# Lecture #3 of 12

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# Review of Physical Chemistry

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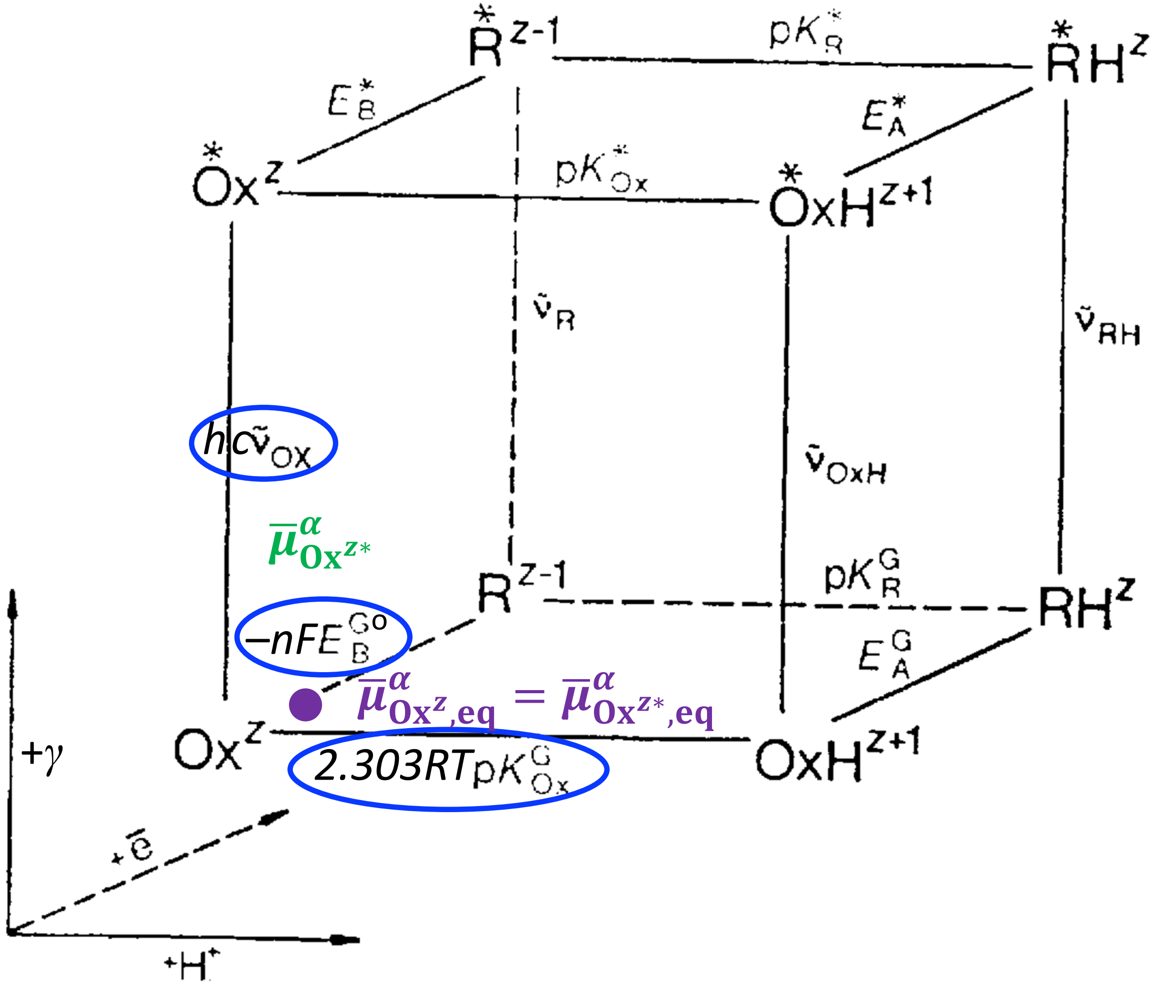
... okay... now let's try this again...



# Förster Cube and Square Schemes




... all of these free energy terms are **standard-state** free energies ($\Delta G^{\mathrm{o}}$)... but what is the actual free energy of the system ($\Delta G$)?

