Lecture #2 of 12

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Review of Physical Chemistry

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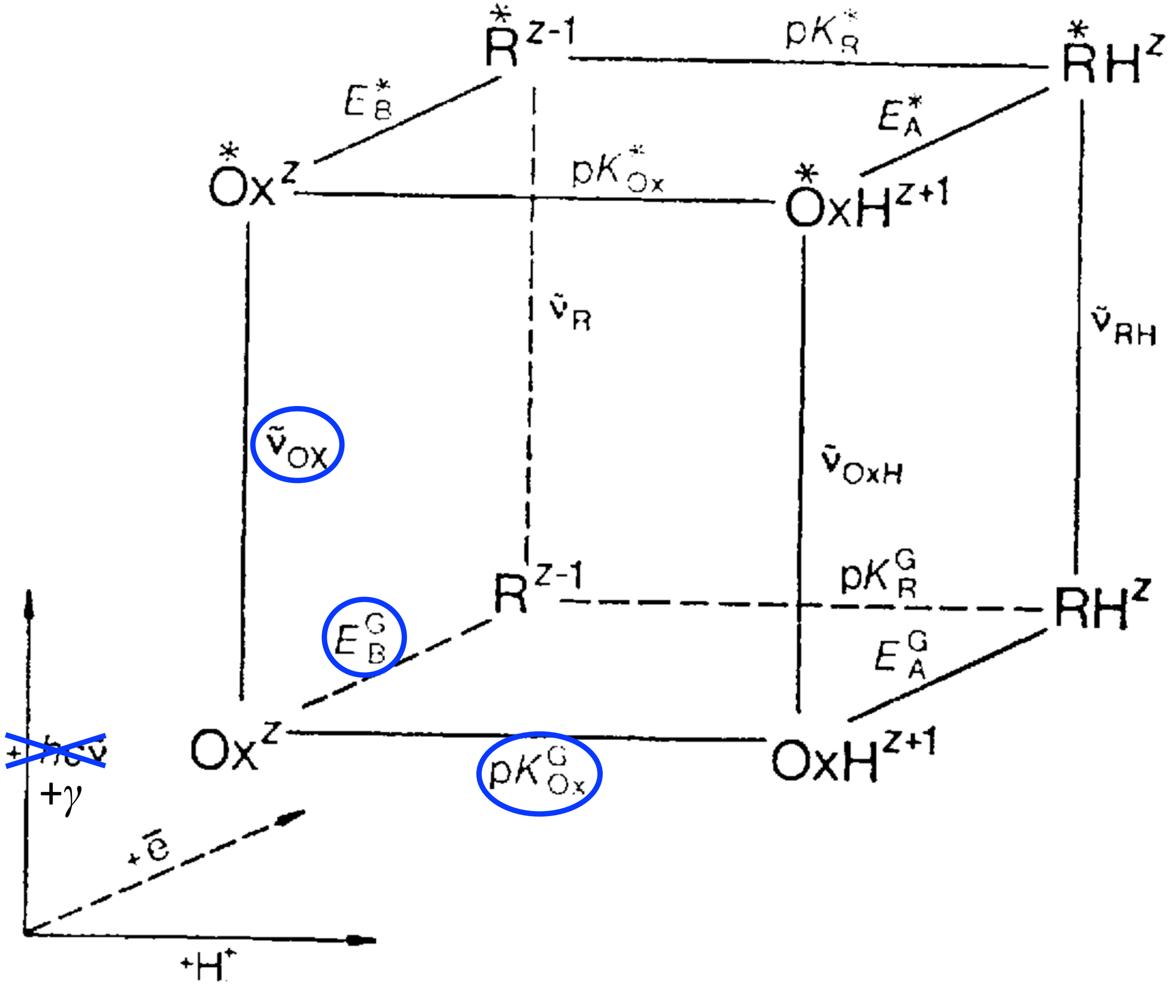
(UPDATED/REVIEW)

Förster Cube and Square Schemes



... let's backtrack a bit... before we add light...
... one must understand dark thermal processes...

Questions to ponder... NOW!

What do the thermodynamic parameters *E*, p*K*, and $\bar{\nu}$ represent?

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

How are they related?

ln 10

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

What is the reference state for each?

$E^o(H_3O^+(aq)/H_2) = 0$; $pK_a(H_3O^+(aq)) = 0$; 0

E. C. Meister, M. Willeke, W. Angst, A. Togni & P. Walde, *Helv. Chim. Acta*, **2014**, *97*, 1–31
T. P. Silverstein & S. T. Heller, *J. Chem. Educ.*, **2017**, *94*, 690–695

