



# Lecture #12 of 14

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

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## Summary of Key Equations and Equilibrium

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**A ⇌ B**

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

(Chemists should be yawning)

$$\bar{\mu}_i^\alpha = \left( \frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{T,p,n_{j \neq i}^\alpha}$$

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

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

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

$$\frac{\partial c_{A,z_0}^\alpha}{\partial t} = -k_f a_A^\alpha + k_b a_B^\alpha = -k_f' c_A^\alpha + k_b' c_B^\alpha = - \frac{\partial c_{B,z_0}^\alpha}{\partial t}$$

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  $K = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = \frac{\gamma_B^\alpha (c_{B,eq}^\alpha/c_B^{\circ,\alpha})}{\gamma_A^\alpha (c_{A,eq}^\alpha/c_A^{\circ,\alpha})}$

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



## Transport as a Chemical Reaction

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

... in a reaction "volume"  $z_0 \dots$   
... that encompasses  $z_1$  and  $z_2$

**A<sup>-</sup><sub>z<sub>1</sub></sub> ⇌ A<sup>-</sup><sub>z<sub>2</sub></sub>**

$$R_A = -k_f c_{A,z_1} + k_b c_{A,z_2} = (k_b - k_f) c_{A,z_1} + k_b \Delta c_A \dots \text{where } c_{A,z_2} = c_{A,z_1} + \Delta c_A$$

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

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

... where  $E'$  is an effective force field

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

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

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





# Chemical Kinetics

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**Quiz Time!**

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## Chemical Kinetics

- Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- 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)
- 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

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## Continuity of Mass

(REVIEW) 331

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

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

"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

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(REVIEW) 332

### Thermodynamics versus Kinetics

Thermodynamics are only as important as their influence on kinetics...

... energetics from thermodynamics dictate **equilibrium concentrations**...

... but it is the **kinetic (and transport) properties** that influence how those conditions change upon perturbation...

rate of change of the (c)oncentration of species A with respect to (t)ime, *in units of*  $M s^{-1} (mol dm^{-3} s^{-1})$

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

rate of change of the molar flux (N) of species A with respect to position (z), e.g.  $N_A = -D \frac{\partial a_A}{\partial z}$  (to a first order, this is driven by differences in electrochemical potential of a single species,  $\mu$ )

mass action (R)ate laws that effect species A, e.g.  $R_A = k_3 a_0 a_0^2 = k_3 [B][D]^2$  (to a first order, this is driven by differences in chemical potential of various species,  $\mu_i$ )

... this master equation describes all kinetic and transport processes for mass... more on this later...

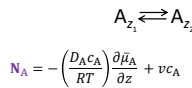


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### 1D Transport in Liquids (solids are simpler)

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

(MechEs should be yawning)



... there are many driving forces for flux of species...  
... convection (vc) is just one (e.g., dT/dx)

Group terms... then mass transfer resembles mass action (assume v = 0 for simplicity)...

$$N_A = -D_A \frac{\partial \left( \frac{\bar{\mu}_A}{RT} \right)}{\partial z} c_A$$

What are the directions for the dimensions of  $D_A$ ?

**BOLD** ((cm<sup>2</sup>/s) / cm) = cm/s... a velocity!  
... and with  $\frac{\partial}{\partial z}$ , units are s<sup>-1</sup>... an inverse time constant!  
... and that equals zero at steady state

(Note that...  $R_{A,total} = -K_f c_A + K_b c_B$ ... with  $K_f$  (s<sup>-1</sup>), an inverse time constant!)



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### 1D Transport in Solids (liquids are "harder")

Let's expand the total differential...

$$\text{Flux}_{x,e} = - \frac{\partial_e d \bar{\mu}_e}{F^2 dz} - S_{e,T_e} \frac{dT_e}{dz} \quad \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \bar{\mu}_i = \mu_i + z_i q \phi$$

$$\text{Flux}_{x,e} = - \frac{D_e n_e}{k T_e} \left( \frac{d \bar{\mu}_e}{dz} - q \frac{d \phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz} \quad \mu_i = \mu_i^0 + k T_i \ln a_i = \mu_i^0 + k T_i \ln \left( \frac{y_i n_i}{n_i^0} \right)$$