**... 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!

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

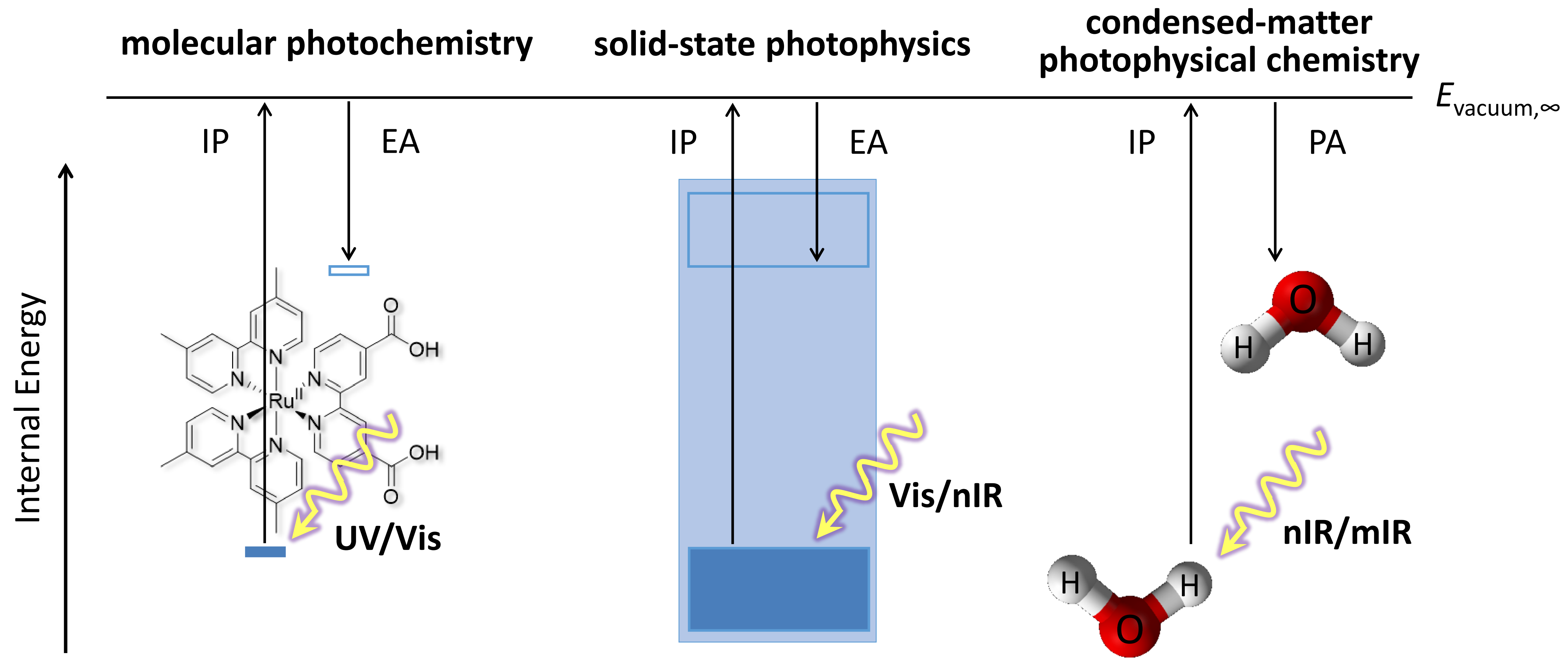
# Today's Critical Guiding Question

*What thermodynamic term indicates whether a processes will net occur, or not, for a chemical reaction, and a single species… and uniquely for today, how does it allow us to quantitatively predict kinetic information?*

# 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**
- **Mass transfer, Transport, Steady state**

# Solid-State Physics Terminology




... is this most relevant to **internal energy (Schrödinger equation)** or **free energy (reactivity)**?

# Solid-State Physics Terminology

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

$$\mathrm{Si_{CB}(h^+) + Si_{VB}(e^-) \rightleftarrows Si_{CB}(e^-) + Si_{VB}(h^+)}$$

At equilibrium,

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(h^+)}} + \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(e^-)}} = \bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(e^-)}} + \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(h^+)}}$$

As reference states, it is useful to define

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(h^+)}} = \bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(e^-)}} = 0$$

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

Anyway… therefore,

$$\bar{\mu}^{\mathrm{Si}}_{\mathrm{CB(e^-)}} = -\bar{\mu}^{\mathrm{Si}}_{\mathrm{VB(h^+)}}$$