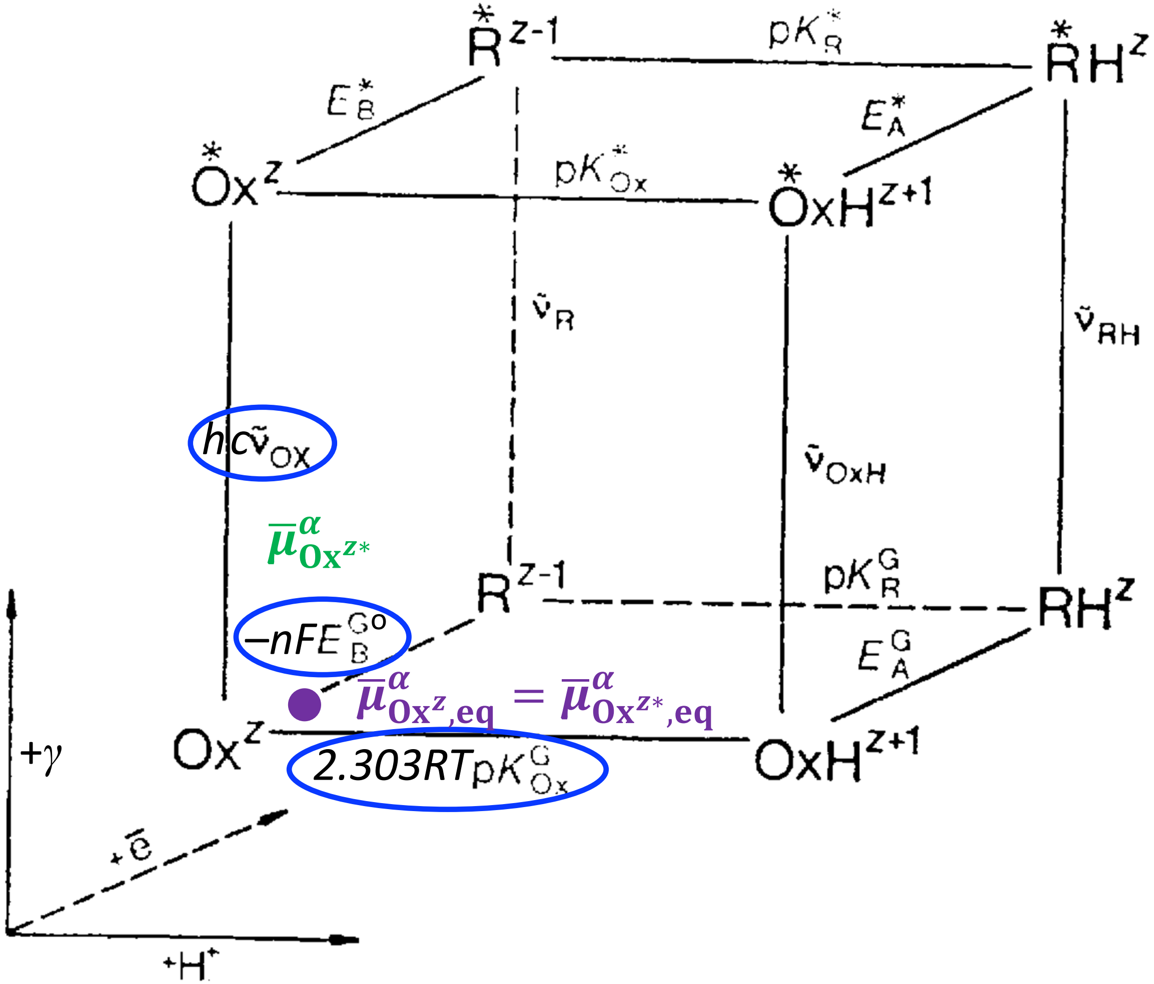
Today’s Critical Guiding Question

What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species?

Review of Physical Chemistry

- **Photochemical applications**
- **Förster cube, Square schemes**
- **Thermodynamics *versus* Kinetics**
- **Schrödinger equation, Internal energy**
- **Free energy, (Electro)Chemical potential, Equilibrium**
- Solid-state physics terminology
- Continuity of mass
- Mass action, Microscopic reversibility
- Activation energy, Rate-determining step
- Mass transfer, Transport, Steady state

Förster Cube and Square Schemes



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

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

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

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

... and if you don't recall all of these physical chemistry details, don't fret... we'll go over them now...

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

Thermodynamics *versus* Kinetics

… but a main benefit of **thermodynamics** ($\boldsymbol{\Delta G_j^o}$; $\boldsymbol{\bar{\mu}_i^o}$) is to predict **kinetics** ($\boldsymbol{k_{jf}}$, $\boldsymbol{k_{jb}}$; $\boldsymbol{D_i}$)…

… energetics from thermodynamics dictate **equilibrium concentrations**…

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

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

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. $R_\mathrm{A} = k_3 a_\mathrm{B} a_\mathrm{C}^2 \approx k_3[\mathrm{B}][\mathrm{C}]^2$
(to a first order, this is driven by differences in chemical potential, μ_i, of various species, ΔG_j)

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

… this master equation describes all kinetic and transport processes… more on this later though…

Schrödinger Equation

Elegant master equation that allows one to determine internal energies, E_n, of a system

$$\widehat{\boldsymbol{H}}\psi_n(x) = \mathbf{E}_{\boldsymbol{n}}\psi_n(x)$$

… but this is not good enough for photochemists where **time-varying** oscillating electromagnetic fields often interact with matter…

$\mathrm{E} = h\nu = \hbar\omega$ (Planck)

$\mathrm{E} = mc^2 = pc$ (Einstein)

$p = \frac{h\nu}{c} = \frac{h}{\lambda} = h\bar{\nu} = \hbar k$ (de Broglie)

$$\widehat{\boldsymbol{H}}\Psi_n(x,t) = \boldsymbol{i\hbar}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial t}}\Psi_n(x,t)$$

… so, how does one solve either of these Schrödinger equations?… We need to know $\widehat{H}$!

$$\widehat{H} = \widehat{T} + \widehat{V}$$

… um… well that didn't really help us at all… anyway, so instead, we need to know $\widehat{T}$ and $\widehat{V}$?

