



Lecture #13 of 14

(3: TThF, 5: MTWThF, 4: MTWTh, 2: TW)

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Chemical Kinetics (*let's review TWTh*)

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- T: Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- W: Mass action, Microscopic reversibility, Förster cube, Square schemes, Rate constants, Activation energies, Transition-state theory, Marcus–Hush theory, Transition-state character, Reorganization energies (outer and inner)
- Th: Linear free energy relationships, Charge transfer across electrified interfaces, Butler–Volmer equation, Fermi's golden rule, Solid-state physics, Marcus–Gerischer theory, Rate-determining step, Steady-state & Pre-equilibrium approximations, Langmuir/Frumkin isotherms

Summary of Key Equations and Equilibrium (REVIEW) 372

$$A \rightleftharpoons B$$

$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j}$$

(Chemists should be yawning)

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

$$R_{A,j} = -k_f a_A \quad R_{B,j} = +k_f a_A \quad k_f \text{ (M/s)} \dots \text{a rate!}$$

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

$$\bar{\mu}_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{T,p,n_{j \neq i}^\alpha} \quad \frac{\partial c_{A,z_0}^\alpha}{\partial t} = -k_f a_A^\alpha + k_b a_B^\alpha = -k_f' c_A^\alpha + k_b' c_B^\alpha = -\frac{\partial c_{A,z_0}^\alpha}{\partial t}$$

Now, consider the reaction to be at equilibrium (3 ways)... $\Delta G^\alpha = 0 = \Delta G^{\circ,\alpha} + RT \ln Q$
... and so, $\Delta G^{\circ,\alpha} = -RT \ln K$, with $K = \frac{a_B^{\alpha,\text{eq}}}{a_A^{\alpha,\text{eq}}} = \frac{\gamma_B^{\alpha,\text{eq}} (c_B^{\alpha,\text{eq}} / c_B^{\circ,\alpha})}{\gamma_A^{\alpha,\text{eq}} (c_A^{\alpha,\text{eq}} / c_A^{\circ,\alpha})}$

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, $\frac{\partial c_{A,z_0}^\alpha}{\partial t} = 0 = -\frac{\partial c_{B,z_0}^\alpha}{\partial t} = -k_f a_{A,\text{eq}}^\alpha + k_b a_{B,\text{eq}}^\alpha \dots$ and so $\frac{k_f}{k_b} = \frac{a_{B,\text{eq}}^\alpha}{a_{A,\text{eq}}^\alpha} = \frac{\gamma_B^{\alpha,\text{eq}} (c_{B,\text{eq}}^\alpha / c_B^{\circ,\alpha})}{\gamma_A^{\alpha,\text{eq}} (c_{A,\text{eq}}^\alpha / c_A^{\circ,\alpha})} = K$

Continuity of Mass

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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

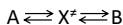
Activation Energies

(REVIEW) 374

Arrhenius (1889)

empirical rate constant equation

$$k_f = A e^{-\frac{E_a}{RT}} \dots \text{pre-exponential factor, } A, \text{ has units of } s^{-1}$$



Eyring-Polanyi-Evans (1930s)

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

$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_B T}{h} K^\ddagger \dots \text{with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

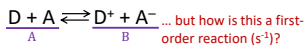
... and $R = N_A k_B \dots$ and $\frac{\kappa k_B T}{h}$ has units of s^{-1}

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

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

Marcus-Hush Theory

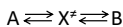
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Marcus-Hush (1950s-1960s)

theoretical (semiclassical) rate constant equation

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



Eyring-Polanyi-Evans (1930s)

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

$$k_f = \kappa \nu K^\ddagger = \frac{\kappa k_B T}{h} K^\ddagger \dots \text{with transmission coefficient, } \kappa, \text{ and vibrational frequency, } \nu \text{ (s}^{-1}\text{)}$$

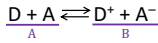
... and $R = N_A k_B \dots$ and $\frac{\kappa k_B T}{h}$ has units of s^{-1}