... assuming a species, e, with valency, z<sub>e</sub>, equal to -1

$$\text{Flux}_{x,e} = - \frac{D_e n_e}{k T_e} \left( \frac{d \bar{\mu}_e^0}{dz} + \frac{k T_e}{y_e} \frac{d y_e}{dz} + \frac{k T_e}{n_e} \frac{d n_e}{dz} - \frac{k T_e}{n_e^0} \frac{d n_e^0}{dz} + k \left( \ln \frac{y_e n_e}{n_e^0} \right) \frac{dT_e}{dz} - q \frac{d \phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz}$$

... other species may have different values for every term, except  $\phi$

$$\text{Flux}_{x,e} = -D_e \left( \frac{n_e}{k T_e} \frac{d \bar{\mu}_e^0}{dz} + \frac{n_e}{y_e} \frac{d y_e}{dz} + \frac{d n_e}{dz} - \frac{n_e}{n_e^0} \frac{d n_e^0}{dz} + \frac{n_e}{T_e} \left( \ln \frac{y_e n_e}{n_e^0} \right) \frac{dT_e}{dz} - \frac{q n_e}{k T_e} \frac{d \phi}{dz} \right) - S_{e,T_e} \frac{dT_e}{dz}$$

Drift-Diffusion equation

$$\text{Flux}_{x,e} = -D_e n_e \left( \frac{d \bar{\mu}_e^0}{k T_e dz} + \frac{q D_e n_e}{k T_e} \frac{d \phi}{dz} \right) \quad \dots \text{assuming spatially invariant } \mu_i^0, \gamma_e, n_e^0, T_e$$

$$\text{Flux}_{x,e} = -D_e n_e \left( \frac{d \bar{\mu}_e^0}{k T_e dz} + \frac{d(\ln \gamma_e)}{dz} + \frac{d(\ln n_e)}{dz} - \frac{d(\ln n_e^0)}{dz} + \frac{d(q \phi)}{k T_e dz} \right) - D_{n_e, \gamma_e, n_e^0, T_e} \frac{dT_e}{dz}$$





### Molecular Orbital Theory

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

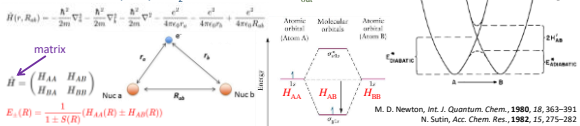
$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^{\ddagger}}{kT}\right)$$

quantum adiabatic  
electronic coupling
classical nuclear free-  
energy dependence

Molecular Orbital Theory  
linear combination of atomic orbitals

(30) The splitting at the intersection is only equal to  $2E_{AB}$  when the overlap of the electronic wave functions can be neglected. More generally it is equal to  $2E_{AB}\sqrt{1+|S_{AB}|^2}$  where  $S_{AB} = \langle \psi_A | \psi_B \rangle$  ... which equals  $(E_+ - E_-)$  from MO Theory

... remember the simplicity of  $H_2^+$  ... which resembles  $\lambda_{\text{good}}$  math

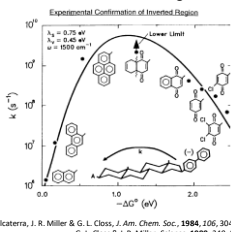
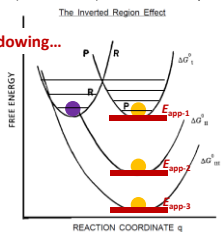


### Observation of Inverted Region Behavior (REVIEW) 339

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

Closs-Miller (1984)  
observation of inverted region

Foreshadowing...



### Linear Free Energy Relationships (LFERs) 340

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

Brønsted-Pedersen (1924)  
empirical LFER for proton transfer

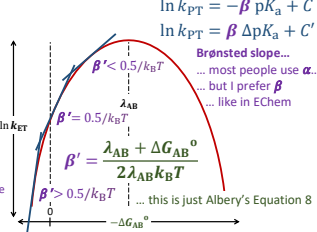
**Linear free-energy relation**

Also contains definition of linear Gibbs energy relation.

A loose correlation between the logarithm of a rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the Brønsted relation and the Hammett equation.