$$\mathbf{E}_{\mathrm{F,e^-}} = \mathbf{E}_{\mathrm{F,h^+}}$$

$$\mathbf{E}_{\mathrm{F,e^-}} = \bar{\mu}_{\mathrm{e^-}}$$

$$\mathbf{E}_{\mathrm{F,h^+}} = -\bar{\mu}_{\mathrm{h^+}}$$

*p-n* JUNCTIONS IN SEMICONDUCTORS 439

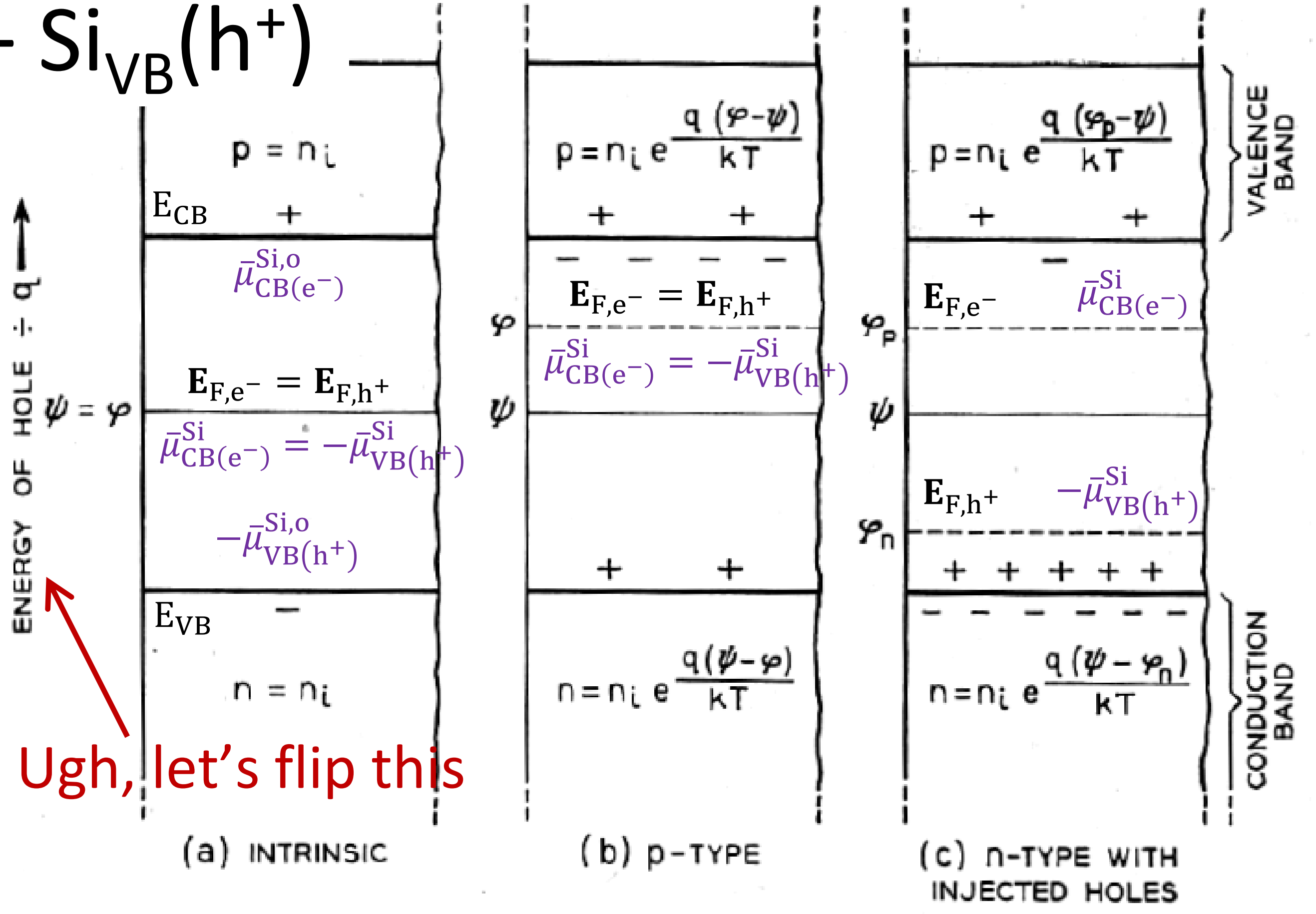


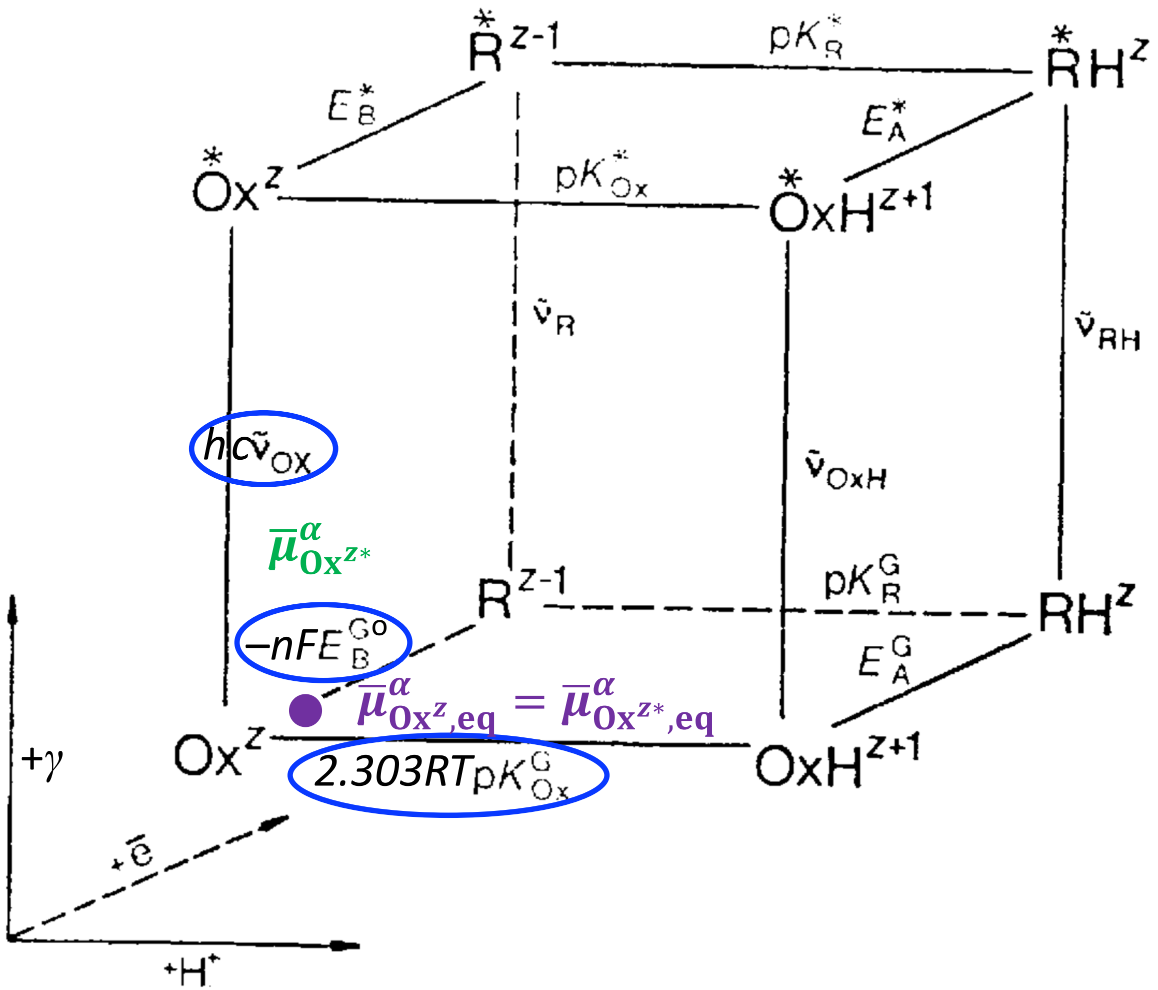

Fig. 2—Electrostatic potential $\psi$, Fermi level $\varphi$ and quasi Fermi levels $\varphi_p$ and $\varphi_n$.
(In order to show electrostatic potential and energies on the same ordinates, the energies of holes, which are minus the energies of electrons, are plotted upwards in the figures in this paper.)

W. Shockley, *The Bell System Technical Journal*, **1949**, *28*, 435–489

... okay... now let's try this again²...



# Förster Cube and Square Schemes

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# Thermodynamics *versus* Kinetics