$\widehat{T}(x) = \mathrm{KE} = \frac{1}{2}m\hat{v}^2 = \frac{\hat{p}^2}{2m}$… with ($\widehat{\boldsymbol{p}}$)momentum = ($m$)ass x ($\hat{v}$)elocity = $-\boldsymbol{i\hbar}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}}$… Wow, right?

$\widehat{V}(x) = \mathrm{PE} = 0$… for particle-in-a-box…

$\widehat{V}(x) = \frac{1}{2}k_f x^2 = \frac{1}{2}m\omega^2 x^2$… for harmonic oscillator, with k_f (force const), ω (angular freq)…

$\widehat{V}(r) = -\frac{q^2}{4\pi\varepsilon_o r}$… for Hydrogen atom, with $F = qN_\mathrm{A}$ (Faraday const), ε_o (vacuum permittivity)

Schrödinger Equation

Poisson's Equation (from Gauss's law)

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -\frac{\rho}{\varepsilon} \qquad \mathbf{E} = -\frac{\partial \phi(x)}{\partial x}$$

for a point charge… look familiar?

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

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

$$\hat{H}\psi_n(x) = (\hat{T} + \hat{V})\psi_n(x) = \mathrm{E}_n \psi(x)$$

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

… 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…

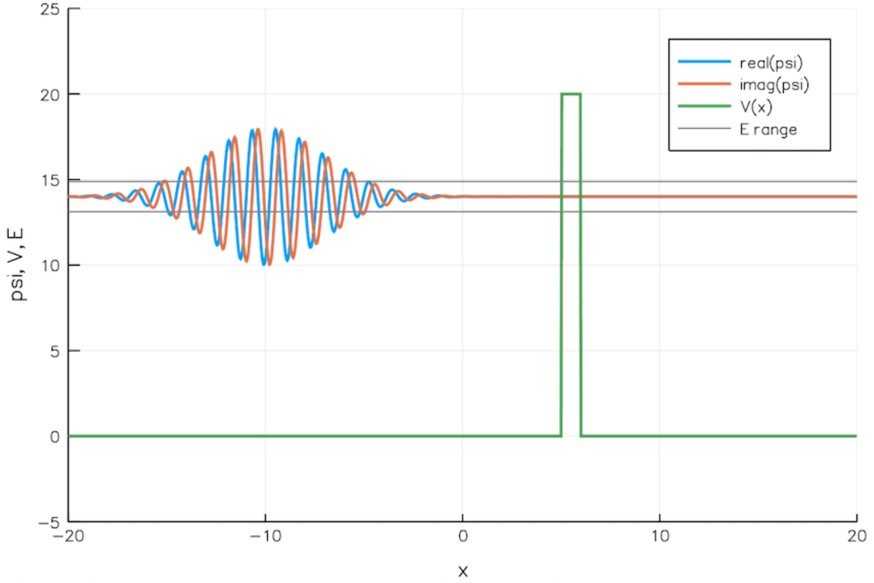
$$\text{Probability Density}(x) = |\psi_n(x)|^2 = \psi_n^*(x)\psi_n(x)$$

… with $\psi_n^*(x)$ (complex conjugate)

$$\text{Overlap integral, } S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x)\, dx = \langle \psi_n | \psi_m \rangle$$

… with $\langle \Psi_n |$ ("bra") and $| \Psi_m \rangle$ ("ket")

$$\text{Mean Energy, } \langle \mathrm{E}_n \rangle = \frac{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\hat{H}\Psi_n(x,t)dx}{\int_{-\infty}^{\infty} \Psi_n^*(x,t)\Psi_n(x,t)dx} = \langle \Psi_n | \hat{H} | \Psi_n \rangle = \langle \hat{H} \rangle$$



https://en.wikipedia.org/wiki/Quantum_tunnelling#/media/File:E14-V20-B1.gif

(UPDATED)

Free Energy

Now that we recall where **internal energy, E**, comes from… also recall **enthalpy, $H = E + pV$**, **Gibbs free energy, $G = H - TS$**, and **Entropy, S**… what in the world is **free energy**?

… total differentials are facile… for example, $dH = dE + pdV + Vdp$ and $dG = dH - TdS - SdT$

Well, it stems from the laws of thermodynamics:

Are these state functions?

(1) Conservation of Energy: $\Delta E_{universe} = 0$ J; $dE_{system} = dQ + dw$… where ***Q* is heat** and ***w* is work**

(2) Increase of Entropy: $\Delta S_{universe} \geq 0$ J K^{-1}, $\Delta G_{system} \leq 0$ J, and $dQ \leq TdS_{system}$

(3) Lower Limit to Entropy and Temperature: $S_{system} \geq 0$ J K^{-1}, $T \geq 0$ K

… where $dw = dw' + -pdV$

Photochemists are primarily interested in non-pdV work, dw', and so using total differentials…

By the 1st law, $dE_{system} = dQ + dw' + -pdV$… and thus $dH_{system} = dQ + dw' + Vdp$

And by the 2nd law, $dw' = dH_{sys} - TdS_{sys} - Vdp$… and thus $\mathbf{dw' = dG_{sys} + S_{sys}dT - Vdp}$

Q flow possible from internal energy

necessary *Q* flow

At constant *T* and *p*, **$(dG_{sys})_{T,p} = dw'$… in chemistry, *w'* is reversible (photo)(electro)chemical work!** … most chemists perform experiments at constant (ambient) pressure and (ambient) temperature

… but what are examples of reversible (photo)(electro)chemical work?… Chemical reactions!

