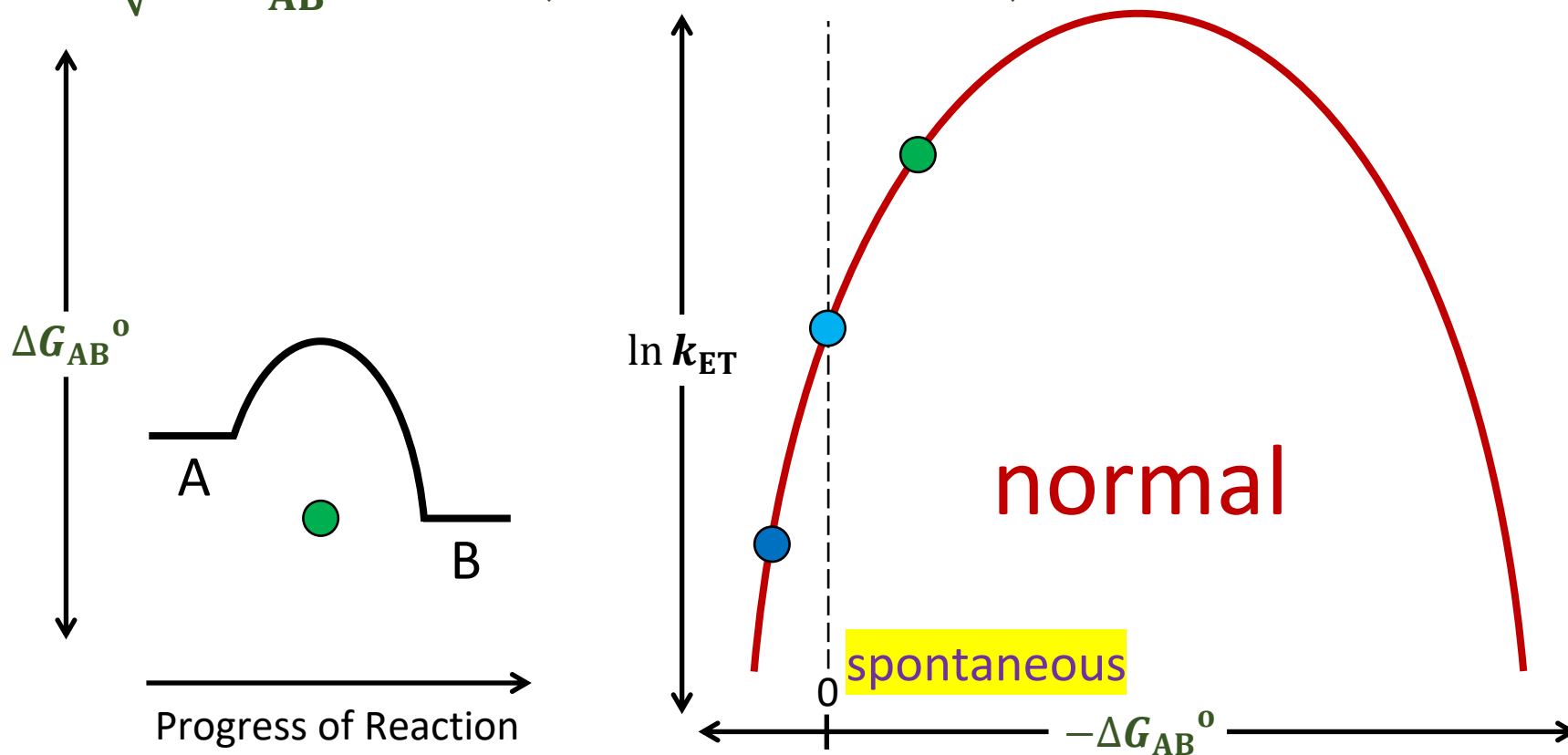
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

How can a thermo-dynamically unfavorable reaction proceed?

Mass Action!

it's a parabola

normal

spontaneous

$-\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$

$\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$

$\ln k_{\mathrm{ET}}$

A

B

0

Progress of Reaction

Marcus–Hush Theory

$$\underline{D + A}_A \rightleftharpoons \underline{D^+ + A^-}_B$$

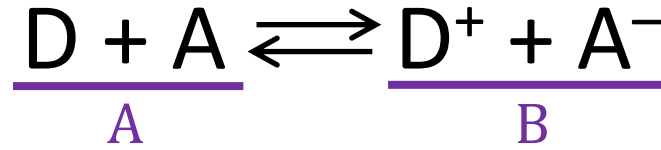**Marcus–Hush** (1950s–1960s)

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

self-exchange reaction ($k_f = k_b$)

