Lecture #3 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: TW)

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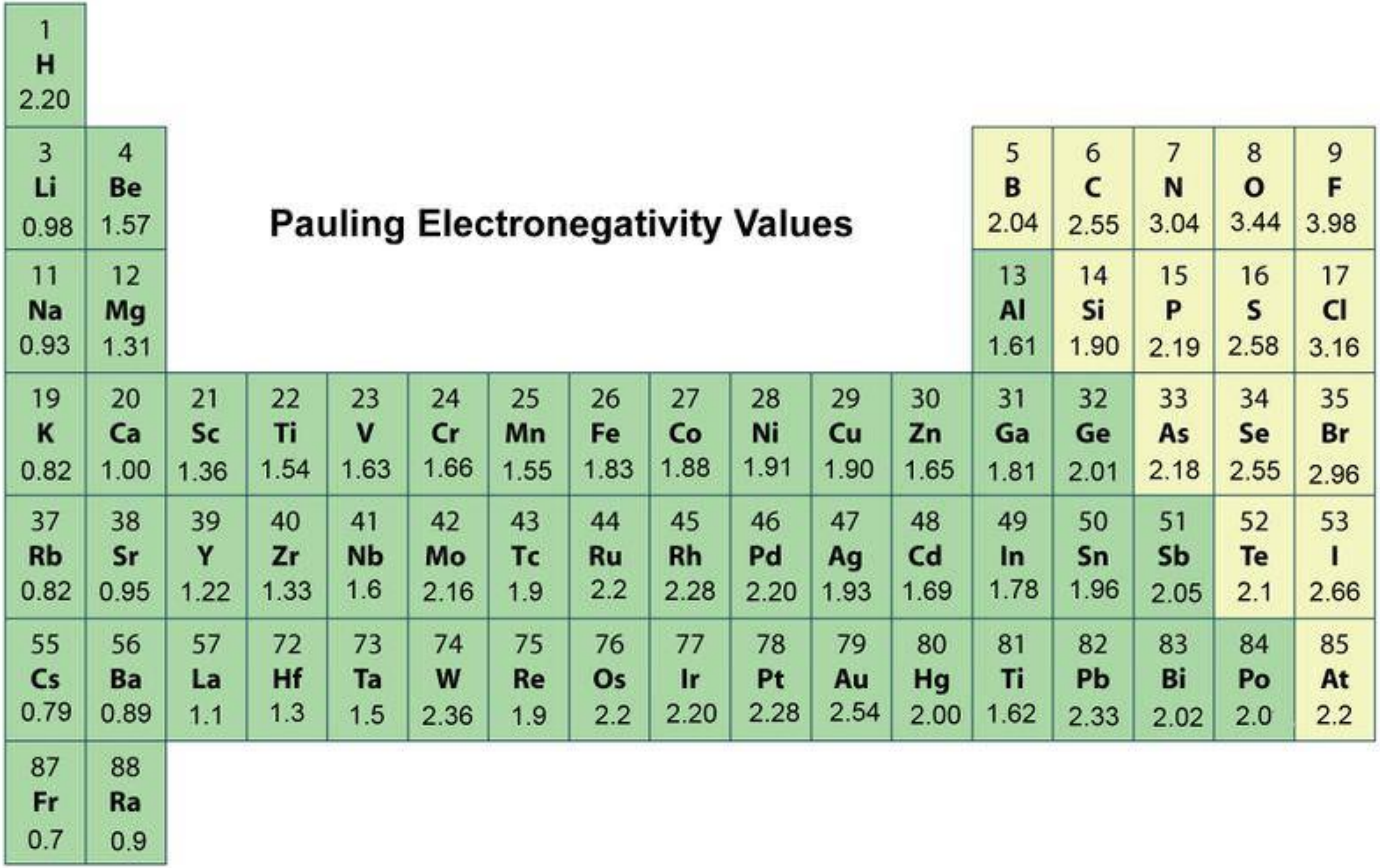