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a constant plus energy relative energy change, and the logarithm of a rate constant is a linear function of the free energy (Gibbs energy) of activation.

It has been suggested that this name should be replaced by linear Gibbs energy relation, but at present there is little sign of acceptance of this change. The sense of physical organic chemists' (particularly physical organic) usage is also unclear. (Source: IUPAC Glossary of Basic Terms in Physical Organic Chemistry, 2004)



... trend looks linear over a small enough  $\Delta G_{AB}^{\ddagger}$  range  
J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, 31, 227-263  
R. A. Marcus, *Farad. Discuss. Chem. Soc.*, **1982**, 74, 7-15

## Marcus Kinetic Behavior

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**Table 13** Applications of the Marcus relation

Electron transfers	Electrochemical	Tafel Law
	Homogeneous	Electrode kinetics at semiconductors
		Correlation with electrochemical
		Cross reactions obey Marcus relation (Eq. 4)
Proton transfers	Marcus relation reduces to Brønsted Law	Explains curved Brønsted plots
	O, N bases and some transfers to C	
Methyl transfers	Concerted reactions	Describes enolization of acetone
	Cross reactions obey Marcus relation	
	Swain-Scott $\rho$ separated into $\rho^+$ and $\rho^-$	$\rho$ D isotope effects measure C <sup>+</sup> character
Nucleophilic additions	Provides alternative explanation to Ritchie relation	Values of $G^\ddagger$ found to be constant for similar species

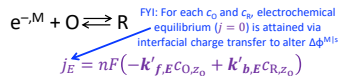
J. Albery, *Ann. Rev. Phys. Chem.*, **1980**, 31, 227-263.  
R. A. Marcus, *Faraday Discuss. Chem. Soc.*, **1982**, 74, 7-15



## Charge Transfer across Electrified Interfaces

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... aren't these so-called "heterogeneous electron-transfer reactions"?... Sure.



$$R_0 = \frac{\partial c_{O,Z_0}}{\partial t} = -k_f c_O + k_b c_R$$

$$j_E = nF(-k'_{f,E} c_{O,Z_0} + k'_{b,E} c_{R,Z_0})$$

...  $R_0$  is a rate... with units of  $M/s$  (=  $\text{mol dm}^{-3} \text{s}^{-1}$ ) ...  $j_E$  is a current density... with units of  $A/\text{cm}^2$  (=  $C \text{ cm}^{-2} \text{ s}^{-1}$ )  
 ...  $k_f$  ( $\text{s}^{-1}$ ) is an inverse time constant! ...  $k'_{f,E}$  ( $\text{cm s}^{-1}$ ) is a velocity!

... as a specific case choose  $E^{0'}$ ... and thus,  $j_{E^{0'}} = nF(-k'_{f,E^{0'}} c_{O,Z_0} + k'_{b,E^{0'}} c_{R,Z_0})$

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

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

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

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

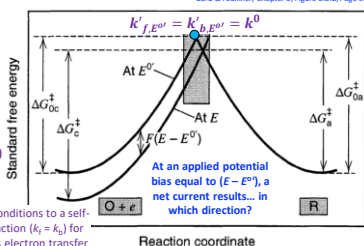


## Charge Transfer across Electrified Interfaces

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### Key Electrochemical Information

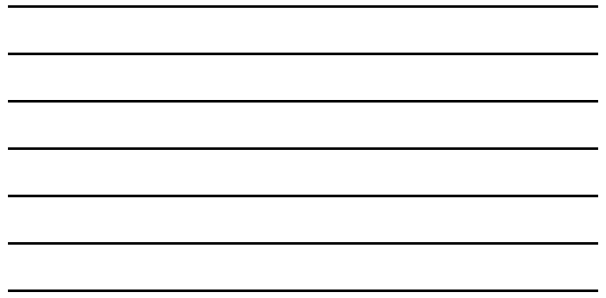
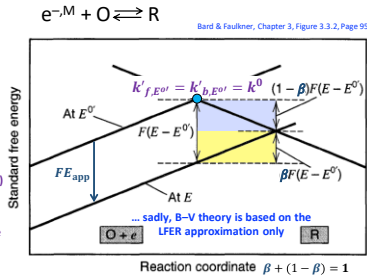
- In electrochemistry, application of a potential,  $E_{app}$ , varies the electrochemical potential of electrons ( $e^-$ ) in the (M)etal working electrode,  $\mu_e^M$
- Based on thermodynamics, when written as a reduction reaction, changing  $\mu_e^M$  alters the free energy (and one assumes also the standard-state free energy) of the reactants, as  $\Delta G_A = \mu_c^M + \mu_O$  (and  $\Delta G_A^\ddagger = \mu_c^M + \mu_O^\ddagger$ )
- The derivation here assumes that the electrode is inert, e.g. not like battery electrodes