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

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

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

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

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)*

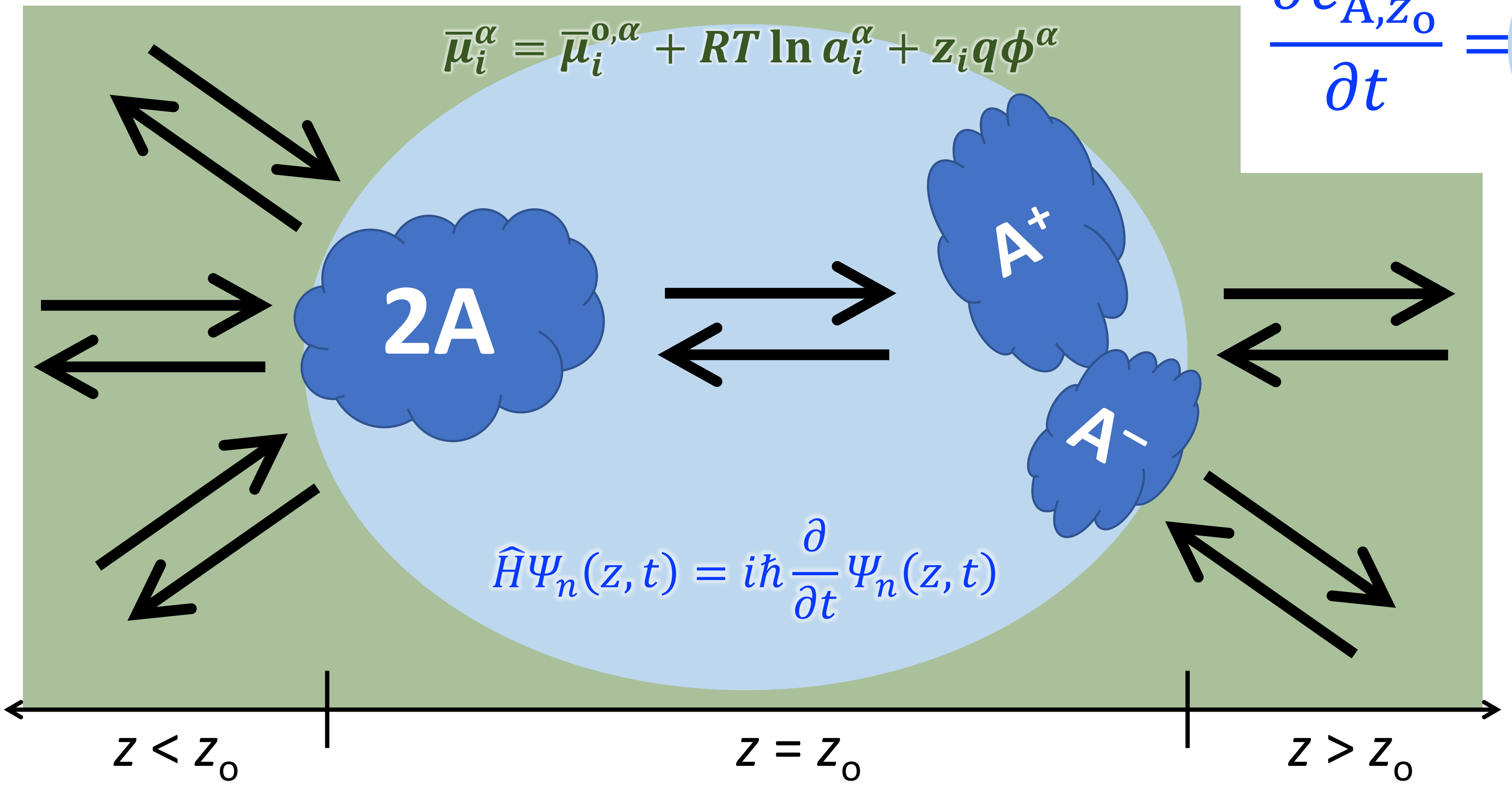
mass action ($R$)ate laws that effect species A,
**e.g. $R_A = k_3 a_B a_C^2 \approx k_3[B][C]^2$**
*(to a first order, this is driven by differences in chemical potential, $\mu_i$, of various species, $\Delta G_j$)*

rate of change of the molar flux (**N**) of species A with respect to position ($z$),
**e.g. $\mathbf{N}_A = -D_A \frac{\partial a_A}{\partial z}$**
*(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... let's go over it in more detail...**

# Continuity of Mass

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




*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

# Mass Action / Microscopic Reversibility

$$\mathrm{A} \rightleftarrows \mathrm{B}$$

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

*(Chemists should be yawning)*

$$\Delta G^{\alpha} = \Delta G^{\mathrm{o},\alpha} + RT\ln Q \text{… where } Q = \frac{a_{\mathrm{B}}^{\alpha}}{a_{\mathrm{A}}^{\alpha}} = \frac{\gamma_{\mathrm{B}}^{\alpha}\left(c_{\mathrm{B}}^{\alpha}/c_{\mathrm{B}}^{\mathrm{o},\alpha}\right)}{\gamma_{\mathrm{A}}^{\alpha}\left(c_{\mathrm{A}}^{\alpha}/c_{\mathrm{A}}^{\mathrm{o},\alpha}\right)}$$

$$R_{\mathrm{A},f} = -\boldsymbol{k_f} a_{\mathrm{A}} \qquad R_{\mathrm{B},f} = +\boldsymbol{k_f} a_{\mathrm{A}}$$

$$R_{\mathrm{A},b} = +\boldsymbol{k_b} a_{\mathrm{B}} \qquad R_{\mathrm{B},b} = -\boldsymbol{k_b} a_{\mathrm{B}}$$

- Law of mass action
- Principle of microscopic reversibility

… and in solid-state physics… $R_{\mathrm{e}^-,\mathrm{total}} = \sum_j \mathrm{Gen}_{\mathrm{e}^-,j} - \sum_j \mathrm{Rec}_{\mathrm{e}^-,j}$

$\boldsymbol{k_j}$ (M/s)… a rate!