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

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Marcus–Hush Theory

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

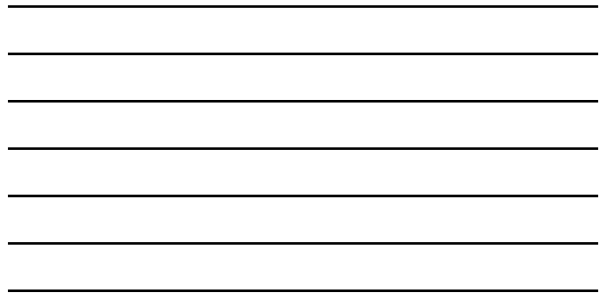
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^{\ddagger}}{kT}\right)$$

quantum adiabatic electronic coupling classical nuclear free-energy dependence

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right) \dots \text{what kind of function is this?}$$

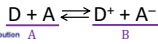
$$\Delta G_{AB}^{\ddagger} = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$$

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{AB}^0 - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right) \dots \text{does this help at all?}$$

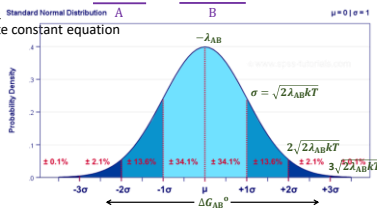


Marcus–Hush Theory

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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 (ΔG_{AB}^0)? ... Yep!

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{AB}^0 - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right) \dots \text{does this help at all?}$$



Charge Transfer across Electrified Interfaces

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... aren't these so-called "heterogeneous electron-transfer reactions"? ... Sure. $e^- + M + O \rightleftharpoons R$ FYI: For each c_O and c_R , electrochemical equilibrium ($j = 0$) is attained via interfacial charge transfer to alter $\Delta\phi^{M|}$.

$$R_O = \frac{\partial c_{O,z_0}}{\partial t} = -k_f c_O + k_b c_R \quad j_E = nF(-k'_{f,E} c_{O,z_0} + k'_{b,E} c_{R,z_0})$$

... R_O is a rate... with units of M/s (= mol dm⁻³ s⁻¹) ... k_f (s⁻¹) is an inverse time constant! ... j_E is a current density... with units of A/cm² (= C cm⁻² s⁻¹) ... $k'_{j,E}$ (cm s⁻¹) is a velocity!

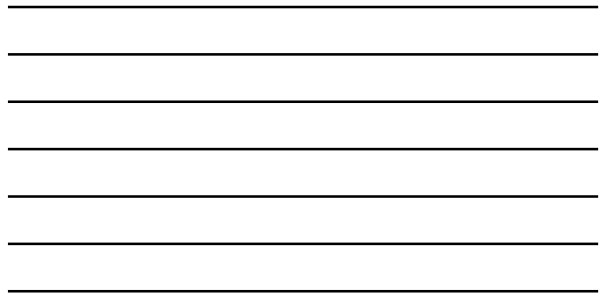
... as a specific case choose $E^{o'}$... and thus, $j_{E^{o'}} = nF(-k'_{f,E^{o'}} c_{O,z_0} + k'_{b,E^{o'}} c_{R,z_0})$

But how does this lead to the Butler–Volmer eqn?... $0 = j_{E^{o'}} = nF(-k'_{f,E^{o'}} c_{O,z_0} + k'_{b,E^{o'}} c_{R,z_0})$

$$j_E = j_0 \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\} \quad K'_{f,E^{o'}} = K'_{b,E^{o'}} = K^0$$

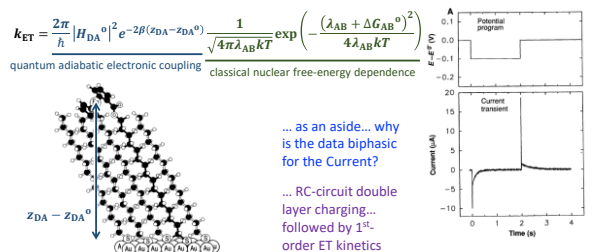
$$\eta = (E - E_{eq}) = E_{app} = \frac{\Delta G^0}{-nF} \dots \text{where } \eta \text{ (V) is overpotential}$$

... this suggests that we will replace $k'_{j,E}$ velocity rate constants...
... with thermodynamic driving force terms!... But how?... M–H!