Pauling Electronegativity Values

1 **H** 2.20																
3 **Li** 0.98	4 **Be** 1.57											5 **B** 2.04	6 **C** 2.55	7 **N** 3.04	8 **O** 3.44	9 **F** 3.98
11 **Na** 0.93	12 **Mg** 1.31											13 **Al** 1.61	14 **Si** 1.90	15 **P** 2.19	16 **S** 2.58	17 **Cl** 3.16
19 **K** 0.82	20 **Ca** 1.00	21 **Sc** 1.36	22 **Ti** 1.54	23 **V** 1.63	24 **Cr** 1.66	25 **Mn** 1.55	26 **Fe** 1.83	27 **Co** 1.88	28 **Ni** 1.91	29 **Cu** 1.90	30 **Zn** 1.65	31 **Ga** 1.81	32 **Ge** 2.01	33 **As** 2.18	34 **Se** 2.55	35 **Br** 2.96
37 **Rb** 0.82	38 **Sr** 0.95	39 **Y** 1.22	40 **Zr** 1.33	41 **Nb** 1.6	42 **Mo** 2.16	43 **Tc** 1.9	44 **Ru** 2.2	45 **Rh** 2.28	46 **Pd** 2.20	47 **Ag** 1.93	48 **Cd** 1.69	49 **In** 1.78	50 **Sn** 1.96	51 **Sb** 2.05	52 **Te** 2.1	53 **I** 2.66
55 **Cs** 0.79	56 **Ba** 0.89	57 **La** 1.1	72 **Hf** 1.3	73 **Ta** 1.5	74 **W** 2.36	75 **Re** 1.9	76 **Os** 2.2	77 **Ir** 2.20	78 **Pt** 2.28	79 **Au** 2.54	80 **Hg** 2.00	81 **Ti** 1.62	82 **Pb** 2.33	83 **Bi** 2.02	84 **Po** 2.0	85 **At** 2.2
87 **Fr** 0.7	88 **Ra** 0.9															

https://www.ck12.org/book/ck-12-chemistry-second-edition/r15/section/9.5/

… this illustrates the tendency for an atom to attract electron density when forming a chemical bond… it is strongly correlated with the first ionization energy… and negatively correlated with the electron affinity

Chemical Properties

Quiz Time!

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Chemical Properties

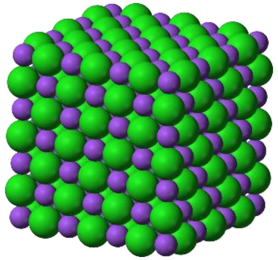
- Molecular nomenclature, Solutions, Balanced chemical reactions
- State functions, Standard states, Thermochemistry
- Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, **Colligative properties, Water activity**
- **Free energy, (X)Chemical potential, Chemical equilibrium, van’t Hoff equation, Activity coefficients, Le Chatelier’s principle**
- Schrödinger equation, Internal energy, Atomic orbitals, Hybridization
- Valence bond theory, Molecular orbital theory, Band diagrams
- Crystal field theory, Ligand field theory

Great online resource: http://www.rnlkwc.ac.in/pdf/study-material/chemistry/Peter_Atkins__Julio_de_Paula__Physical_Chemistry__1_.pdf

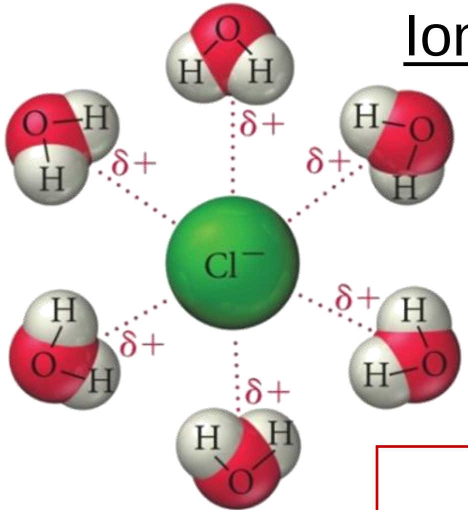
Intermolecular Forces

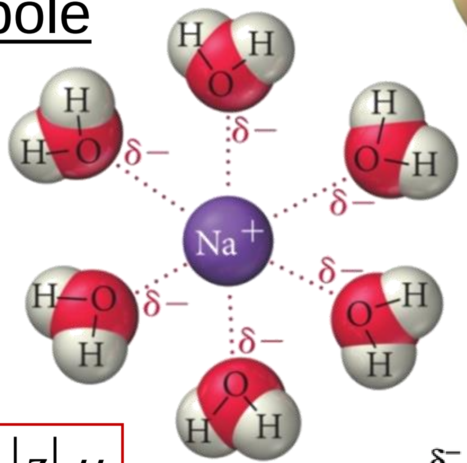
(REVIEW)

What does salt (NaCl) look like in the Newport Beach ocean?