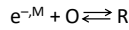
### Charge Transfer across Electrified Interfaces 344

**Key Electrochemical Information**

- In electrochemistry, application of a potential,  $E_{app}$ , varies the electrochemical potential of electrons ( $e^-$ ) in the (M)etal working electrode,  $\mu_e^M$
- Based on thermodynamics, when written as a reduction reaction, changing  $\mu_e^M$  alters the free energy (and one assumes also the standard-state free energy) of the reactants, as  $\Delta G_A = \mu_e^M + \mu_O$  (and  $\Delta G_A^0 = \mu_e^0 + \mu_O^0$ )
- Based on approximations, altering  $\Delta G_A$  changes all  $\Delta G$  values on the reaction coordinate relative to  $\Delta G_A$ , and not the parabolic/linear shape of the reactant "surface"... **Should it?**



### Butler–Volmer equation 345



$j_E = nF(k'_{b,E}c_{R,z_0} - k'_{f,E}c_{O,z_0})$  ... for this example, let's assume that  $n = 1...$

$j_E = Fk^0 \left\{ c_{R,z_0} \exp\left(\frac{(1-\beta)F(E-E^{0'})}{RT}\right) - c_{O,z_0} \exp\left(\frac{-\beta F(E-E^{0'})}{RT}\right) \right\}$  **Current–Potential Characteristic**

$j_E = j_0 \left\{ \frac{c_{R,z_0}}{c_R^*} \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \frac{c_{O,z_0}}{c_O^*} \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$  **Current–Overpotential Equation**

$j_0 = Fk^0 \frac{c_R^{\beta} c_O^{1-\beta}}{c_R^* c_O^*}$

...  $c^*$  means bulk concentration... conversion is trivial using  $E_{eq} = E^{0'} - \frac{RT}{nF} \ln \frac{c_R}{c_O}$

$j_E = j_0 \left\{ \exp\left(\frac{(1-\beta)F\eta}{RT}\right) - \exp\left(\frac{-\beta F\eta}{RT}\right) \right\}$  **Butler–Volmer Equation**

... assuming one rapidly stirs

**Tafel Slopes**

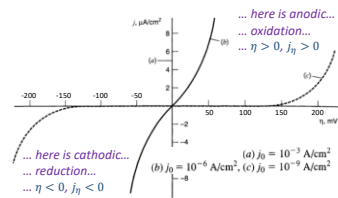
$TS_{cath}^{-1} = \left(\frac{d(\log |j_E|)}{d\eta}\right)_{cath} = \frac{-\beta F}{2.303RT}$

$TS_{an}^{-1} = \left(\frac{d(\log |j_E|)}{d\eta}\right)_{an} = \frac{(1-\beta)F}{2.303RT}$



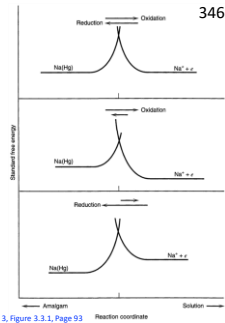
### Butler–Volmer equation 346

... let's examine effects of  $j_0$  (or  $k^0$ )...