Marcus–Gerischer Theory

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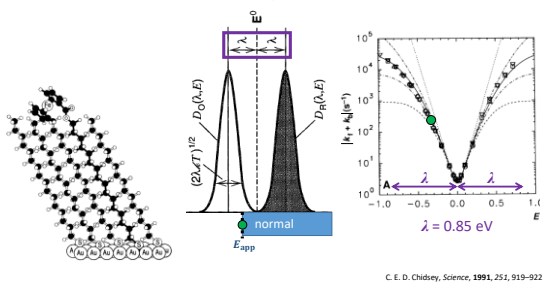


C. E. D. Chidsey, *Science*, **1991**, 251, 919-922
 H. D. Sikes, J. F. Smalley, S. P. Dutek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, **2001**, 291, 1519-1523



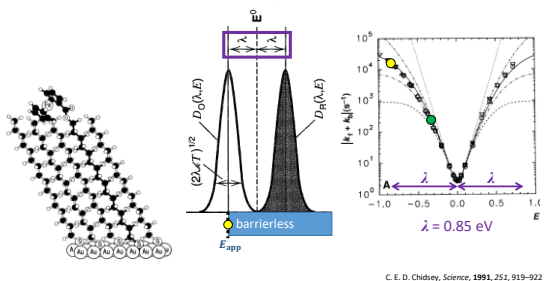
Marcus–Gerischer Theory

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Marcus–Gerischer Theory

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Marcus–Gerischer Theory

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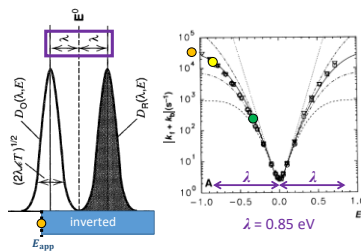
• It is easy to sweep/vary the driving force, ΔG_{app} , by simply changing the electrochemical potential of electrons (e^-) in the [Metal] working electrode, μ_e^M , through variations in E_{app}

• But evidence of the inverted region is a little challenging to clearly observe

... what if Chidsey had plotted the derivative of his data on the right?

... what do you expect that would have looked like?... a nice Marcus parabola!

... I wish he had done that!

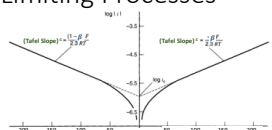


C. E. D. Chidsey, Science, 1991, 251, 919-922

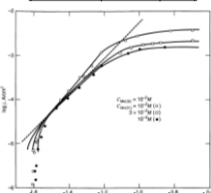


Limiting Processes

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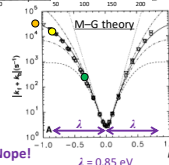


B-V theory (Current-Overpotential Equation)



Bard & Faulkner, Chapter 3, Figure 3.4.5, Page 104

Since Butler-Volmer theory is based on the LFER approximation only, can it report on aspects of the inverted region? ... Nope!



... but why do these current densities, j_E , and rate constants, $k'_{j,E,obs}$, plateau at large overpotential, η ? ... Not for the same reasons!

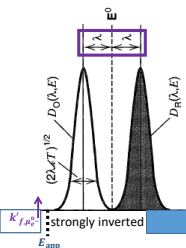


Marcus–Gerischer Theory

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• Use of a semiconductor limits the electronic states to those with (approximately) a single μ_e^S , which makes analysis of data simpler, i.e. one does not need to consider a distribution of states in the electrode

• But one cannot alter the driving force, ΔG_{app} , by simply changing the electrochemical potential of electrons (e^-) in the [Semiconductor] working electrode, μ_e^S , through variations in E_{app} , because instead that typically changes the concentration of e^-



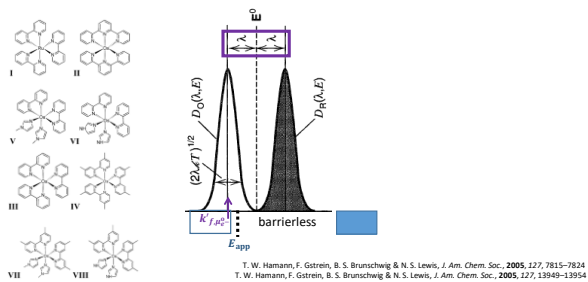
How can one use a semiconductor to study the inverted region?