ΔG_{AB}^{o}

A   B

Progress of Reaction

$\ln k_{ET}$

normal

0   spontaneous

$-\Delta G_{AB}^{o}$

Marcus–Hush Theory

$$\underline{D + A} \rightleftharpoons \underline{D^+ + A^-}$$
$$\quad A \qquad\qquad B$$

Marcus–Hush (1950s–1960s)

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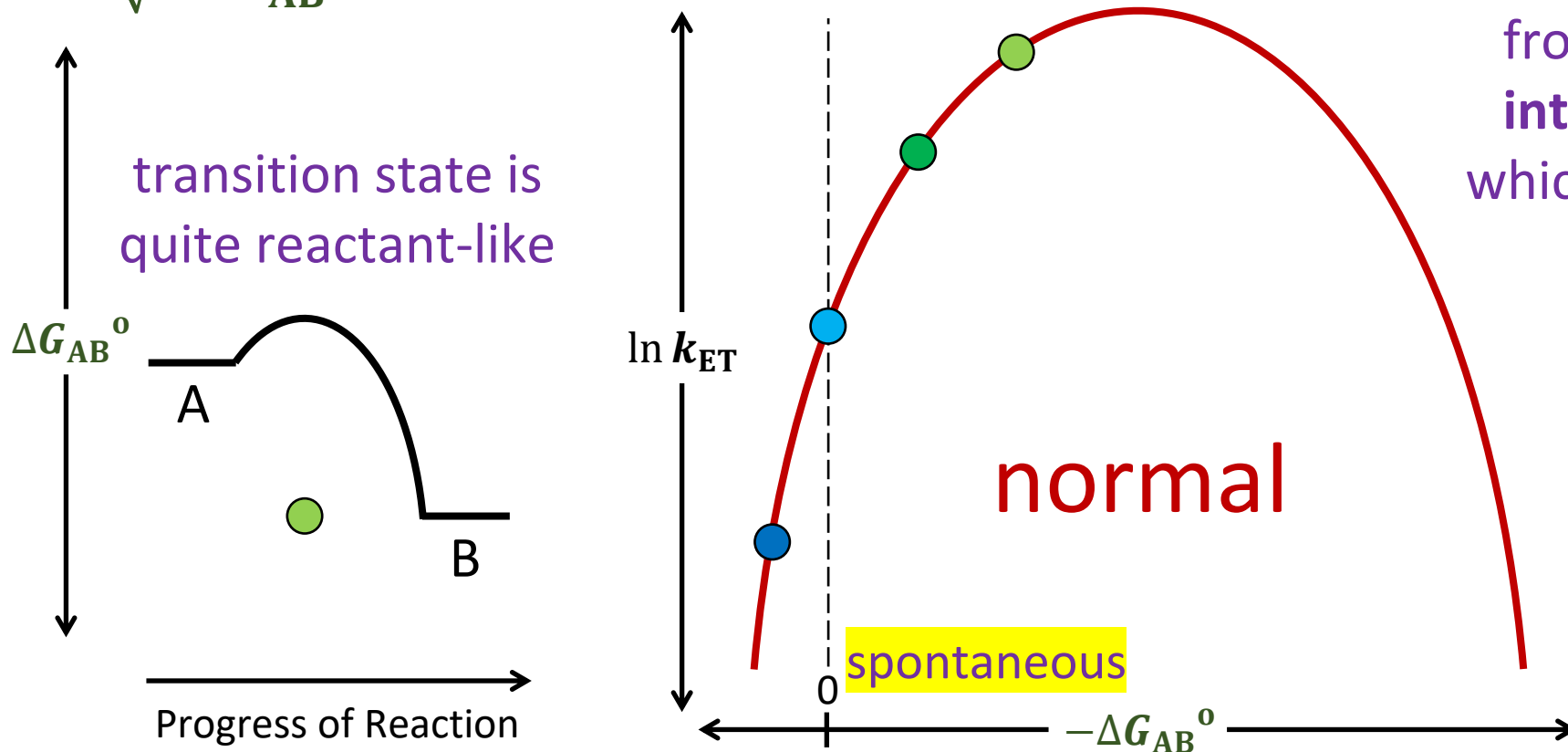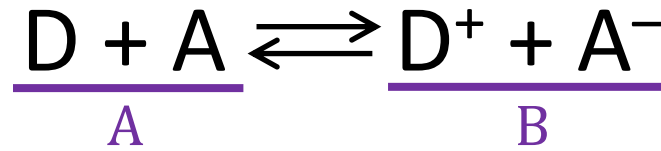
$\Delta G_{\text{AB}}{}^{\text{o}}$