$\boldsymbol{k_j'}$ ($\mathrm{s}^{-1}$)… an inverse time constant!

Now, consider the reaction to be at equilibrium… $\Delta G^{\alpha} = 0 = \Delta G^{\mathrm{o}',\alpha} + RT\ln Q' = \bar{\mu}_{\mathrm{B}}^{\alpha} - \bar{\mu}_{\mathrm{A}}^{\alpha}$

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

But also, $\dfrac{\partial c_{\mathrm{A}}}{\partial t} = 0 = -\boldsymbol{k_f} a_{\mathrm{A,eq}}^{\alpha} + \boldsymbol{k_b} a_{\mathrm{B,eq}}^{\alpha}$… $\dfrac{\boldsymbol{k_f}}{\boldsymbol{k_b}} = \dfrac{a_{\mathrm{B,eq}}^{\alpha}}{a_{\mathrm{A,eq}}^{\alpha}} = K = K'\dfrac{\gamma_{\mathrm{B}}^{\alpha}}{\gamma_{\mathrm{A}}^{\alpha}}$ … it can get messy

Or equivalently, $\dfrac{\partial c_{\mathrm{A}}}{\partial t} = 0 = -\boldsymbol{k_f'} c_{\mathrm{A,eq}}^{\alpha} + \boldsymbol{k_b'} c_{\mathrm{B,eq}}^{\alpha}$… $\dfrac{\boldsymbol{k_f'}}{\boldsymbol{k_b'}} = \dfrac{c_{\mathrm{B,eq}}^{\alpha}}{c_{\mathrm{A,eq}}^{\alpha}} = K'\dfrac{c_{\mathrm{B}}^{\mathrm{o},\alpha}}{c_{\mathrm{A}}^{\mathrm{o},\alpha}} = K\dfrac{\gamma_{\mathrm{A}}^{\alpha}}{\gamma_{\mathrm{B}}^{\alpha}}\dfrac{c_{\mathrm{B}}^{\mathrm{o},\alpha}}{c_{\mathrm{A}}^{\mathrm{o},\alpha}}$

# 1D Transport in Liquids (solids are simpler)

$$\mathrm{A}_{z_1} \rightleftarrows \mathrm{A}_{z_2}$$

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

*(MechEs should be yawning)*

$$\mathbf{N}_\mathrm{A} = -\left(\frac{D_\mathrm{A} c_\mathrm{A}}{RT}\right)\frac{\partial \bar{\mu}_\mathrm{A}}{\partial z} + v c_\mathrm{A}$$

… 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)…

$$\mathbf{N}_\mathrm{A} = -\boldsymbol{D}_\mathbf{A}\frac{\boldsymbol{\partial}\left(\bar{\boldsymbol{\mu}}_\mathbf{A}/\boldsymbol{RT}\right)}{\boldsymbol{\partial z}} c_\mathrm{A}$$

**What are the directions for the dimensions of $\boldsymbol{D}_\mathbf{A}$?**

**BOLD** ((cm$^2$/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**

(Recall that… $R_{\mathrm{A,total}} = -\boldsymbol{k}_{\boldsymbol{f}}' c_\mathrm{A} + \boldsymbol{k}_{\boldsymbol{b}}' c_\mathrm{B}$… with $\boldsymbol{k}_{\boldsymbol{j}}'$ (s$^{-1}$), an inverse time constant!)