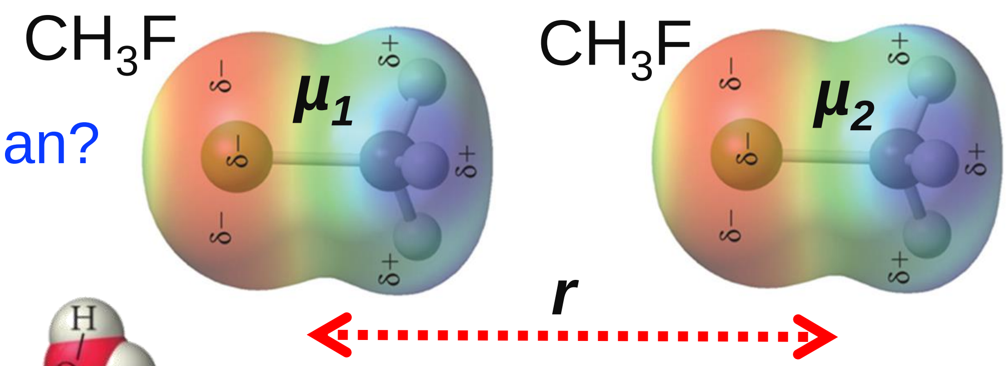
Ion–Dipole





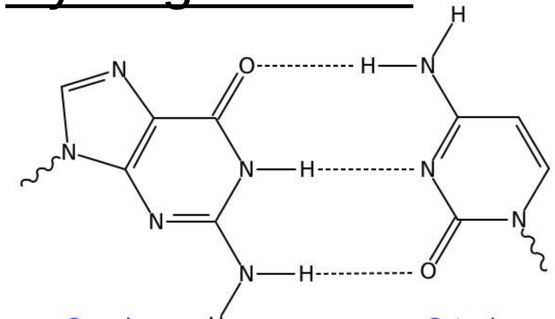
$$E_{binding} \propto \frac{|z|\mu}{r^2}$$

Dipole–Dipole

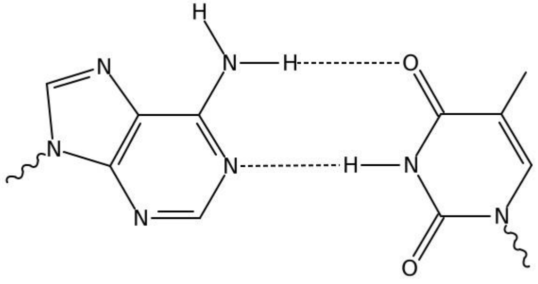


$$E_{binding} \propto \frac{\mu_1 \mu_2}{r^3}$$

Hydrogen Bond



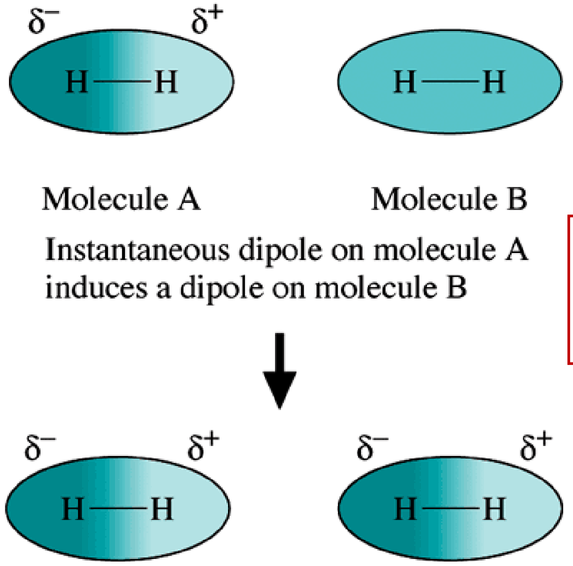
Guanine Cytosine



Adenine Thymine

… like in DNA, proteins, water, ice, etc.

