

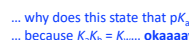
DISSOCIATION CONSTANTS OF ORGANIC ACIDS AND BASES

This table lists the dissociation constants of most 1075 organic acids, bases, and amphoterics compounds. All data apply to dilute aqueous solutions and are presented as values of pK_a , which is defined as the negative of the logarithm of the equilibrium constant K_a for the reaction:



where [H₃O⁺] etc. represent the concentrations of the respective species in mol/L. It follows that $pK_a = -\log K_a = -\log \frac{[A^-][H_3O^+]}{[HA]}$, so that a solution with 50% dissociation has pK_a equal to the pH of the acid.

Data for bases are presented as pK_b values for the conjugate acid, i.e., for the reaction:



$pK_b = pK_a - 14.00$ (at 25°C) ... $pBLAH = -\log a_{BLAH}$

... why does this state that $pK_b + pK_a = pK_w$?
 ... because $K_b K_a = K_w$... **okaaaayyyy**... but why?
 ... because $\exp(-(\Delta G_b^\circ + \Delta G_a^\circ)) = \exp(-\Delta G_w^\circ)$...
 ... **Ahhhhh!**... enough with the algebra already!
 ... but wait!... for B, BH⁺ this looks like Hess's law!
 ... **so, let's add up these chemical reactions!**
 ... and that gives us water dissociation... Nice!

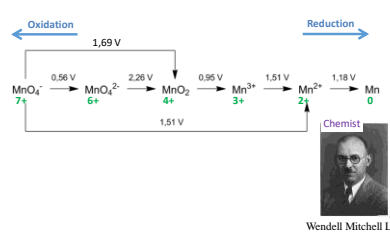
... **and again**, the CRC Handbook has a lot of chemical information... including tables of values...
 ... also those in the **Acidity/Basicity Series**...
 ... Do you know what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?

(REVIEW) 240

Ref. Name	Name	Step	pK _a	Ref. Name	Name	Step	pK _a
CR001	Carbonic acid	1	6.37	CR001	Carbonic acid	2	10.33
CR002	Formic acid	1	3.75	CR002	Formic acid	2	10.25
CR003	Acetic acid	1	4.76	CR003	Acetic acid	2	10.25
CR004	Propionic acid	1	4.87	CR004	Propionic acid	2	10.25
CR005	Butyric acid	1	4.82	CR005	Butyric acid	2	10.25
CR006	Pyruvic acid	1	2.49	CR006	Pyruvic acid	2	10.25
CR007	Oxalic acid	1	1.27	CR007	Oxalic acid	2	4.26
CR008	Malonic acid	1	3.44	CR008	Malonic acid	2	10.25
CR009	Succinic acid	1	4.21	CR009	Succinic acid	2	10.25
CR010	Tartronic acid	1	3.34	CR010	Tartronic acid	2	10.25
CR011	Malic acid	1	3.40	CR011	Malic acid	2	10.25
CR012	Fumaric acid	1	3.03	CR012	Fumaric acid	2	10.25
CR013	Maleic acid	1	1.92	CR013	Maleic acid	2	10.25
CR014	Phthalic acid	1	2.89	CR014	Phthalic acid	2	10.25
CR015	Benzoic acid	1	4.20	CR015	Benzoic acid	2	10.25
CR016	Chloroacetic acid	1	2.86	CR016	Chloroacetic acid	2	10.25
CR017	Bromoacetic acid	1	2.90	CR017	Bromoacetic acid	2	10.25
CR018	Iodoacetic acid	1	3.19	CR018	Iodoacetic acid	2	10.25
CR019	Phosphoric acid	1	2.12	CR019	Phosphoric acid	2	7.21
CR020	Sulfuric acid	1	-3.00	CR020	Sulfuric acid	2	-1.99
CR021	Hydrofluoric acid	1	3.17	CR021	Hydrofluoric acid	2	11.31
CR022	Hydrochloric acid	1	-7.00	CR022	Hydrochloric acid	2	-7.00
CR023	Hydrobromic acid	1	-9.00	CR023	Hydrobromic acid	2	-9.00
CR024	Hydroiodic acid	1	-10.00	CR024	Hydroiodic acid	2	-10.00
CR025	Perchloric acid	1	-16.00	CR025	Perchloric acid	2	-16.00
CR026	Chlorous acid	1	2.00	CR026	Chlorous acid	2	5.95
CR027	Bromous acid	1	2.00	CR027	Bromous acid	2	5.95
CR028	Iodosulfuric acid	1	2.00	CR028	Iodosulfuric acid	2	5.95
CR029	Chlorous acid	1	2.00	CR029	Chlorous acid	2	5.95
CR030	Bromous acid	1	2.00	CR030	Bromous acid	2	5.95
CR031	Iodosulfuric acid	1	2.00	CR031	Iodosulfuric acid	2	5.95
CR032	Chlorous acid	1	2.00	CR032	Chlorous acid	2	5.95
CR033	Bromous acid	1	2.00	CR033	Bromous acid	2	5.95
CR034	Iodosulfuric acid	1	2.00	CR034	Iodosulfuric acid	2	5.95
CR035	Chlorous acid	1	2.00	CR035	Chlorous acid	2	5.95
CR036	Bromous acid	1	2.00	CR036	Bromous acid	2	5.95
CR037	Iodosulfuric acid	1	2.00	CR037	Iodosulfuric acid	2	5.95
CR038	Chlorous acid	1	2.00	CR038	Chlorous acid	2	5.95
CR039	Bromous acid	1	2.00	CR039	Bromous acid	2	5.95
CR040	Iodosulfuric acid	1	2.00	CR040	Iodosulfuric acid	2	5.95