Bard & Faulkner, Chapter 3, Figure 3.4.2, Page 101

... recall that...  $\eta = (E - E_{eq}) = E_{app} - \frac{\Delta G^0}{-nF}$



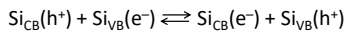
Bard & Faulkner, Chapter 3, Figure 3.3.1, Page 93







### Solid-State Physics Terminology $\bar{\mu}_i^{\text{SI}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$ 350



At equilibrium,  $\bar{\mu}_{\text{CB}}^{\text{SI}}(\text{h}^+) + \bar{\mu}_{\text{VB}}^{\text{SI}}(\text{e}^-) = \bar{\mu}_{\text{CB}}^{\text{SI}}(\text{e}^-) + \bar{\mu}_{\text{VB}}^{\text{SI}}(\text{h}^+)$

As reference states, it is useful to define  $\bar{\mu}_{\text{CB}}^{\text{SI}}(\text{h}^+) = \bar{\mu}_{\text{VB}}^{\text{SI}}(\text{e}^-) = 0$

... you can define up to one more  $\bar{\mu}_i^{\text{SI}}$ , but the last  $\bar{\mu}_i^{\text{SI}}$  has to be defined based on calorimetry data

Anyway... therefore,  $E_{\text{F},\text{e}^-} = \bar{\mu}_{\text{e}^-}$   
 $\bar{\mu}_{\text{CB}}^{\text{SI}}(\text{e}^-) = -\bar{\mu}_{\text{VB}}^{\text{SI}}(\text{h}^+)$   $E_{\text{F},\text{h}^+} = -\bar{\mu}_{\text{h}^+}$   
 $E_{\text{F},\text{e}^-} = E_{\text{F},\text{h}^+}$

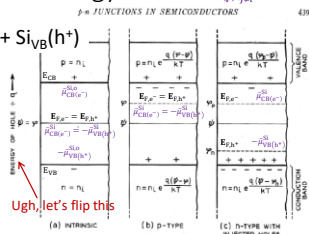
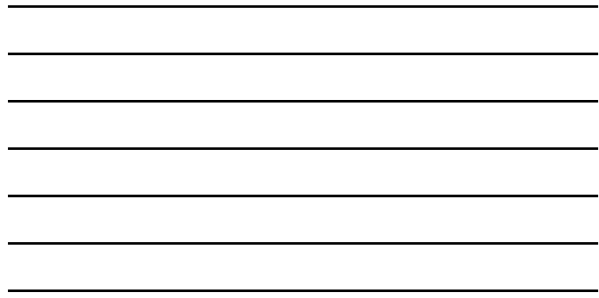
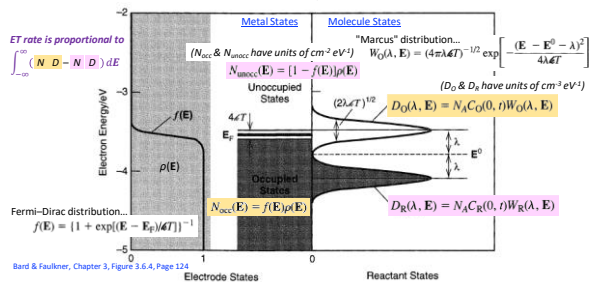


Fig. 2—Electrostatic potential  $\phi$ , Fermi level  $\mu$  and quasi Fermi levels  $\mu_e$  and  $\mu_h$ . In order to show electrostatic potential and energies on the same ordinate, the energies of holes, which are minus the energies of electrons, are plotted upwards in the figure in this paper. W. Shockley, *The Bell System Technical Journal*, 1949, 28, 435-489



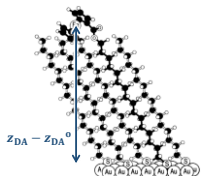
### Marcus–Gerischer Theory 351



### Marcus–Gerischer Theory 352

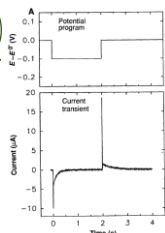
$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}|^2 e^{-2\beta(z_{\text{DA}} - z_{\text{DA}}^0)} \frac{1}{\sqrt{4\pi\lambda_{\text{AB}}kT}} \exp\left(-\frac{(\lambda_{\text{AB}} + \Delta G_{\text{AB}}^0)^2}{4\lambda_{\text{AB}}kT}\right)$$

quantum adiabatic electronic coupling      classical nuclear free-energy dependence

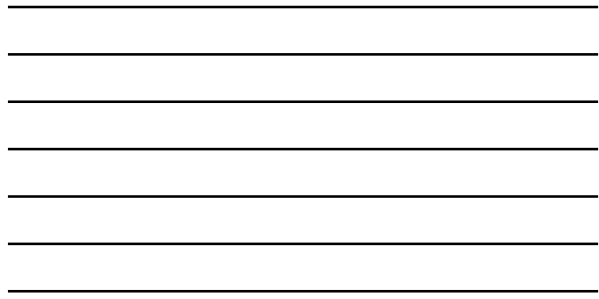


... as an aside... why is the data biphasic for the Current?