# 1D Transport in Solids

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

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

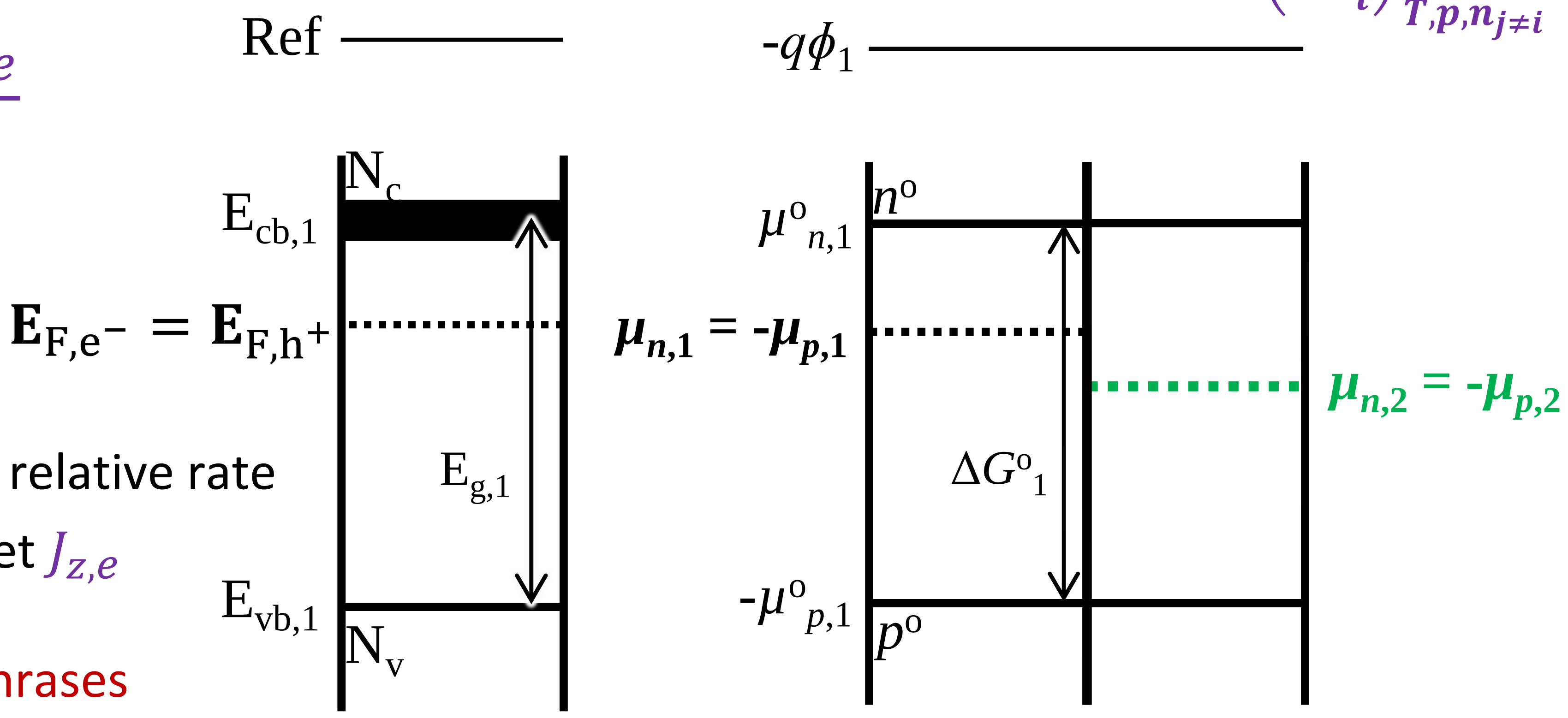
($z$ is a direction; $e$ means $z_e = -1$)

$\frac{d\bar{\mu}_e}{dz}$ dictates directionality

… multiply by $\sigma_e = \frac{F^2 D_e c_e}{RT}$ to get relative rate

… multiply $\text{Flux}_{z,e}$ by "$z_e F$" to get $J_{z,e}$

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




Band diagram

"Ardo" diagram

A hybrid internal energy / free energy diagram shows several useful things at once, but (possibly usefully) glosses over details of other transport processes… let's see which ones…

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

Let's expand the total differential…

… assuming a species, $e$, with valency, $z_e$, equal to −1

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

$$\text{Flux}_{z,e} = -\frac{\sigma_e}{F^2}\frac{d\bar{\boldsymbol{\mu}}_e}{dz} - S_{e,\boldsymbol{T}_e}\frac{d\boldsymbol{T}_e}{dz}$$

$$\left(\frac{\partial \boldsymbol{G}}{\partial \boldsymbol{n}_i}\right)_{\boldsymbol{T},\boldsymbol{p},\boldsymbol{n}_{j\neq i}} = \bar{\boldsymbol{\mu}}_i = \boldsymbol{\mu}_i + z_i q\phi$$

$$\text{Flux}_{z,e} = -\frac{D_e\boldsymbol{n}_e}{k\boldsymbol{T}_e}\left(\frac{d\boldsymbol{\mu}_e}{dz} - q\frac{d\phi}{dz}\right) - S_{e,\boldsymbol{T}_e}\frac{d\boldsymbol{T}_e}{dz}$$

$$\boldsymbol{\mu}_i = \boldsymbol{\mu}_i^{\mathbf{o}} + k\boldsymbol{T}_i \ln \boldsymbol{a}_i = \boldsymbol{\mu}_i^{\mathbf{o}} + k\boldsymbol{T}_i \ln\left(\frac{\boldsymbol{\gamma}_i\boldsymbol{n}_i}{\boldsymbol{n}_i^{\mathbf{o}}}\right)$$

… $\boldsymbol{n}_i$ is proportional to $\boldsymbol{c}_i$ in a single phase… divide by $\boldsymbol{V}_{\text{phase}}$