Two diagrams of empirical standard potentials... (REVIEW) 241

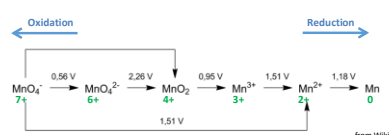
A **Latimer diagram** is a summary of the E° values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



Latimer, The oxidation states of the elements and their potentials in aqueous solution, 1938

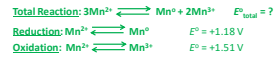
Two diagrams of empirical standard potentials... 242

A **Latimer diagram** is a summary of the E° values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



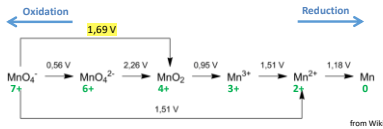
Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule (the opposite is **comproportionation** (AKA: **sympportionation**))

- (1) Does Mn²⁺ disproportionate? **NO**. E° = E_{red} - E_{ox} = 1.18 - 1.51 = -0.33 V
- (2) What is the standard reduction potential of MnO₂ to MnO₄²⁻?



Two diagrams of empirical standard potentials...

A Latimer diagram is a summary of the E° values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule (the opposite is comproportionation (AKA: symproportionation))

(1) Does Mn^{2+} disproportionate? NO. $E^\circ = E_{red} - E_{ox} = 1.18 - 1.51 = -0.33 V$
 (2) What is the standard reduction potential of MnO_4^- to MnO_2 ?

$\Delta G^\circ = -nFE^\circ = -3FE^\circ$

$\Delta G^\circ = -nFE^\circ_{MnO_4^- \rightarrow MnO_2} = -F(1 \times 0.56 V) + (2 \times 2.26 V) = -F(5.08 V)$

Set them equal to each other, and thus, $3E^\circ = 5.08$ and $E^\circ = 1.69 V$

... for #1, you can work with E° only (do not need ΔG°), because the reaction is always balanced/equal in the number of electrons

243



Two diagrams of empirical standard potentials...

A Latimer diagram is a summary of the E° values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



Recall from before...

$Mn^{2+} + 2e = Mn$	1.185
$Mn^{3+} + e = Mn^{2+}$	1.513
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.224
$MnO_4^- + e = MnO_4^{2-}$	0.558
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.679
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.507
$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$	0.595
$MnO_4^- + 2H_2O + 2e = MnO_2 + 4OH^-$	0.660
$Mn(OH)_2 + 2e = Mn + 2OH^-$	-1.56
$Mn(OH)_2 + e = Mn(OH) + OH^-$	0.15
$Mn_2O_3 + 6H^+ + e = 2Mn^{2+} + 3H_2O$	1.485

... because they are at basic/alkaline standard state with ~1 M OH⁻

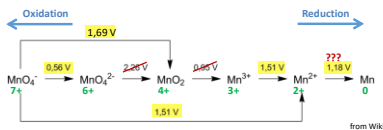
... anyway, why are these bottom E° values not on the Latimer diagram?

244



Two diagrams of empirical standard potentials...

A Latimer diagram is a summary of the E° values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



Recall from before...

$Mn^{2+} + 2e = Mn$	1.185
$Mn^{3+} + e = Mn^{2+}$	1.513
$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	1.224
$MnO_4^- + e = MnO_4^{2-}$	0.558
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.679
$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	1.507
$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$	0.595
$MnO_4^- + 2H_2O + 2e = MnO_2 + 4OH^-$	0.660
$Mn(OH)_2 + 2e = Mn + 2OH^-$	-1.56
$Mn(OH)_2 + e = Mn(OH) + OH^-$	0.15
$Mn_2O_3 + 6H^+ + e = 2Mn^{2+} + 3H_2O$	1.485

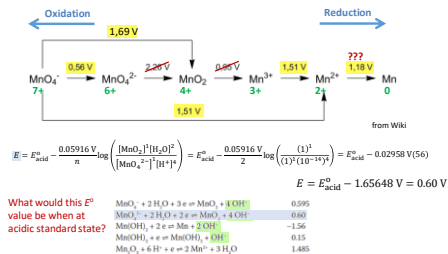
What would this E° value be when at acidic standard state?