... RC-circuit double layer charging... followed by 1<sup>st</sup>-order ET kinetics

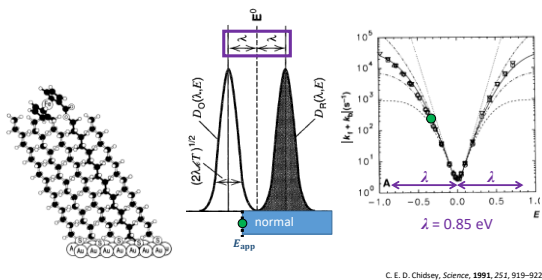


C. E. D. Chidsey, *Science*, 1991, 251, 919-922  
 H. D. Sikas, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey & S. W. Feldberg, *Science*, 2001, 292, 1519-1523



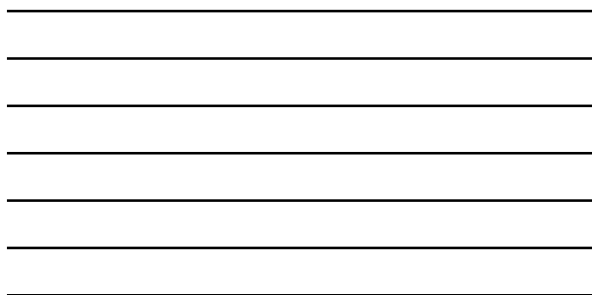
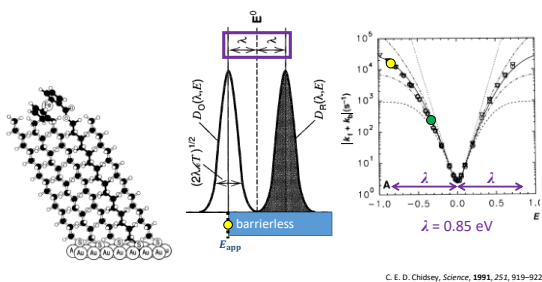
### Marcus–Gerischer Theory

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### Marcus–Gerischer Theory

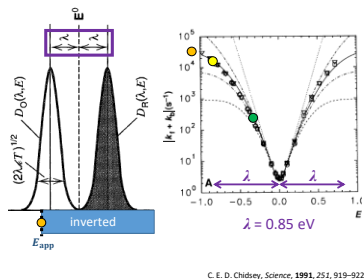
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### Marcus–Gerischer Theory

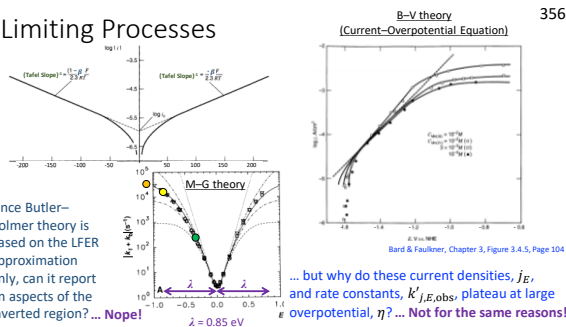
355

- It is easy to sweep/vary the driving force,  $\Delta G_{app}$ , by simply changing the electrochemical potential of electrons ( $e^-$ ) in the [M]etal working electrode,  $\mu_e^M$ , 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!



### Limiting Processes

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

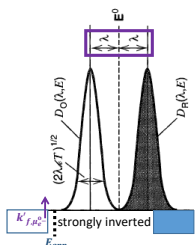
... but why do these current densities,  $j_E$ , and rate constants,  $k_{f,E,obs}^0$ , plateau at large overpotential,  $\eta$ ? ... Not for the same reasons!