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

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

Drift–Diffusion equation

$$\text{Flux}_{z,e} = -D_e\frac{d\boldsymbol{n}_e}{dz} + \frac{qD_e\boldsymbol{n}_e}{k\boldsymbol{T}_e}\frac{d\phi}{dz}$$

… assuming spatially invariant $\boldsymbol{\mu}_e^{\mathbf{o}}$, $\boldsymbol{\gamma}_e$, $\boldsymbol{n}_e^{\mathbf{o}}$, $\boldsymbol{T}_e$

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

# 1D Transport in Solids

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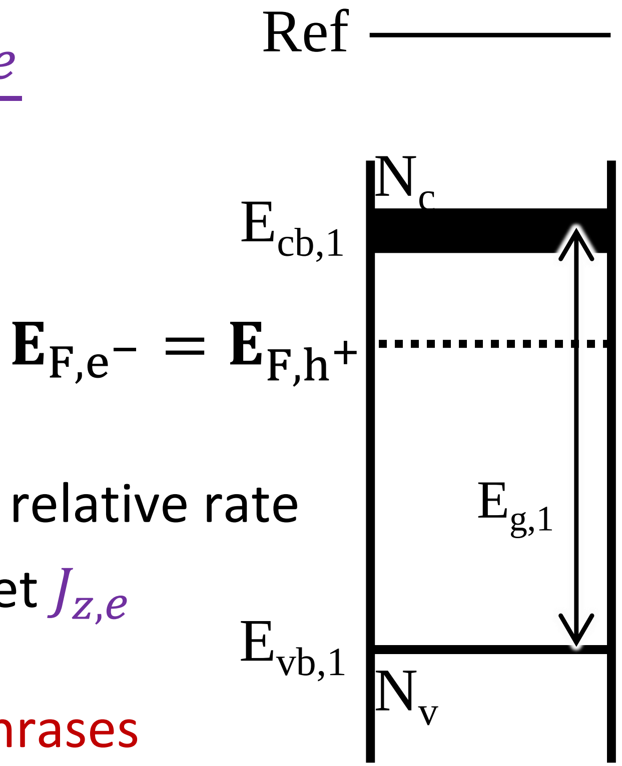


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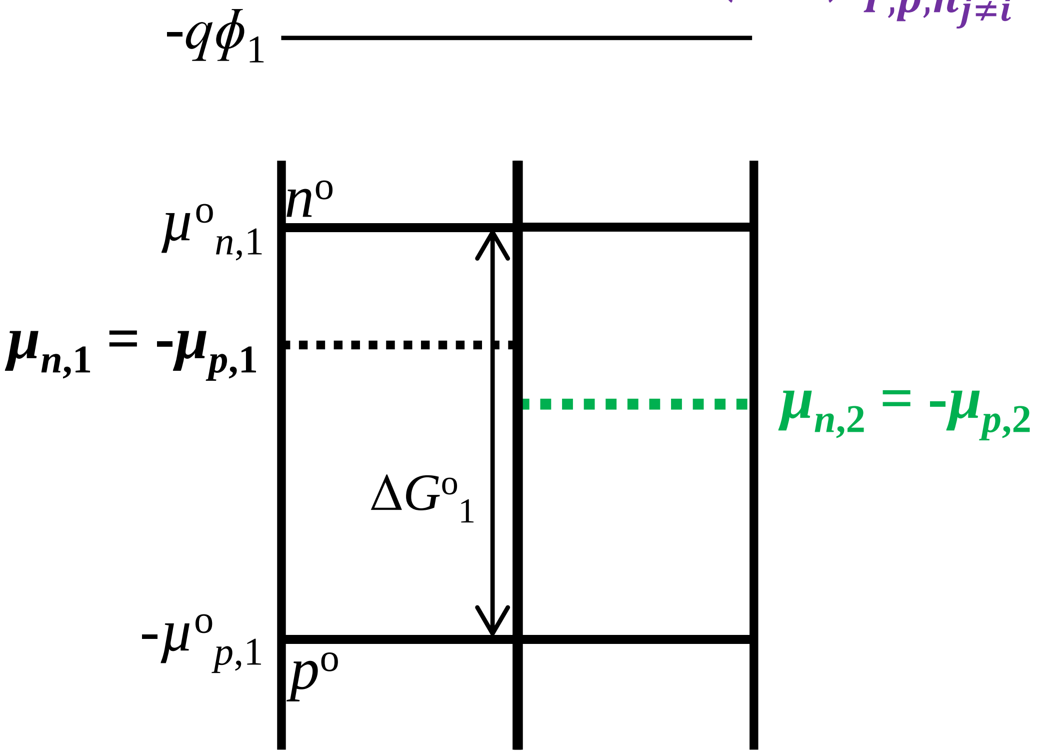


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