(Electro)Chemical Potential

What if we could determine the contribution from each species, i, to the ability of the system to perform useful (photo)(electro)chemical work? That might be good to know, right?

Well, we're in luck… that is the definition of the **(electro)chemical potential:** $\boldsymbol{\bar{\mu}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}}$

… it's the <u>change in Gibbs free energy</u>, ∂G, for every infinitesimal change in the amount, ∂n_i

with $T, p, n_{j\neq i}$ held constant

So, let's expand the differential as $dG = \left(\sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \partial n_i\right)$ and integrate from 0 to some amount of each n_i to form (R)eactants, and separately to form (P)roducts, and one gets

$$G_{\mathrm{R}} = \sum_r \bar{\mu}_r n_r \qquad\qquad G_{\mathrm{P}} = \sum_p \bar{\mu}_p n_P$$

So, ΔG for converting reactants to products is then $\Delta G_{\mathrm{rxn}} = \sum_p \bar{\mu}_p n_p - \sum_r \bar{\mu}_r n_r$

… which seems to make sense… to me at least

… and there is nothing special about "electro" above… this could be "magneto", "gravito", "weak force-o", etc.

(Electro)Chemical Potential

So, let’s take a deeper look at this process for a simple reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$

Assume this reaction has a negative free energy difference… its infinitesimal change is…

$dG = \left(\frac{\partial G}{\partial n_{\mathrm{A}}}\right)\partial n_{\mathrm{A}} + \left(\frac{\partial G}{\partial n_{\mathrm{B}}}\right)\partial n_{\mathrm{B}} = \bar{\mu}_{\mathrm{A}}\partial n_{\mathrm{A}} + \bar{\mu}_{\mathrm{B}}\partial n_{\mathrm{B}}$… but since every loss of A has a gain of B

$dG = (\bar{\mu}_{\mathrm{B}} - \bar{\mu}_{\mathrm{A}})\partial n_{\mathrm{B}}$… and so this is a detailed thermodynamic version of an ICE table!

$\mathrm{A} \rightleftharpoons \mathrm{B}$	$\mathrm{A} - x;\ \mathrm{B} + x$	$\mathrm{A} \rightleftharpoons \mathrm{B}$
(I)nitial	(C)hange	(E)quilibrium

But hold on… at equilibrium, what is dG? **0** Yet based on the equation, won’t all A turn into B?

… the answer is that $\bar{\mu}_i$ are not constants with ∂n_i… and ultimately $\bar{\mu}_{\mathrm{B}}^{\alpha} = \bar{\mu}_{\mathrm{A}}^{\alpha}$, at equilibrium

… and seen *(next)* by its definition: $\boldsymbol{\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\mathrm{o},\alpha} + k_{\mathrm{B}}T \ln a_i^{\alpha} + z_i q \phi^{\alpha}}$ in phase α…

(Electro)Chemical Potential

So where does the fundamental equation, $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\mathrm{o},\alpha} + k_{\mathrm{B}}T\ln a_i^{\alpha} + z_i q\phi^{\alpha}(x)$, come from?

… recall that, by definition, $\mathbf{d}\boldsymbol{w}' = \mathbf{dG}_{\mathbf{sys}} + \mathbf{S}_{\mathbf{sys}}\mathbf{d}\boldsymbol{T}_{\mathbf{sys}} - \boldsymbol{V}_{\mathbf{sys}}\mathbf{d}\boldsymbol{p}_{\mathbf{sys}}$ and $\bar{\mu}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T_{\mathrm{sys}},p_{\mathrm{sys}},n_{j\neq i}}$

… and thus for species i, at constant T_{sys} and p_{sys}… one has $\mathbf{d}\boldsymbol{w}'/\mathbf{d}\boldsymbol{n}_i = \bar{\mu}_i - \boldsymbol{V}_i\,\mathbf{d}\boldsymbol{p}_i$

… where $\boldsymbol{V}_i$ is partial molar volume, $\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}}$, and $\boldsymbol{p}_i$ is partial pressure

… then assuming ideal gas law behavior, $\boldsymbol{V}_i = k_{\mathrm{B}}T/p_i$… and so one has $\bar{\mu}_i = \boldsymbol{k}_{\mathbf{B}}\boldsymbol{T}\,(\mathbf{1}/\boldsymbol{p}_i)\,\mathbf{d}\boldsymbol{p}_i + \mathbf{d}\boldsymbol{w}'_i$