Think solution studies... vary the molecule!



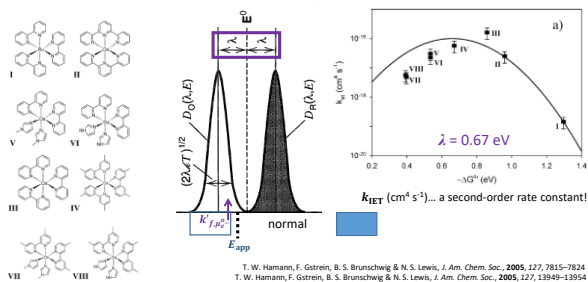
Marcus–Gerischer Theory

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Marcus–Gerischer Theory

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UCI PHYSICS/CHEM207 – Applied Physical Chemistry, Summer 2022

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Photochemistry

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

Straight into Groups!

Quiz(zes) Time!

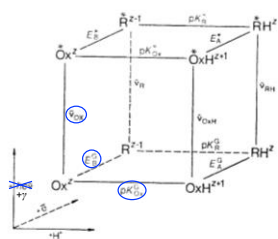
Photochemistry

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- Blackbody radiation, Light–Matter interactions, Photon properties, Conservation laws
- Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule, Thexi state, Stokes shift, Luminescence processes
- Born–Oppenheimer approximation, Franck–Condon principle, Harmonic oscillator model, Transition dipole moment operator, Selection rules, Spin–orbit coupling, Heavy-atom effect
- Photochemical length and time scales, Electromagnetic spectrum
- Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, E–k diagrams

Förster Cube and Square Schemes

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Questions to ponder...
 In this figure, what do the thermodynamic parameters E , pK , and $\bar{\nu}$ represent?
 $E = E^0$ (standard-state reduction potential)
 $pK = pK_s = -\log K_s$ (acid dissociation constant)
 $\bar{\nu} = \frac{1}{\lambda}$ (wavenumber)

How are they related?
 Redox: $E^0 = -\Delta G^0/nF$
 Acidity: $pK_s = -\log K_s = \Delta G^0/(2.303RT)$
 Light: $hc\bar{\nu} = \frac{hc}{\lambda} = h\nu = E_{\text{photon}}$

What is the reference state for each?
 $E^0(\text{H}^+(\text{aq})/\text{H}_2) = 0$; $pK_s(\text{H}^+(\text{aq})) = 0$; 0

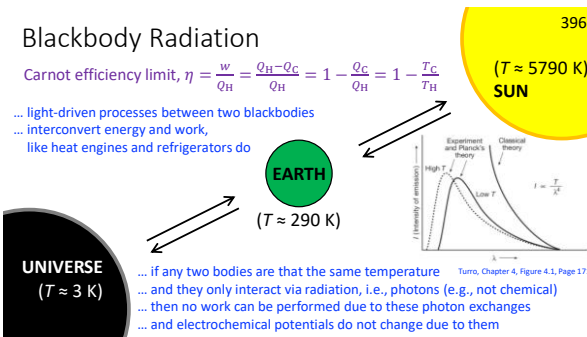
... before we add light... let's backtrack a bit...
 ... first we must understand dark thermal processes... Z. R. Grabowski & W. Rubaszewska, *J. Chem. Soc. Faraday Trans. 1*, 1977, 73, 11–28

Blackbody Radiation

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Carnot efficiency limit, $\eta = \frac{w}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$

- ... light-driven processes between two blackbodies
- ... interconvert energy and work,
- ... like heat engines and refrigerators do



... if any two bodies are that the same temperature
 ... and they only interact via radiation, i.e., photons (e.g., not chemical)
 ... then no work can be performed due to these photon exchanges
 ... and electrochemical potentials do not change due to them

Turno, Chapter 4, Figure 4.1, Page 171

Photon Properties & Conservation Laws

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Where does light come from?