Induced Dipole–Induced Dipole



Instantaneous dipole on molecule A induces a dipole on molecule B

$$E_{binding} \propto \frac{\alpha_1 \alpha_2}{r^6}$$

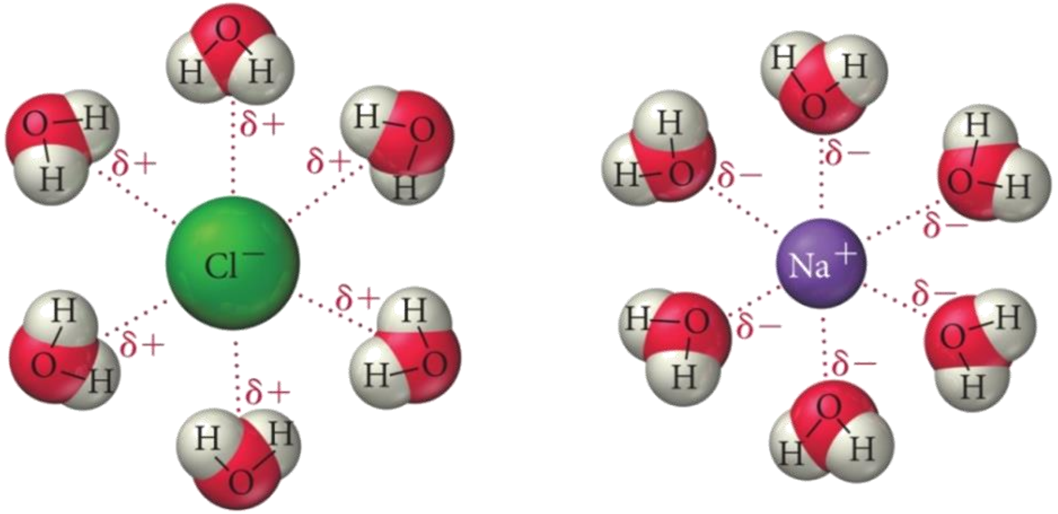
Explains viscosity, vapor pressure, capillary action, surface tension, osmotic pressure, boiling/freezing point

Colligative Properties

Colligative properties depend on the number of particles present, **not** on the charge or chemical nature of the particle… so how is this chemistry?

This implies that substances that produce a pair of ions upon solvation (e.g., NaCl) contribute more than 1 particle: $NaCl \rightarrow Na^+(aq) + Cl^-(aq)$

The van’t Hoff factor indicates the actual number of particles that contribute to the colligative properties.



Does this cartoon possibly indicate why this is chemical?

$$i = \frac{\text{actual number of particles upon solvation}}{\text{number of units dissolved in solution}}$$

Boiling-point elevation: $\Delta T_b = i\, K_b\, m$

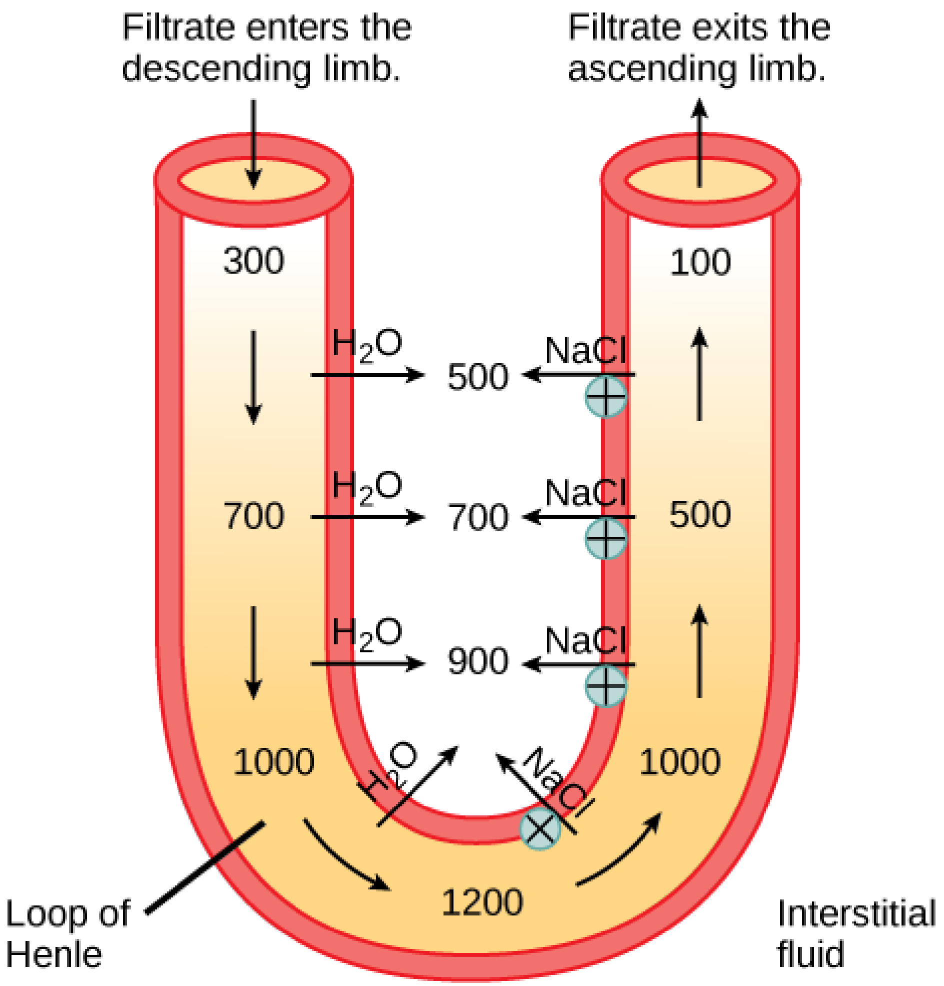
Freezing-point depression: $\Delta T_f = i\, K_f\, m$