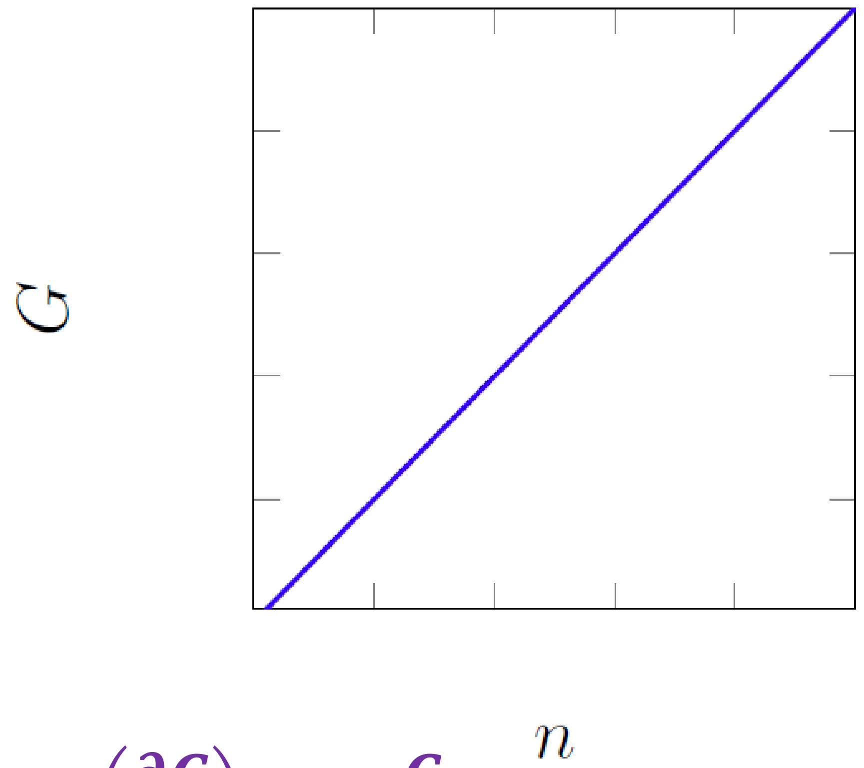
… integration from $\bar{\mu}_i^{\mathrm{o},\alpha}$ to $\bar{\mu}_i^{\alpha}$ results in $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\mathrm{o},\alpha} + k_{\mathrm{B}}T\ln\left(p_i^{\alpha}/p_i^{\mathrm{o},\alpha}\right) + \boldsymbol{w}'_i$

… and when species i is non-ideal, the natural log term is more accurate as $a_i^{\alpha} = \gamma_i^{\alpha}\left(p_i^{\alpha}/p_i^{\mathrm{o},\alpha}\right)$

… and/or when species i is charged, $z_i \neq 0$, then spatial effects due to $\phi^{\alpha}(x)$ (**E**-fields) matter

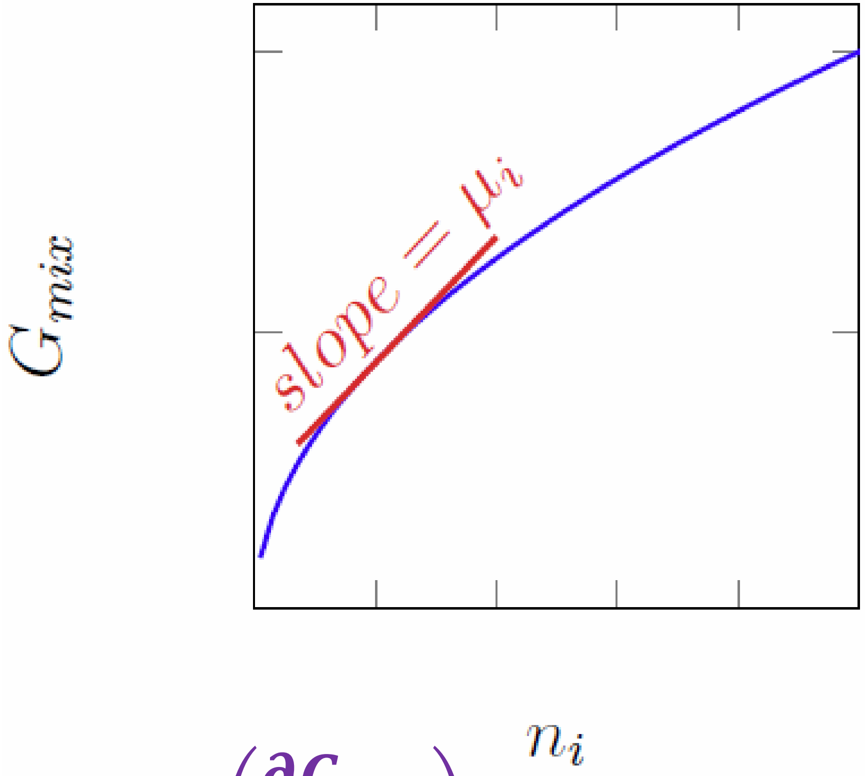
(Electro)Chemical Potential

Pure substance



$$\bar{\mu}^{\alpha} = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \frac{G}{n}$$

Mixture or Solution



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

Figures from Prof. Mark Lonergan (Univ. of Oregon)

Equilibrium

classical version of $\hat{V}$ for effects outside of the Hamiltonian "box"

So in summary, as it relates to the fundamental equation, $\boldsymbol{\bar{\mu}_i^\alpha = \bar{\mu}_i^{o,\alpha} + RT\ln a_i^\alpha + z_i q \phi_x^\alpha}$

... recall that for species in solution, $\boldsymbol{a_i^\alpha = \gamma_i^\alpha \frac{c_i^\alpha}{c_i^{o,\alpha}}}$