245



Two diagrams of empirical standard potentials...

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur

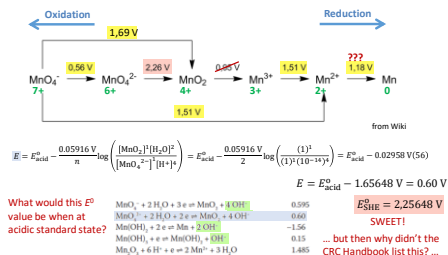


246



Two diagrams of empirical standard potentials...

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur

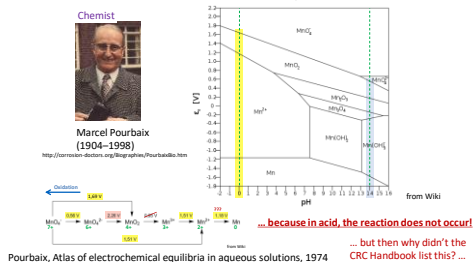


247



... a second diagram of (not truly) empirical standard potentials... (REVIEW) 248

A **Pourbaix diagram** is a map of the predominant equilibrium species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable ... mostly based on thermochemical data



Chemical Kinetics

252

- 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

... So, let’s start with the simple equations that Chemical Engineers use...

253

... mass transfer in chemical systems is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)...

... *We need to understand mass transfer!* ...

... *but first, because it relates directly to mass transfer, I need to introduce the governing equation for the continuity of mass, which is even more stringent than the law of the conservation of mass!*

... and later, let’s step our game up and do a more rigorous PChem / Physics derivation!

Thermodynamics *versus* Kinetics

254

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...

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

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

mass action (R)ate laws that effect species A, e.g. $R_A = k_c \sigma_A \sigma_{e^-}^2 = k_s [B][D]^2$ (to a first order, this is driven by differences in *chemical potential* of various species, μ_i)

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

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

mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion, migration/drift, and convection*

258

the Nernst-Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

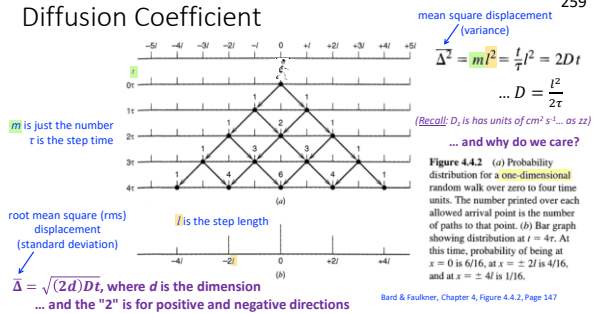
B&F, 1.4.2 & 4.1.8

↑
the diffusive flux of reactant *i* to a flat electrode where *D_i* is the diffusion coefficient for species, *i* (*D* has units of cm² s⁻¹)



Diffusion Coefficient

259



mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion, migration/drift, and convection*

260

the Nernst-Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

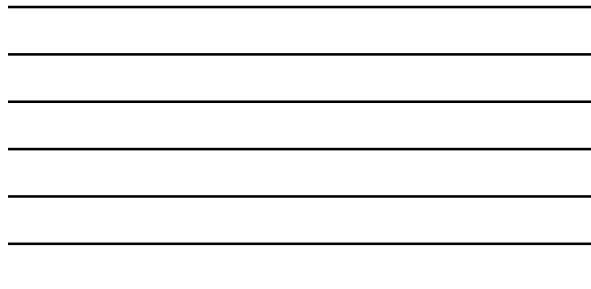
B&F, 1.4.2 & 4.1.8

... migration/drift relies on the electric-field-driven variant of the random walk diffusion coefficient... obviously the ability for a species to random walk is still important, but on top of that an electric field will drive the species directionally... this is called the *mobility*, μ

$$\mu_i = \frac{|z_i|FD_i}{RT}$$

↑
the flux due to migration/drift of reactant *i* where *z_i* is the charge on species *i*, and $\partial\phi/\partial x$ is the gradient in electric potential (which is equal to the negative of the electric field, *E*)

... this is the Einstein-Smoluchowski equation... sorry that *mobility* and *chemical potential* have the same symbol... ugh!



mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: *diffusion, migration/drift, and convection*

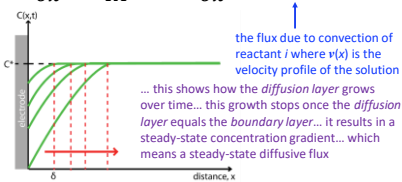
261

the Nernst-Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

B&F, 1.4.2 & 4.1.8

... convection forms a boundary layer that to a first approximation is fixed for a given stir rate... which sets a slope for the concentration gradient to dictate maximum diffusive flux... stirring faster shrinks this boundary layer, which increases the limiting mass transfer flux



Mass transfer... where analogous equations exist for heat transfer...