Particle Type: Boson

Mass: 0

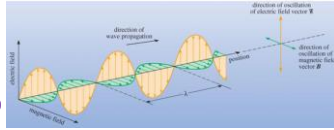
Charge: 0

Energy: $E = \hbar\nu = \hbar\omega$

Linear Velocity: $v = \left(\frac{c}{n}\right)v = \lambda'v$

Linear Momentum: $p = \frac{h}{\lambda'} = \frac{\hbar\nu}{c} \approx 0$

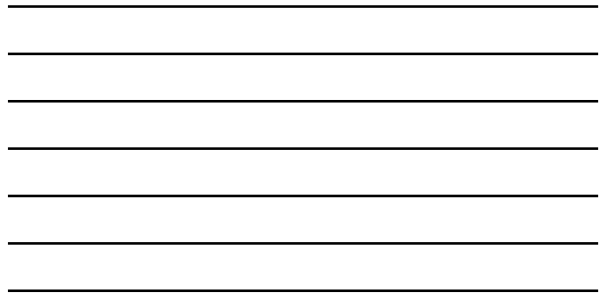
Linear Polarization: \vec{E} and \vec{B}



z-Direction Angular Momentum / Circular Polarization / Chirality / Helicity / Spin: $\pm\hbar = \pm \frac{h}{2\pi}$

Wait... is a light a wave or a particle?
 ... I mean, is matter a wave or particle?
 ... I mean, **doesn't everything exhibit wave-like and particle-like properties?**

[Fermion Angular Momentum \(Orbital, Spin\)](#)
 Magnitude: $\hbar\sqrt{j(j+1)}$
 z-Direction: $m_j\hbar, m_j = [-j, j]$ in steps of 1
 Multiplicity/Degeneracy, $g_j: 2j + 1$



Light-Matter Interactions

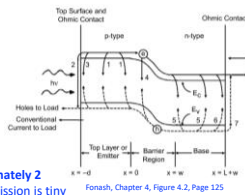
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$$\frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

What value of j have we considered thus far? ≥ 2

How large is j for actual systems? **Quite large, likely!**

What is the smallest value that j can be? **3... but approximately 2**
 ... stimulated emission is tiny



Fonash, Chapter 4, Figure 4.2, Page 125

Given a box at temperature, T , by what processes can heat be transferred to something inside it?
 Okay, now what if inside the box was a vacuum?

(Blackbody) radiation only! $A + \hbar\nu_{BB} \rightleftharpoons A^*$

... at a microscopically reversible **equilibrium**, rate is equal to $\%A(\nu) \times \text{PhotonFlux}(\nu)$, integrated over ν
 ... $\bar{\mu}_A = \bar{\mu}_{A^*}$... with additional (sun)light absorption, $\bar{\mu}_A < \bar{\mu}_{A,eq}$ and $\bar{\mu}_{A^*} > \bar{\mu}_{A^*,eq}$ = **useful work!**



Light-Matter Interactions

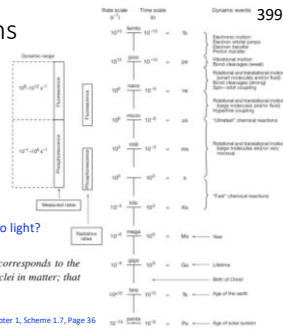
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Turro, Chapter 4, Page 184
 Total force exerted on an electron by a light wave

$$\mathbf{F} = e\mathbf{E} + \frac{e(\mathbf{H}\mathbf{v})}{c}$$
 Electrical force Magnetic force

$c_{light} = 3 \times 10^{18} \text{ nm s}^{-1}$
 $v_{electron} = 10^{15} - 10^{16} \text{ nm s}^{-1}$
 $v_{nuclei} = 10^{13} - 10^{14} \text{ nm s}^{-1}$

... so which term dominates the resonant response to light?