... where $\boldsymbol{\gamma_i^\alpha}$ are **activity coefficients**

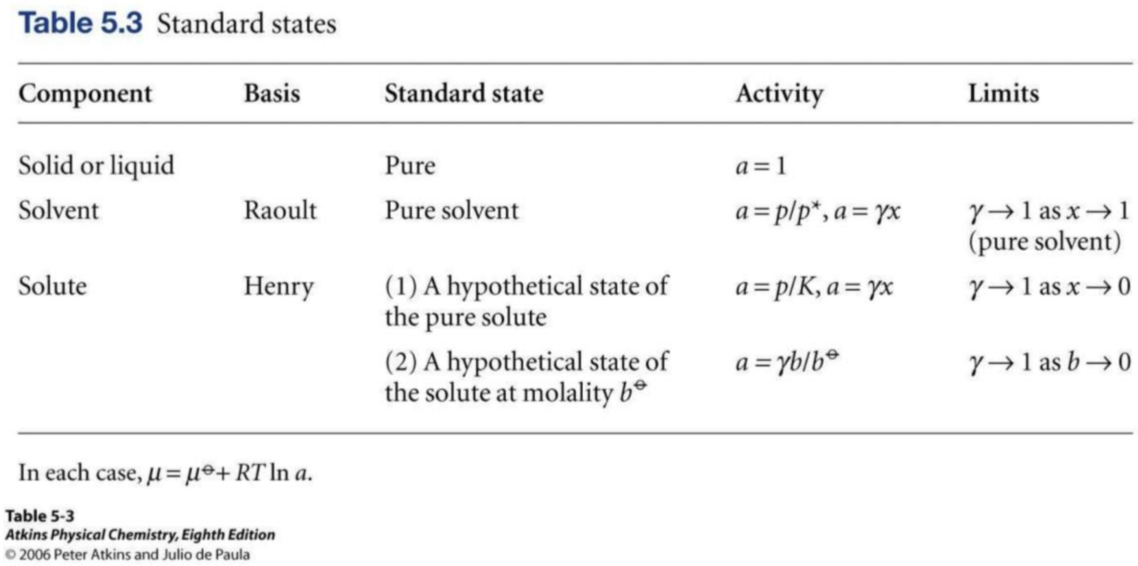


Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*, a = \gamma x$	$\gamma \to 1$ as $x \to 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K, a = \gamma x$	$\gamma \to 1$ as $x \to 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a = \gamma b/b^\ominus$	$\gamma \to 1$ as $b \to 0$

In each case, $\mu = \mu^\ominus + RT\ln a$.

Table 5-3
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$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

And back to $dG = (\bar{\mu}_\mathrm{B}^\alpha - \bar{\mu}_\mathrm{A}^\alpha)\partial n_\mathrm{B}$... the latter ∂n_B is like the **progress of the reaction**, and so...

$\Delta G = \left(\bar{\mu}_\mathrm{B}^\alpha - \frac{v_\mathrm{A}}{v_\mathrm{B}}\bar{\mu}_\mathrm{A}^\alpha\right)$... with v_A (stoichiometric number)

... when $\Delta G < 0$ the reaction is **exoergic/exergonic**, and net proceeds as written
... when $\Delta G > 0$ the reaction is **endoergic/endergonic**, and net proceeds opposite of as written
... when $\Delta G = 0$ the reaction is at **equilibrium** and proceeds equally in both directions (net is 0)

Entropic Mixing

Now in the previous example, imagine that A and B <u>are ideal gases</u>…

… they cannot react… n_A and n_B (mol) are independent and constant

Then, using $\boldsymbol{\bar{\mu}_i^\alpha = \bar{\mu}_i^{\mathrm{o},\alpha} + RT \ln a_i^\alpha + z_i F \phi_x^\alpha}$

$$\bar{\mu}_\mathrm{A}^\alpha = \bar{\mu}_\mathrm{A}^{\mathrm{o},\alpha} + RT \ln a_\mathrm{A}^\alpha + (0) F \phi_x^\alpha$$

$$\bar{\mu}_\mathrm{B}^\alpha = \bar{\mu}_\mathrm{B}^{\mathrm{o},\alpha} + RT \ln a_\mathrm{B}^\alpha + (0) F \phi_x^\alpha$$

classical version of $\hat{V}$ for effects outside of the Hamiltonian "box"

Defining the free energy change upon mixing is facile as

$$G_\mathrm{initial} = \bar{\mu}_\mathrm{A}^\alpha n_\mathrm{A} + \bar{\mu}_\mathrm{B}^\alpha n_\mathrm{B} \qquad G_\mathrm{final} = \bar{\mu}_\mathrm{A,eq}^\alpha n_\mathrm{A} + \bar{\mu}_\mathrm{B,eq}^\alpha n_\mathrm{B}$$

$$\Delta G_\mathrm{mix} = n_\mathrm{A}\left(RT \ln \frac{a_\mathrm{A,eq}^\alpha}{a_\mathrm{A}^\alpha}\right) + n_\mathrm{B}\left(RT \ln \frac{a_\mathrm{B,eq}^\alpha}{a_\mathrm{B}^\alpha}\right)$$

… with total number, $n = n_\mathrm{A} + n_\mathrm{B}$, and mole fraction, $x_i = \frac{n_i}{n}$…

$$\Delta G_\mathrm{mix} = nRT\left(x_\mathrm{A,eq}^\alpha \ln x_\mathrm{A,eq}^\alpha + x_\mathrm{B,eq}^\alpha \ln x_\mathrm{B,eq}^\alpha\right) = nRT(\ln 0.5) = -0.69nRT$$

… since this assumed ideal gases, $\Delta H_\mathrm{mix} = 0$ and the driving force is purely entropic ($\Delta S_\mathrm{mix} \geq 0$)…

… this is the driving force for **diffusion**!