A

B

Progress of Reaction

$\ln k_{\text{ET}}$

normal

0

spontaneous

$-\Delta G_{\text{AB}}{}^{\text{o}}$

Marcus–Hush Theory

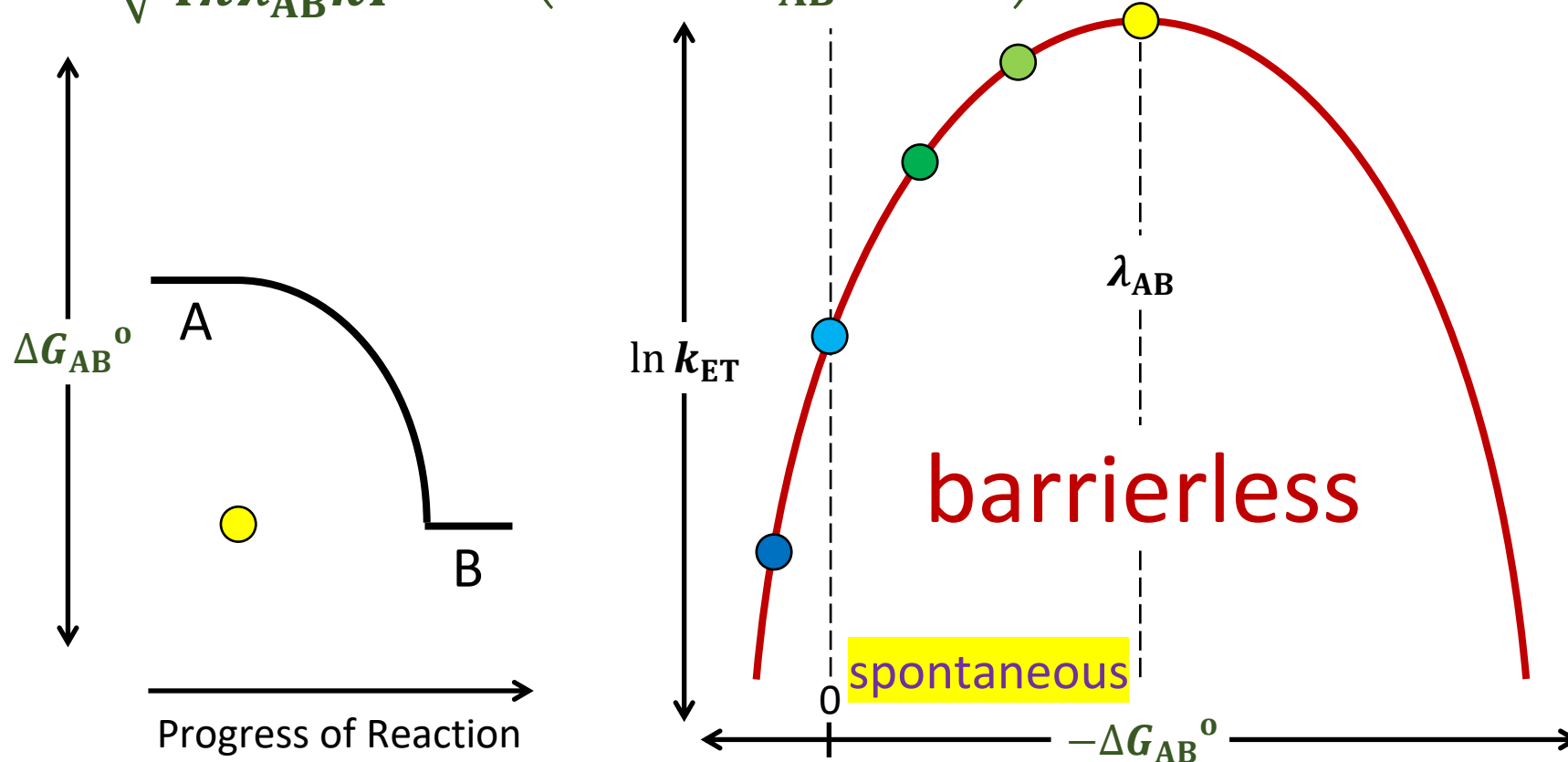$$\underbrace{\text{D} + \text{A}}_{\text{A}} \rightleftharpoons \underbrace{\text{D}^+ + \text{A}^-}_{\text{B}}$$
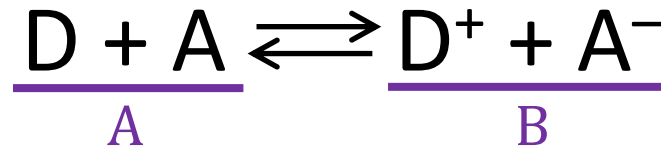
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transition state is
quite reactant-like