### Marcus-Gerischer Theory

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- Use of a semiconductor limits the electronic states to those with (approximately) a single  $\mu_e^*$ , 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,  $\Delta G_{obs}^0$ , by simply changing the electrochemical potential of electrons ( $e^-$ ) in the (Semi)Conductor working electrode,  $\mu_e^*$ , through variations in  $E_{app}$ , because instead that changes the concentration of  $e^-$

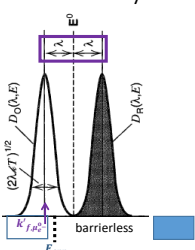
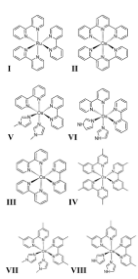


How can one use a semiconductor to study the inverted region?  
Think solution studies... vary the molecule!



### Marcus-Gerischer Theory

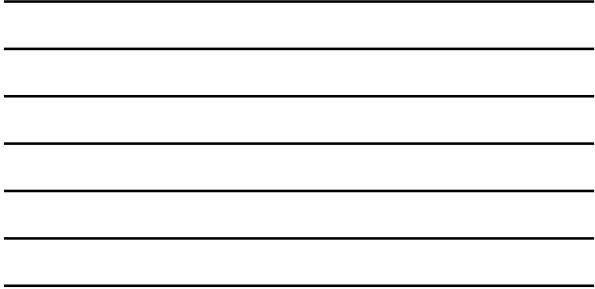
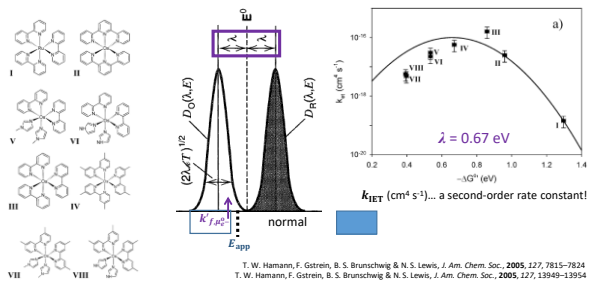
358



T. W. Hamann, F. Gotstein, B. S. Brunenschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, 127, 7815–7824  
T. W. Hamann, F. Gotstein, B. S. Brunenschwig & N. S. Lewis, *J. Am. Chem. Soc.*, **2005**, 127, 13949–13954



### Marcus–Gerischer Theory



### Charge Transfer across Electrified Interfaces

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 and Z. Nagy<sup>2</sup>  
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### Symmetry Factor and Transfer Coefficient

*A source of confusion in electrode kinetics*

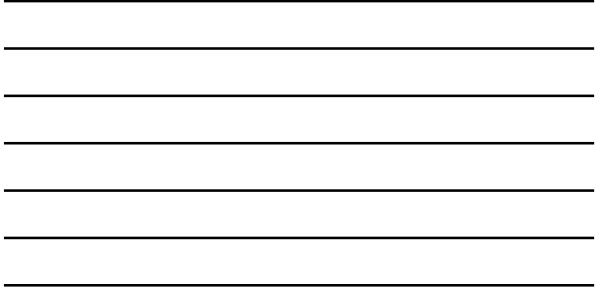
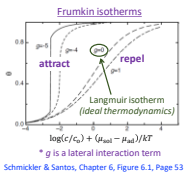
**Symmetry factor ( $\beta$ ):** change in the activation free energy of the cathodic elementary reaction step, expressed as a fraction of  $E_{app}$

**Transfer coefficient ( $\alpha$ ):** change in the total observed (cathodic/ anodic) reaction rate expressed as a change in observed activation free energies as a fraction of  $E_{app}$

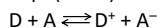
Do the two transfer coefficients always have to sum to one?

$$TS_{cath}^{-1} = \left( \frac{d(\log |j_c|)}{d|q|} \right)_{cath} = \frac{-\alpha_{cath} F}{2.303RT}$$

$$TS_{an}^{-1} = \left( \frac{d(\log |j_a|)}{dq} \right)_{an} = \frac{\alpha_{an} F}{2.303RT}$$



### Rate-Determining Step (RDS)



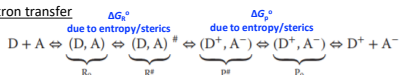
But wait... is this the elementary reaction step for electron transfer between a (D)onor and an (A)ccceptor in solution?  
**Nope!**