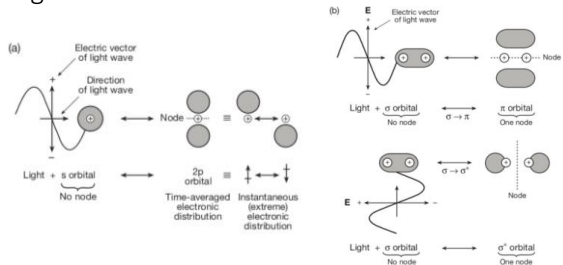
In more concrete chemical terms, the oscillation of the dipoles corresponds to the movements of electrons in bonds relative to positively charged nuclei in matter; that is, electrons oscillate about the nuclear framework of molecules.

Turro, Chapter 1, Scheme 1.7, Page 36



Light-Matter Interactions

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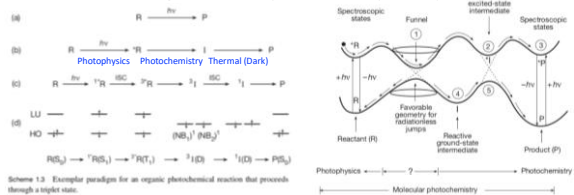


Turro, Chapter 4, Figure 4.6, Page 189



Jablonski Diagram & Spin Multiplicity

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Turro, Chapter 1, Scheme 1.3, Page 13

Turro, Chapter 1, Scheme 1.5, Page 21

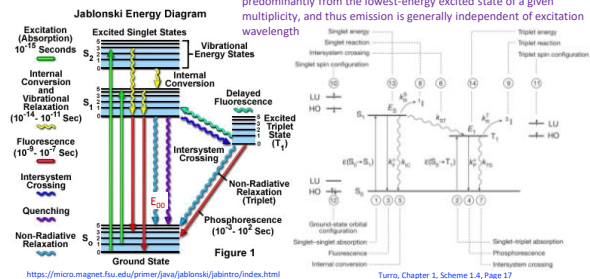
- ... Angular Momentum Energy Degeneracy, $g_j: 2J + 1$
- ... when $J = 0, g_j = 1...$ sounds like a "Singlet (S or 1X)"
- ... when $J = 1, g_j = 3...$ sounds like a "Triplet (T or 3X)"



Jablonski Diagram

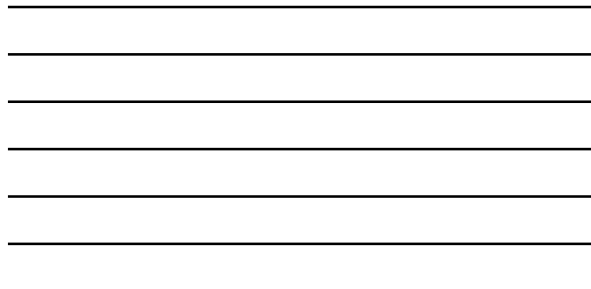
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Kasha-Vavilov "rule": polyatomic molecular entities emit and react predominantly from the lowest-energy excited state of a given multiplicity, and thus emission is generally independent of excitation wavelength



<https://micro.magnet.fsu.edu/primer/java/jablonski/jabintro/index.html>

Turro, Chapter 1, Scheme 1.4, Page 17



Photochemistry (*summary for today*)

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- **Blackbody radiation, Light–Matter interactions, Photon properties, Conservation laws**
- **Jablonski diagram, Internal conversion, Intersystem crossing, Kasha–Vavilov rule**, Thexi state, Stokes shift, Luminescence processes
- Born–Oppenheimer approximation, Franck–Condon principle, Harmonic oscillator model, Transition dipole moment operator, Selection rules, Spin–orbit coupling, Heavy-atom effect
- Photochemical length and time scales, Electromagnetic spectrum
- Beer–Lambert law, Absorption coefficient, Einstein coefficients, Oscillator strength, Absorptance, E – k diagrams