$\Delta G_{\text{AB}}^{\text{o}}$

A

B

Progress of Reaction

$\ln k_{\text{ET}}$

normal

0 spontaneous

$-\Delta G_{\text{AB}}^{\text{o}}$

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

Marcus–Hush Theory

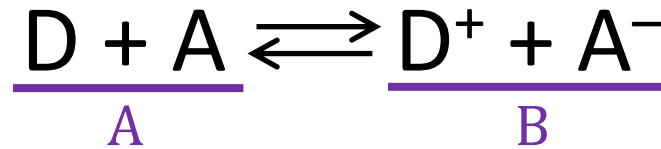$$\underbrace{D + A}_{A} \rightleftharpoons \underbrace{D^+ + A^-}_{B}$$

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

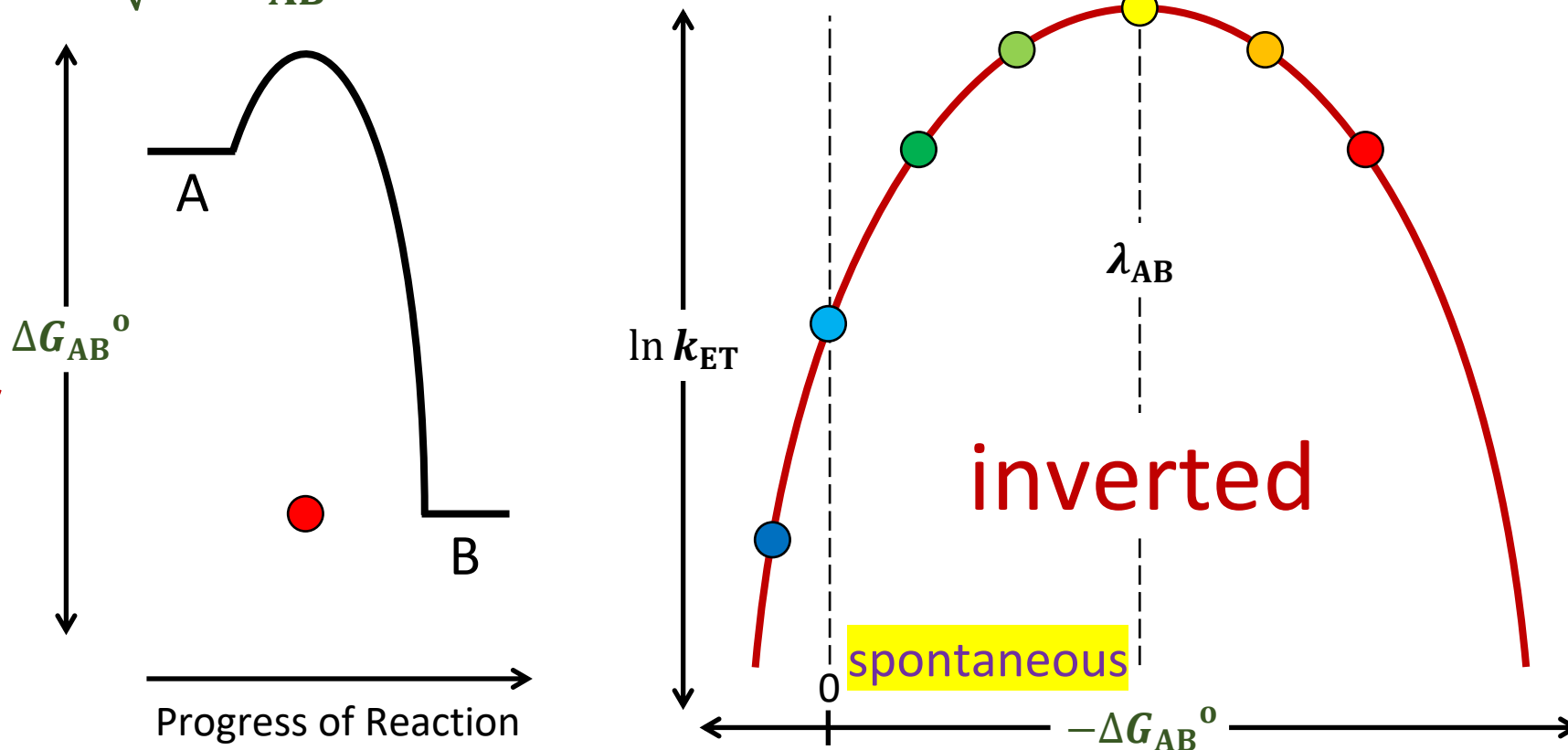$$\underline{D + A} \rightleftharpoons \underline{D^+ + A^-}$$
$$\quad\;\; A \qquad\qquad B$$