Poisson's Equation (from Gauss's law)

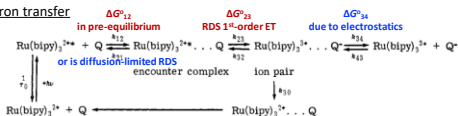
$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\epsilon} \quad E = -\frac{\partial \phi(x)}{\partial x}$$

$$\phi(r) = \frac{q}{4\pi\epsilon r}$$

#### Ground-state electron transfer



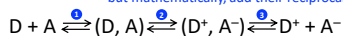
#### Excited-state electron transfer



## RDS: Pre-Equilibrium Approximation

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... seemingly totally unrelated... how does one determine the **observed** resistance of 3 resistors in parallel, or 3 capacitors in series? ... it's approximately equal to the smaller one... okay...  
but mathematically, add their reciprocals... and reciprocate



... so how does one determine the **observed** rate constant for 3 reactions in series?

... it's the same general idea...  $\frac{1}{k_{f,obs}} = \frac{1}{k_{1f}} + \frac{1}{k_{2f}'} + \frac{1}{k_{3f}}$  ... where  $\frac{\partial[D]}{\partial t} = \frac{\partial[A]}{\partial t} = -k_{f,obs}[D][A]$

... except that **Step 2** is preceded by **Step 1**... and **Step 3** is preceded by **Steps 1 and 2**

... and only one of those **Steps** will dictate the observed rate when it is the slowest step

... so the (pre)ceding steps must be much faster... thus assume they are in equilibrium...

$$\frac{1}{k_{f,obs}} = \frac{1}{k_{1f}} + \frac{1}{k_{1f}k_{2f}} + \frac{1}{k_{1f}k_{2f}k_{3f}} = \frac{1}{k_{1f}} + \frac{k_{1b}}{k_{1f}k_{2f}} + \frac{k_{1b}k_{2b}}{k_{1f}k_{2f}k_{3f}}$$

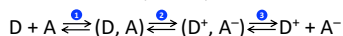
... and for completion, what if 3 (same-order) reactions are in **parallel**?

... it's as easy as it seems...  $k_{f,obs} = k_{1f} + k_{2f} + k_{3f} = \frac{1}{\tau_{1f}} + \frac{1}{\tau_{2f}} + \frac{1}{\tau_{3f}} = \frac{1}{\tau_{f,obs}}$

## RDS: Steady-State Approximation

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... but what if we want to determine  $\frac{\partial[D^+]}{\partial t} = \frac{\partial[A^-]}{\partial t}$  ... and some preceding steps are fast?  
... when all are fast, **except Step 1**, won't  $k_{f,obs} = k_{1f}$  then?... not always...



Assume that the middle steps come and go quickly... so each has a small steady-state conc...

$$\frac{\partial[(D,A)]}{\partial t} = 0 = -k_{2f}[(D,A)] + k_{1f}[D][A] \dots \text{and thus } [(D,A)] = \frac{k_{1f}[D][A]}{k_{2f}}$$

$$\frac{\partial[(D^+,A^-)]}{\partial t} = 0 = -k_{3f}[(D^+,A^-)] + k_{2f}[(D,A)] \dots \text{and thus } [(D^+,A^-)] = \frac{k_{2f}[(D,A)]}{k_{3f}}$$

$$\dots \text{which means that } [(D^+,A^-)] = \frac{k_{1f}k_{2f}[D][A]}{k_{2f}k_{3f}} = \frac{k_{1f}[D][A]}{k_{3f}}$$

... since  $\frac{\partial[D^+]}{\partial t} = \frac{\partial[A^-]}{\partial t} = k_{3f}[(D^+,A^-)]$ ... this is just equal to  $k_{1f}[D][A]$ ... and  $k_{f,obs} = k_{1f}$

... which is what the pre-equilibrium approximation would have predicted too, so... unexciting!

## Chemical Kinetics (summary for today)

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- Continuity of mass, Mass transfer, Nernst–Planck equation, Diffusion, Diffusion coefficient, Migration, Mobility, Convection, Boundary layer
- 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)
- **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**

Paper Time!