262

- (1) **Migration / Drift** (*no analogous term for heat, as heat is not charged*) Flux ($\text{mol cm}^{-2} \text{s}^{-1}$) of **charged species** due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions



<http://wps.prenhall.com/wps/media/object/3313/3392587/bb2003.html>

Mass transfer... where analogous equations exist for heat transfer...

263

- (1) **Migration / Drift** (*no analogous term for heat, as heat is not charged*) Flux ($\text{mol cm}^{-2} \text{s}^{-1}$) of **charged species** due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions
- (2) **Diffusion** (*analogous heat transfer is down a temperature gradient*) Net flux of **species** due to a spatial gradient in their concentration and random thermal motion (no real "force")



Diffusion

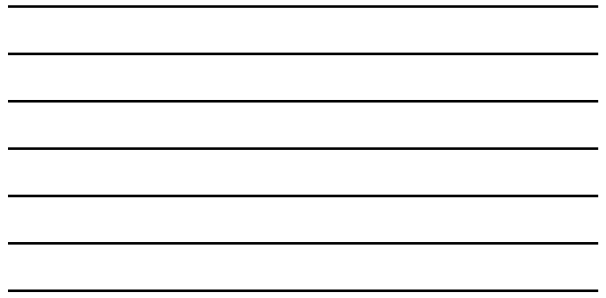
<http://en.wikipedia.org/wiki/Diffusion>

Mass transfer... where analogous equations exist for heat transfer...

264

- (1) **Migration / Drift** (*no analogous term for heat, as heat is not charged*)
Flux (mol cm⁻² s⁻¹) of **charged species** due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions
- (2) **Diffusion** (*analogous heat transfer is down a temperature gradient*)
Net flux of **species** due to a spatial gradient in their concentration and random thermal motion (no real "force")
- (3) **Convection** (*analogous heat transfer is fluid/gas motion*)
Hydrodynamic movement (e.g. forced convection (stirring)) of **species**, where charged species still remain near each other (Coulombic attraction)

... FVI: even without intentional forced convection, unintentional forced convection (e.g. vibrations) influences an electrochemical experiment after ~30 seconds



1D Transport in Solids... *the heavy lift*

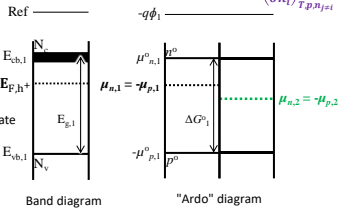
265

$$\text{Flux}_{x,e} = N_e = -\frac{\sigma_e d\bar{\mu}_e}{F^2 dz}$$

(z is a direction; e means z_e = -1)

$\frac{d\bar{\mu}_e}{dz}$ dictates directionality
... multiply by $\sigma_e = \frac{F^2 D_e c_e}{RT}$ to get relative rate
... multiply Flux_{x,e} by "z_eF" to get J_{x,e}

Solar cell experts say colloquial phrases like "band bending for charge separation" and "selective contacts"... I'm not a fan



A hybrid internal energy / free energy diagram shows several useful things at once, but (possibly usefully) glosses over details of other transport processes



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

266

Let's expand the total differential... $\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j \neq i}} = \bar{\mu}_i = \mu_i + z_i q \phi$

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

... assuming a species, e, with valency, z_e, equal to -1

$$\text{Flux}_{x,e} = -\frac{D_e n_e}{kT_e} \left(\frac{d\mu_e^0}{dz} + \frac{kT_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{kT_e}{n_e} \frac{dn_e}{dz} - \frac{kT_e}{n_e^0} \frac{dn_e^0}{dz} + k \left(\ln \frac{\gamma_e m_e}{n_e^0} \right) \frac{dT_e}{dz} - q \frac{d\phi}{dz} \right) - S_e T_e \frac{dT_e}{dz}$$