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Marcus–Hush Theory

$$D + A \underset{B}{\overset{A}{\rightleftharpoons}} D^+ + A^-$$
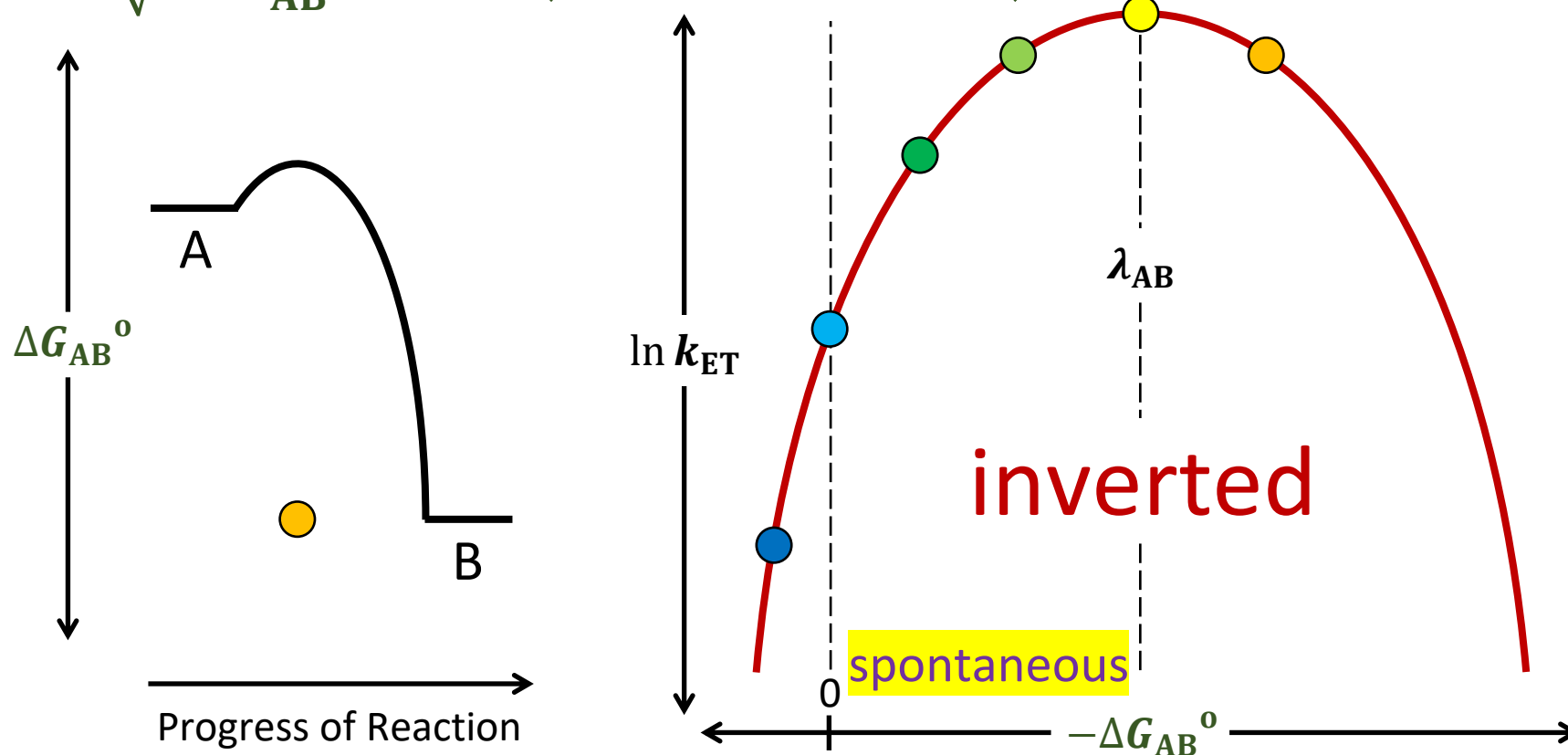
Marcus–**Hush** (1950s–1960s)