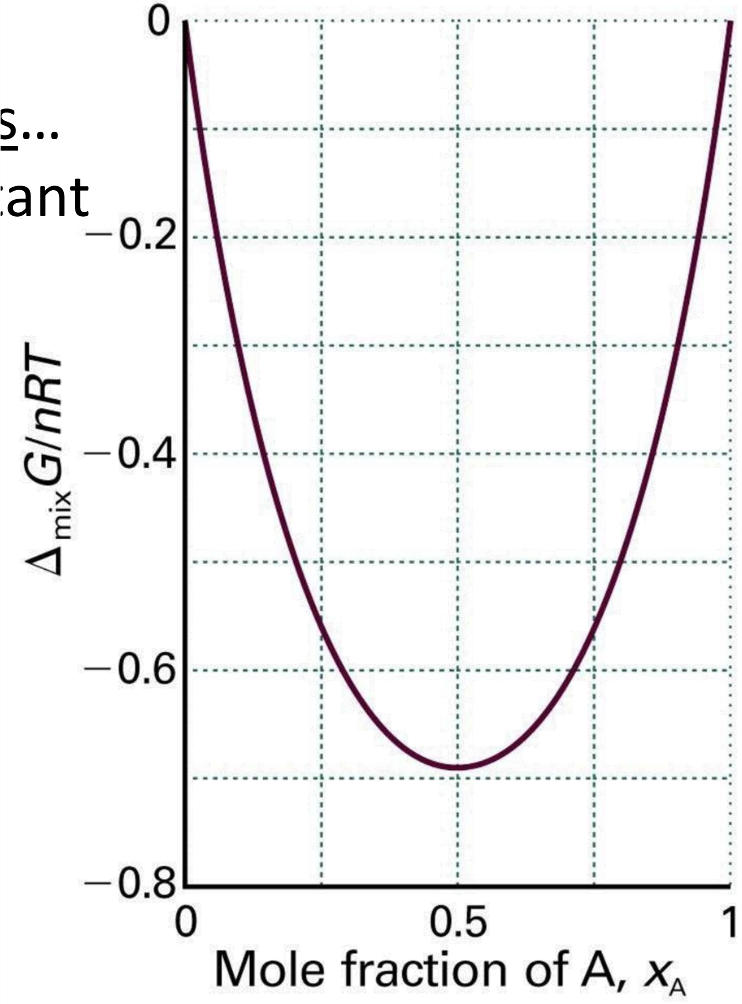

Figure 5-7
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(Electro)Chemical (and Thermal) Equilibrium

Given $\Delta G = (\bar{\mu}_{\mathrm{B}}^{\alpha} - \bar{\mu}_{\mathrm{A}}^{\alpha})$… which could have ν_i too…

and using $\boldsymbol{\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{o,\alpha} + RT\ln a_i^{\alpha} + z_i F\phi_x^{\alpha}}$

$$\Delta G = \bar{\mu}_{\mathrm{B}}^{o,\alpha} + RT\ln a_{\mathrm{B}}^{\alpha} + z_{\mathrm{B}}F\phi_x^{\alpha} - \left(\bar{\mu}_{\mathrm{A}}^{o,\alpha} + RT\ln a_{\mathrm{A}}^{\alpha} + z_{\mathrm{A}}F\phi_x^{\alpha}\right)$$

Which means that, at a single position, x_o,

$$\Delta G = (\bar{\mu}_{\mathrm{B}}^{o,\alpha} - \bar{\mu}_{\mathrm{A}}^{o,\alpha}) + RT\ln\frac{a_{\mathrm{B}}^{\alpha}}{a_{\mathrm{A}}^{\alpha}} + \Delta zF(0)$$

$\Delta G = \Delta G^{o,\alpha} + RT\ln Q$… where $Q = \frac{a_{\mathrm{B}}^{\alpha}}{a_{\mathrm{A}}^{\alpha}}$, and…

$\Delta G = \Delta G^{o',\alpha} + RT\ln Q'$… where $Q' = \frac{c_{\mathrm{B}}^{\alpha}/c_{\mathrm{B}}^{o,\alpha}}{c_{\mathrm{A}}^{\alpha}/c_{\mathrm{A}}^{o,\alpha}}$

… where $\Delta G^{o',\alpha}$ contains the activity coefficients, γ_i^{α}

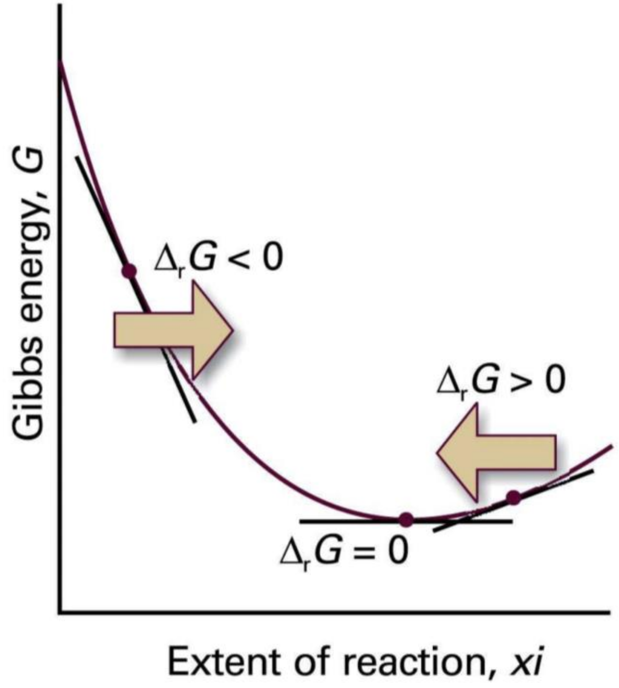
For an uncharged species: $\bar{\mu}_i^{\alpha} = \mu_i^{\alpha}$