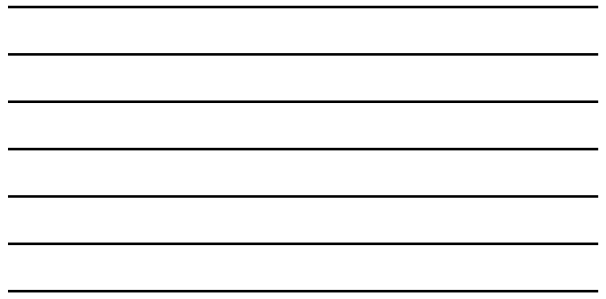
... other species may have different values for every term, except φ

$$\text{Flux}_{x,e} = -D_e \left(\frac{n_e}{kT_e} \frac{d\mu_e^0}{dz} + \frac{n_e}{\gamma_e} \frac{d\gamma_e}{dz} + \frac{dn_e}{dz} - \frac{n_e}{n_e^0} \frac{dn_e^0}{dz} + \frac{n_e}{T_e} \left(\ln \frac{\gamma_e m_e}{n_e^0} \right) \frac{dT_e}{dz} - \frac{qn_e}{kT_e} \frac{d\phi}{dz} \right) - S_e T_e \frac{dT_e}{dz}$$

Drift-Diffusion equation

$$\text{Flux}_{x,e} = -D_e \frac{dn_e}{dz} + \frac{qD_e n_e}{kT_e} \frac{d\phi}{dz} \quad \dots \text{assuming spatially invariant } \mu_e^0, \gamma_e, n_e^0, T_e$$

$$\text{Flux}_{x,e} = -D_e n_e \left(\frac{d\mu_e^0}{kT_e dz} + \frac{d(\ln \gamma_e)}{dz} + \frac{d(\ln n_e)}{dz} - \frac{d(\ln n_e^0)}{dz} + \frac{d(q\phi)}{kT_e dz} \right) - D_e n_e \gamma_e \frac{dT_e}{dz}$$



Continuity of Mass

(REVIEW) 267

"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

Thermodynamics versus Kinetics

(REVIEW) 268

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_i)

mass action (R)ate laws that effect species A, e.g. $R_+ = k_1 a_A a_B^2 = k_1 [B][D]^2$ (to a first order, this is driven by differences in chemical potential of various species, mu_j)

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

1D Transport in Liquids (solids are simpler)

(REVIEW) 269

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

(MechEs should be yawning)

$$N_A = - \left(\frac{D_{AC_A}}{RT} \right) \frac{\partial \bar{\mu}_A}{\partial z} + v c_A$$

... 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 ((cm²/s) / cm) = cm/s... a velocity!
 ... and with $\frac{\partial}{\partial z}$, units are s⁻¹... 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_j (s⁻¹), an inverse time constant!)

270

Mass Action / Microscopic Reversibility

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

(Chemists should be yawning)

... and in solid-state physics... $R_{e^{-}total} = \sum_j Ge_{n,e^{-},j} - \sum_j Re_{e^{-},j}$



$$\Delta G^\alpha = \Delta G^{0,\alpha} + RT \ln Q \dots \text{where } Q = \frac{a_B^\alpha}{a_A^\alpha} = \frac{y_B^\alpha (c_B^\alpha / c_A^\alpha)}{y_A^\alpha (c_A^\alpha / c_A^\alpha)}$$

$$R_{A,f} = -k_f a_A \quad R_{B,f} = +k_f a_A \quad \bullet \text{ Law of mass action}$$

$$R_{A,b} = +k_b a_B \quad R_{B,b} = -k_b a_B \quad \bullet \text{ Principle of microscopic reversibility}$$

k_j (M/s)... a rate!
 k_j (s⁻¹)... an inverse time constant!

Now, consider the reaction to be at equilibrium... $\Delta G^\alpha = 0 = \Delta G^{0,\alpha} + RT \ln Q' = \bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha$

So, $\Delta G^{0,\alpha} = -RT \ln K'$, with $K' = \frac{c_{B,eq}^\alpha / c_{A,eq}^\alpha}{c_{A,eq}^\alpha / c_{A,eq}^\alpha}$... and, of course, $K' = \exp\left(-\frac{\Delta G^{0,\alpha}}{RT}\right)$

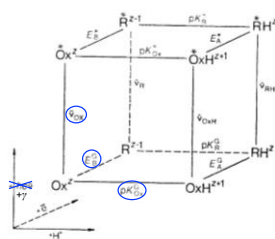
But also, $\frac{\partial c_A}{\partial t} = 0 = -k_f a_{A,eq}^\alpha + k_b a_{B,eq}^\alpha \dots \frac{k_f}{k_b} = \frac{a_{B,eq}^\alpha}{a_{A,eq}^\alpha} = K = K' \frac{y_B^\alpha}{y_A^\alpha}$... it can get messy

Or equivalently, $\frac{\partial c_A}{\partial t} = 0 = -k'_f c_{A,eq}^\alpha + k'_b c_{B,eq}^\alpha \dots \frac{k'_f}{k'_b} = \frac{c_{B,eq}^\alpha}{c_{A,eq}^\alpha} = K' \frac{y_A^\alpha c_{B,eq}^\alpha}{y_B^\alpha c_{A,eq}^\alpha}$



271

Förster Cube and Square Schemes



Questions to ponder...