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… this looks odd…

… but what did we expect from a General Chemistry cartoon

$\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$

A

B

Progress of Reaction

$\ln k_{\mathrm{ET}}$

λ_{AB}

inverted

spontaneous

$-\Delta G_{\mathrm{AB}}{}^{\mathrm{o}}$

0

Outer Reorganization Energy

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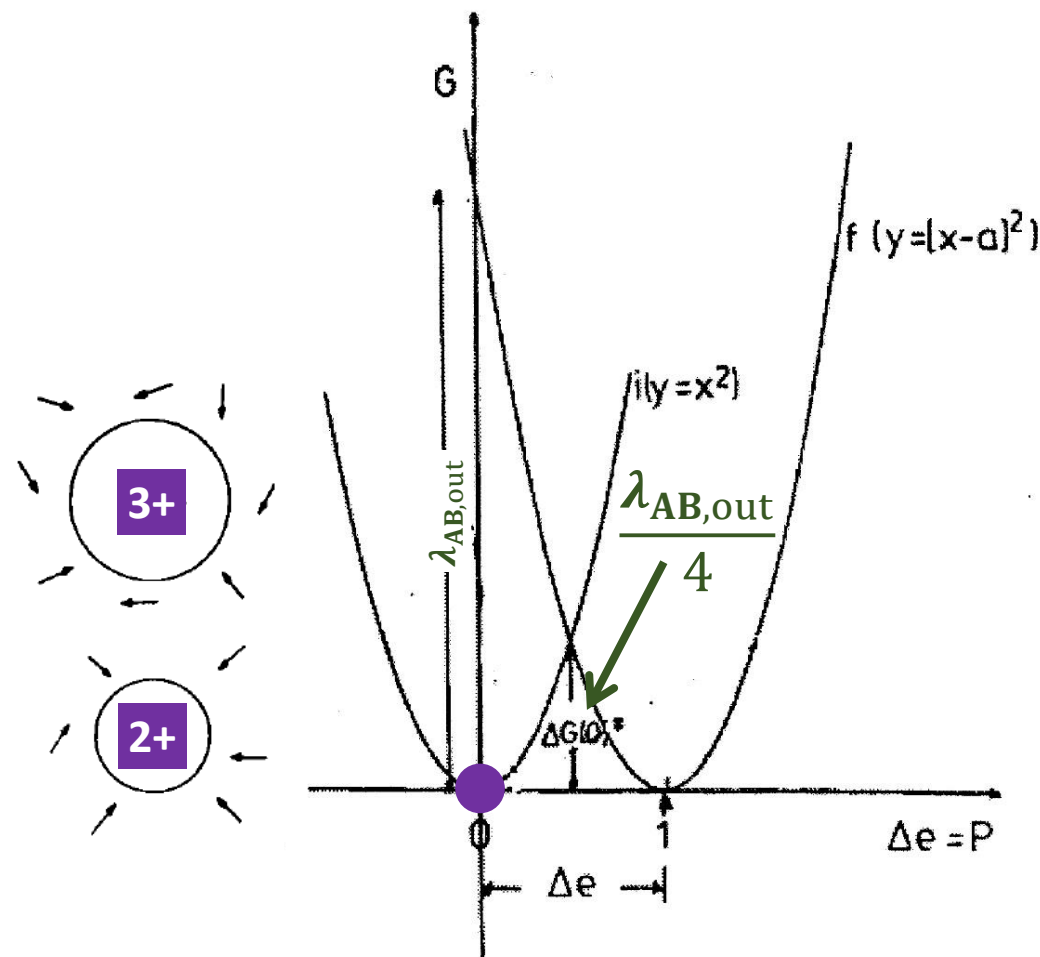
theoretical (semiclassical) rate constant equation

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

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

… but what causes this parabolic relationship?…

… what physical expression results in a quadratic dependence on **charge**?

… classical electrostatics… of the solvent!

… dielectric continuum model…

  … $G_{\mathrm{out}} \approx 1$ eV in water
  … G_{out} decreases as permittivity decreases

$$\lambda_{\mathrm{out}} = \left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right)\left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{\mathrm{s}}}\right)(\Delta e)^2$$