For any substance: $\mu_i^{\alpha} = \mu_i^{0\alpha} + RT\ln a_i^{\alpha}$

For any pure phase at unit activity $\mu_i^{\alpha} = \mu_i^{0\alpha}$

For electrons in a metal $(z = -1)$: $\bar{\mu}_e^{\alpha} = \mu_e^{0\alpha} - F\phi^{\alpha}$

For equilibrium of species i between phases α and β: $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\beta}$



As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

Figure 7-1
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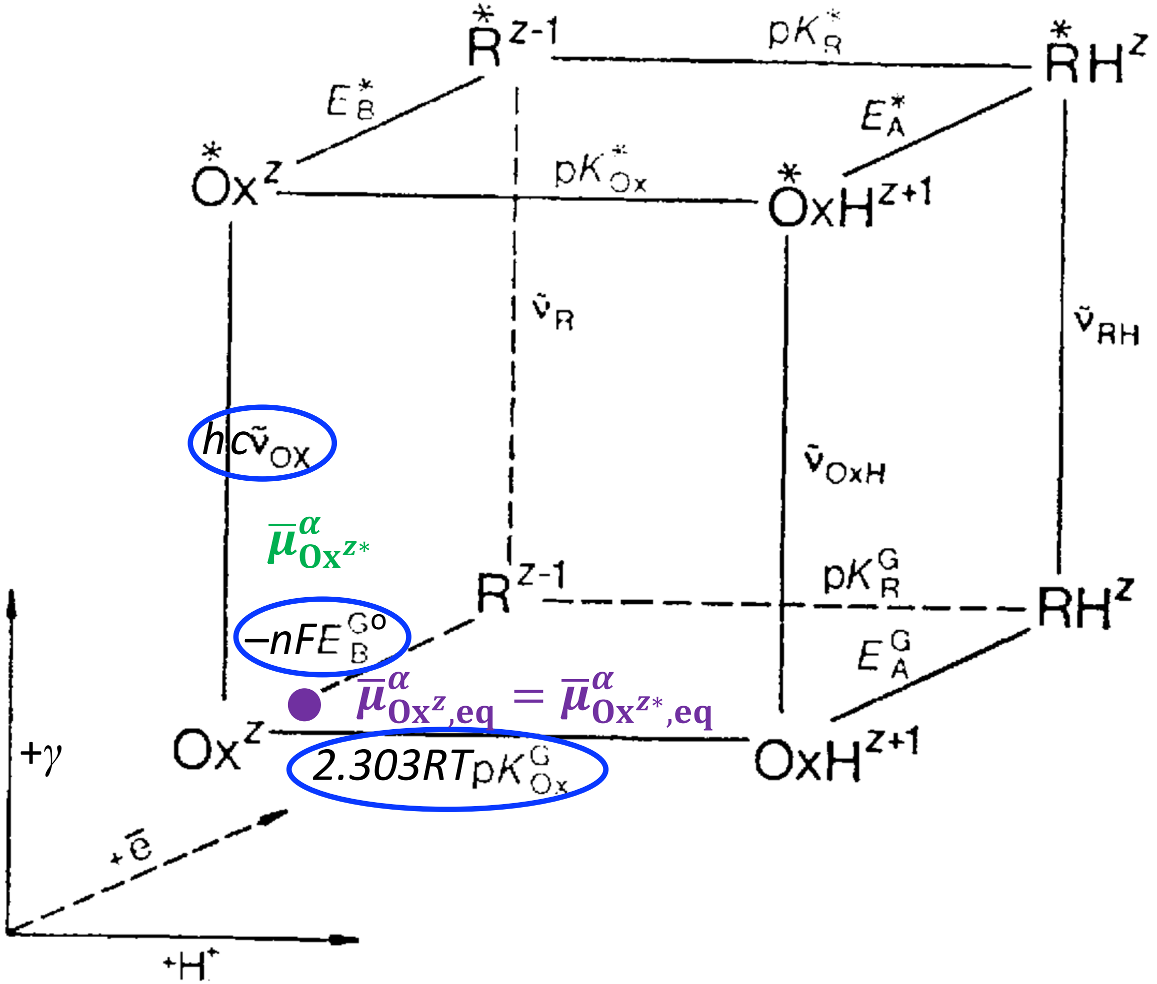
At equilibrium, $\bar{\mu}_{\mathrm{B}} - \bar{\mu}_{\mathrm{A}} = 0 = \Delta G^{o',\alpha} + RT\ln Q'_{\mathrm{eq}}$, so $\Delta G^{o',\alpha} = -RT\ln K'$ with $K' = \frac{c_{\mathrm{B,eq}}^{\alpha}/c_{\mathrm{B}}^{o,\alpha}}{c_{\mathrm{A,eq}}^{\alpha}/c_{\mathrm{A}}^{o,\alpha}}$

... okay... now let's try this again...

(UPDATED)

Förster Cube and Square Schemes



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

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

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

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

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Today’s Critical Guiding Question

What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species?