In this figure, what do the thermodynamic parameters E , pK , and $\bar{\nu}$ represent?

- $E = E^0$ (standard-state reduction potential)
- $pK = pK_a = -\log K_a$ (acid dissociation constant)
- $\bar{\nu} = \frac{1}{\lambda}$ (wavenumber)

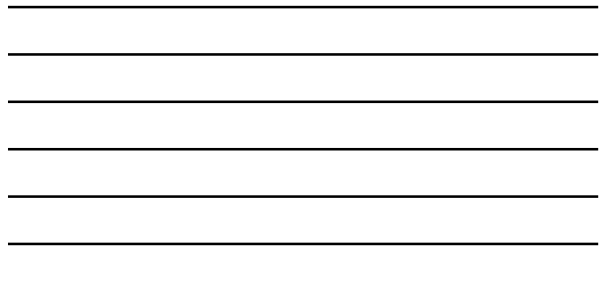
How are they related?

- Redox: $E^0 = -\Delta G^0/nF$
- Acidity: $pK_a = -\log K_a = \Delta G^0/(2.303RT)$
- Light: $hc\bar{\nu} = \frac{hc}{\lambda} = h\nu = E_{\text{photon}}$

What is the reference state for each?
 $E^0(H^+(aq)/H_2) = 0$; $pK_a(H^+(aq)) = 0$; 0

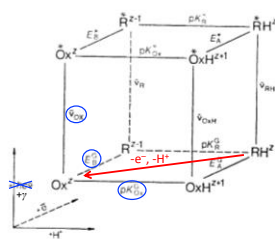
... before we add light... let's backtrack a bit...

... first we must understand dark thermal processes... Z. R. Grabowski & W. Rubaszewska, J. Chem. Soc. Faraday Trans. 1, 1977, 73, 11-28



272

Förster Cube and Square Schemes



Does this obey Hess's law?

- Redox: $E^0 = -\Delta G^0/nF$
- Acidity: $pK_a = -\log K_a = \Delta G^0/(2.303RT)$
- Thus, $E^0 = -pK_a \times (2.303RT/nF) = -59.2 \text{ mV} \times pK_a$
- Does Bottom Route = Top Route?
 $10(-0.0592V) + (-0.8V) = -1.5V + -2(-0.0592V)$
 $-0.59V + -0.8V = -1.5V + 0.12V \dots \text{so, "yes!"}$

... anyway... but is the concerted path possible? R. Tyburski, T. Liu, S. D. Glover & L. Hammarström, J. Am. Chem. Soc., 2021, 143, 560-576



Förster Cube and Square Schemes

273

... oh, I see... by moving oppositely charged species in a concerted fashion, electrostatic (Born solvation) energy will be much smaller

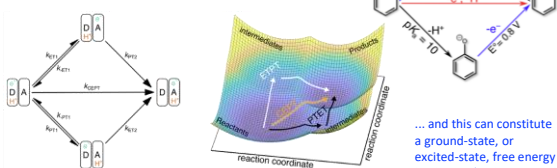


Figure 2. (Left) Square scheme that summarizes the mechanisms by which proton-coupled electron transfer can proceed. The edges of the square show the sequential mechanisms with EPT and PTE on the top and bottom, respectively. The pathways bisecting the square is concerted, where e^- and H^+ are transferred without the formation of an intermediate species. Note that the donor and acceptor sites for ET and PT can be the same or different species. (Right) Illustration of the three main mechanisms for PCET, each with a distinct transition state.

R. Tyburnski, T. Liu, S. D. Glover & L. Hammarström, *J. Am. Chem. Soc.*, **2021**, *143*, 560-576

... and this can constitute a ground-state, or excited-state, free energy landscape (N-dimensional potential energy surface)



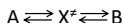
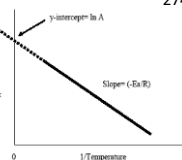
Activation Energies

274

Arrhenius (1889)

empirical rate constant equation

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



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}

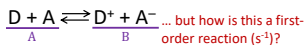
$$k_f = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{and so } A \text{ contains } \Delta S^\ddagger$$

... 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

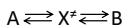
275



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}

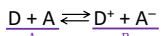
$$k_f = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) = \frac{\kappa k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \dots \text{and so } A \text{ contains } \Delta S^\ddagger$$