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
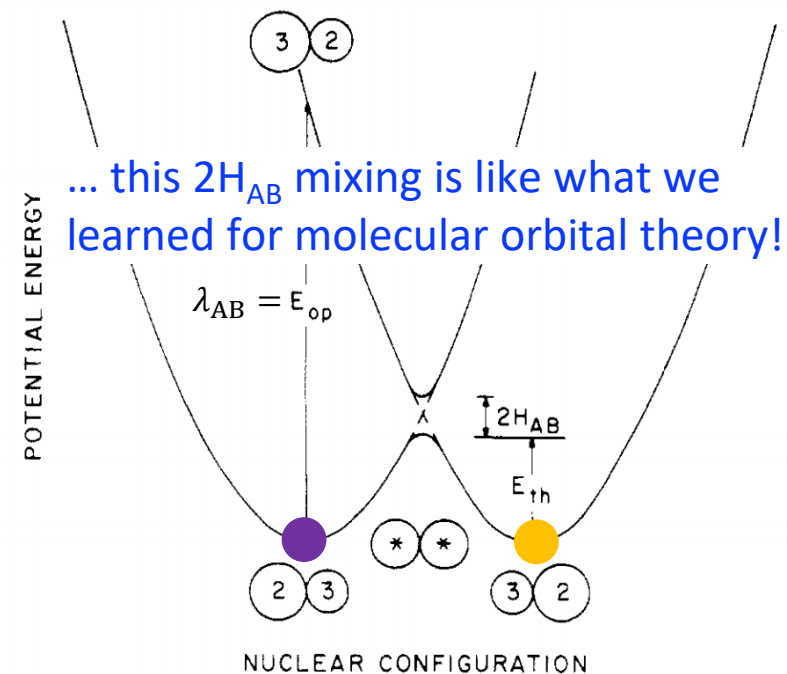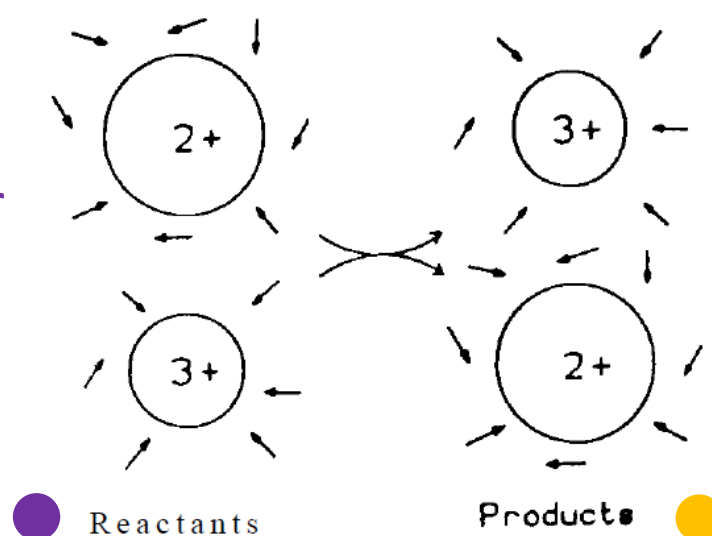
Electron Transfer in Solution

$$\lambda_{AB} = \lambda_{in} + \lambda_{out}$$

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

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

... and yes, it's another parabola!

Reactants ●   Products ●

... this 2H$_{AB}$ mixing is like what we learned for molecular orbital theory!

$$\lambda_{AB} = E_{op}$$

POTENTIAL ENERGY

2H$_{AB}$

E$_{th}$

NUCLEAR CONFIGURATION

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?

Transport as a Chemical Reaction

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

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

$$A^-_{z_1} \rightleftharpoons A^-_{z_2}$$
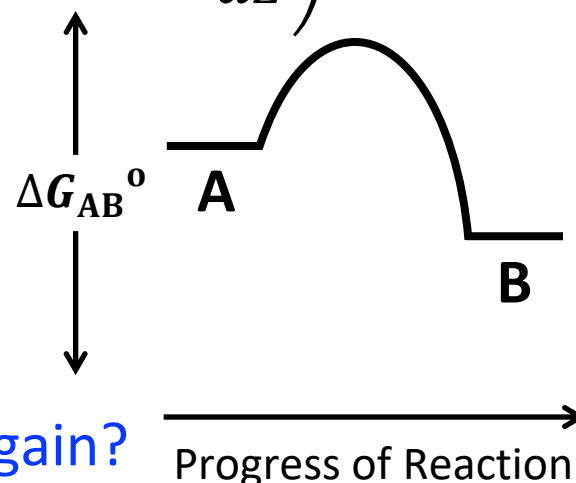
Reactants   Products

A   **B**
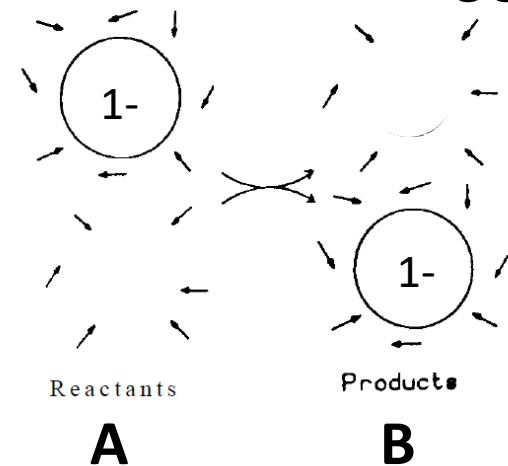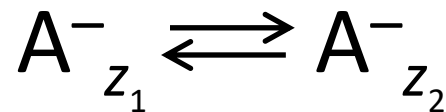
$$R_A = -k_f c_{A_{z_1}} + k_b c_{A_{z_2}} = (k_b - k_f)c_{A_{z_1}} + k_b \Delta c_A \text{ ... where } c_{A_{z_2}} = c_{A_{z_1}} + \Delta c_A$$

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

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

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

ΔG_{AB}^o A

B

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

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

Progress of Reaction

... since the reaction volume is >1 Å³ , l > 1 Å... and D(aq) < 10^{-4} cm²/s... $k_{D(aq)}$ < **10^{12} s⁻¹ = (>1 ps)⁻¹**

Diffusion Coefficient

mean square displacement
(variance)
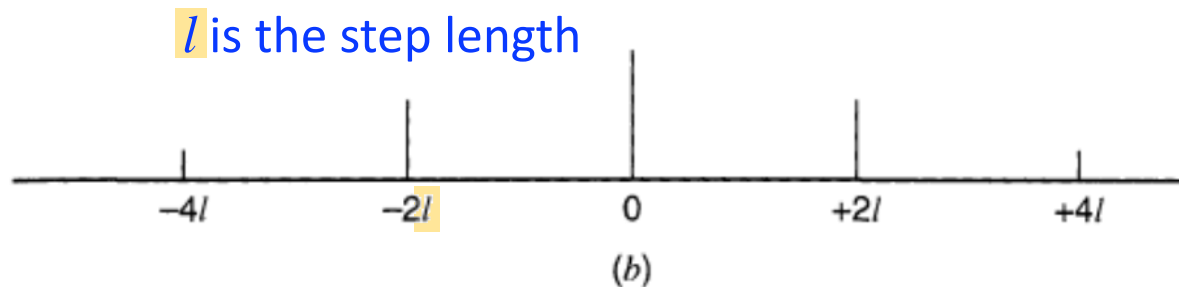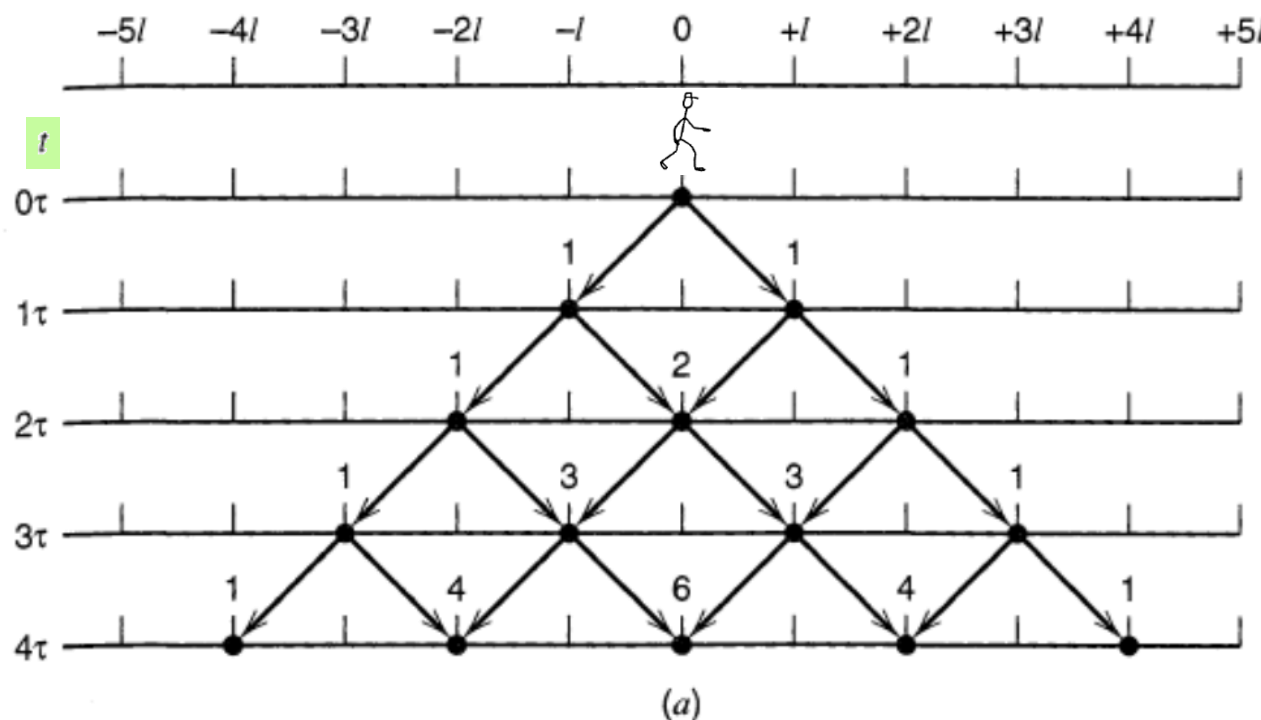
$$\overline{\Delta^2} = m\,l^2 = \frac{t}{\tau}l^2 = 2Dt$$

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

(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

root mean square (rms)
displacement
(standard deviation)

l is the step length

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.

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

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