... 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

276



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

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{\Delta G_{AB}^\ddagger}{kT}\right) \quad \frac{\partial c_{A,z_0}}{\partial t} = \sum_j R_{A,j} - \frac{\partial N_A}{\partial z}$$

quantum adiabatic electronic coupling classical nuclear free-energy dependence

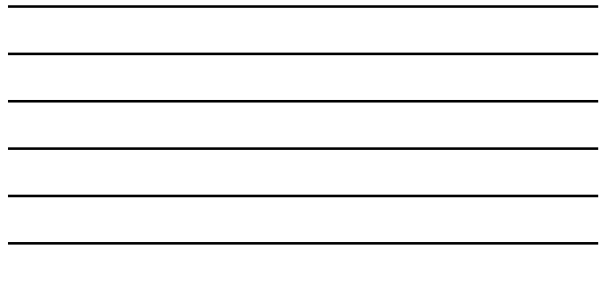
proportional to $\frac{d\mu_A}{dz}$

proportional to $(\lambda_{AB} + \Delta G_{AB}^0)^2$

... 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?

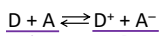
$$\Delta G_{AB}^\ddagger = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$$

... wait... there is a direct relation between thermodynamics (ΔG_{AB}^0) and kinetics (ΔG_{AB}^\ddagger)?
 ... this makes sense since $\frac{d\mu_A}{dz}$ drives transport... which can be written as a chemical reaction
 ... but that key relationship is quadratic... meaning a parabola? Huh?!?!?!?



Marcus–Hush Theory

277



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

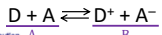
$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda_{AB}kT}} \exp\left(-\frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}kT}\right)$... what kind of function is this?
 $\Delta G_{AB}^\ddagger = \frac{(\lambda_{AB} + \Delta G_{AB}^0)^2}{4\lambda_{AB}}$

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



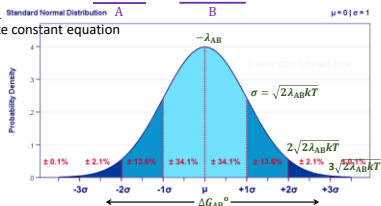
Marcus–Hush Theory

278



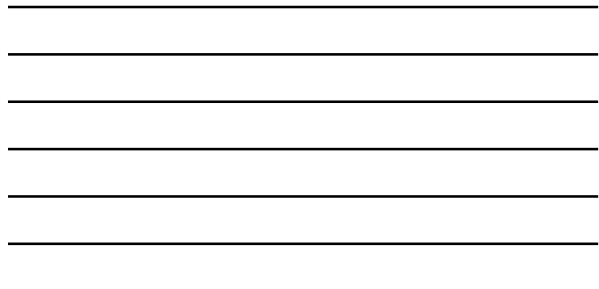
Marcus–Hush (1950s–1960s) Standard Normal Distribution theoretical (semiclassical) rate constant equation

... 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!

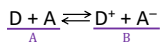


$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{2\pi}\sqrt{2\lambda_{AB}kT}} \exp\left(-\frac{1}{2} \left(\frac{\Delta G_{AB}^0 - (-\lambda_{AB})}{\sqrt{2\lambda_{AB}kT}}\right)^2\right)$$

... does this help at all?



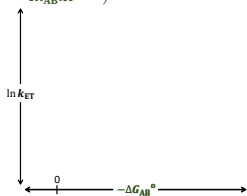
Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

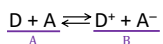
theoretical (semiclassical) rate constant equation

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



279

Marcus–Hush Theory



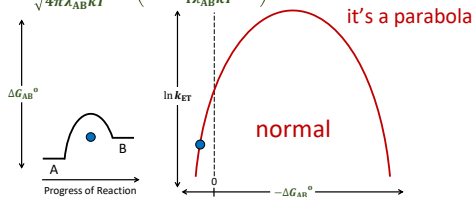
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

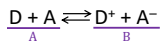
How can a thermodynamically unfavorable reaction proceed?

Mass Action!



280

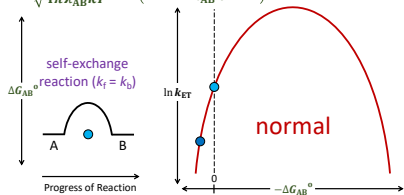
Marcus–Hush Theory



Marcus–Hush (1950s–1960s)

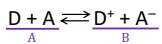
theoretical (semiclassical) rate constant equation

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



281

Marcus–Hush Theory

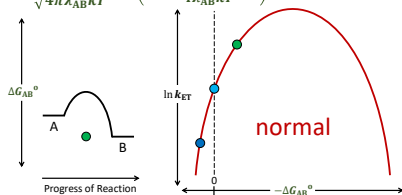


282

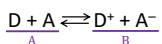
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



Marcus–Hush Theory

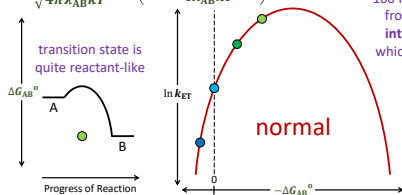


283

Marcus–Hush (1950s–1960s)

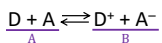
theoretical (semiclassical) rate constant equation

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



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

Marcus–Hush Theory

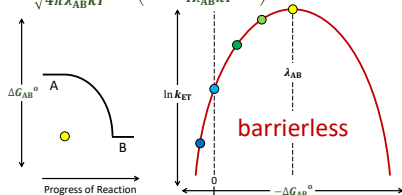


284

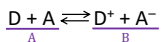
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



Marcus–Hush Theory

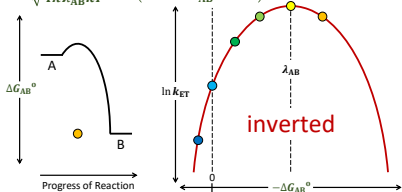


285

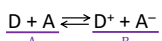
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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



Marcus–Hush Theory



286

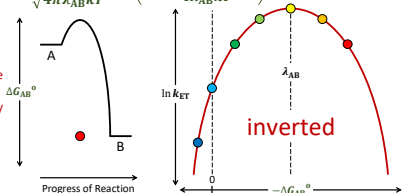
Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

... this looks odd...

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



Outer Reorganization Energy

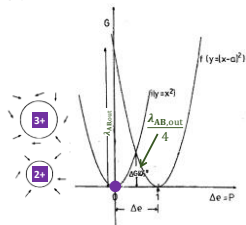
287

Marcus–Hush (1950s–1960s)

theoretical (semiclassical) rate constant equation

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

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



... 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 Energy

288

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

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

$\lambda_i = \sum_j \lambda_{i,j} = \frac{1}{2} \sum_j f_j (\Delta q_{i,j})^2$

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

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

MO Diagram: This 2H_{1s} mixing is like what we learned for molecular orbital theory!

$\lambda_{AB} = E_{in} - E_{out}$

$E_{in} = \frac{1}{2} \sum_j f_j (\Delta q_{i,j})^2$

$E_{out} = \frac{1}{2} \sum_j f_j (\Delta q_{o,j})^2$

N. Sutin, Acc. Chem. Res., 1982, 15, 275-282

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

More Quantum Mechanics

289

But you still didn't tell us why we need to recall this equation

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = E_n\psi_n(x)$$

... we need to fill internal energies, E_n , with particles... okay.

Poisson's Equation (from Gauss's law)

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

for a point charge... $\phi(r) = \frac{q}{4\pi\epsilon r}$
look familiar?

... and that under most chemical conditions, potential energy, $\hat{V}(x)$, is **electrostatic**, $\phi(x)$
... which is actually not so limiting because there are only 4-ish forces of Nature

... and while we're at it, let's (re)learn **overlap integral** (S_{nm}), **expectation value** ($\langle p_n \rangle$), **bra-ket notation** ($\langle \psi_n | \psi_m \rangle$), and exponential **tunneling probability**...

Probability Density (x) = $|\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$
... with $\psi_n^*(x)$ (complex conjugate)

Overlap integral, $S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x) dx = \langle \psi_n | \psi_m \rangle$
... with $\langle \psi_n |$ ("bra") and $|\psi_m \rangle$ ("ket")

Mean Energy, (E_n) = $\frac{\int_{-\infty}^{\infty} \psi_n^*(x)\hat{H}\psi_n(x) dx}{\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x) dx} = \langle \psi_n | \hat{H} | \psi_n \rangle = \langle E \rangle$

https://en.wikipedia.org/wiki/Quantum_tunnelling#/media/File:E14-V20-81.gif

Molecular Orbital Theory

290

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

Molecular Orbital Theory
linear combination of atomic orbitals

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

quantum adiabatic electronic coupling classical nuclear free-energy dependence

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

... remember the simplicity of H₂⁺... which resembles λ_{out} math

$$\hat{H}(r, R_{AB}) = \frac{\hbar^2}{2m} \nabla_1^2 + \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R_{AB}}$$

matrix

$$\hat{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

Nuc. a Nuc. b

Atomic orbital (Atom A) Molecular orbital (Mol. Orb.) Atomic orbital (Atom B)

H_{AA} H_{AB} H_{BB}

ψ_A ψ_{AB} ψ_B

M. D. Newton, Int. J. Quantum Chem., 1980, 18, 363-391
N. Sutin, Acc. Chem. Res., 1982, 15, 275-282

Chemical Kinetics (*summary for today*)

291

- 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