Osmotic pressure: $\pi = i\, RT\, M$

Vapor-Pressure lowering: $P_1 \neq i\, P_1^o\, X_1$

Water Activity

My kidneys thank you, osmolyte, for influencing water activity and thus osmotic pressure…



The loop of Henle acts as a countercurrent multiplier that uses energy to create concentration gradients. The descending limb is water permeable. Water flows from the filtrate to the interstitial fluid, so osmolality inside the limb increases as it descends into the renal medulla. At the bottom, the osmolality is higher inside the loop than in the interstitial fluid. Thus, as filtrate enters the ascending limb, Na^+ and Cl^- ions exit through ion channels present in the cell membrane. Further up, Na^+ is actively transported out of the filtrate and Cl^- follows. Osmolarity is given in units of milliosmoles per liter (mOsm/L).

https://opentextbc.ca/biology/chapter/22-2-the-kidneys-and-osmoregulatory-organs/

Free Energy

1^{st} Law of Thermodynamics

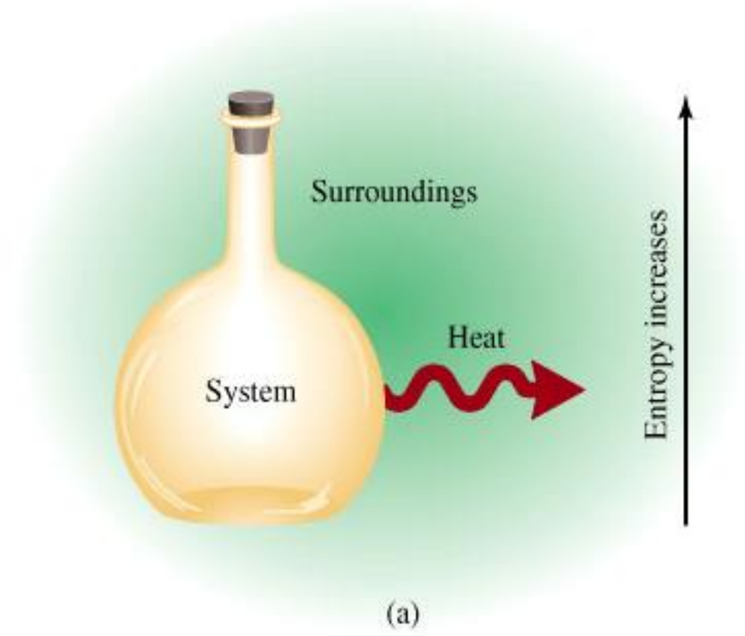
Energy can be converted from one form to another, but it cannot be created or destroyed.

$$\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$$

2^{nd} Law of Thermodynamics

The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$



In this example, is $\Delta H_{system} > 0$ or < 0?

What is relation between heat flow (dQ) and change in entropy ΔS?

So, is $\Delta S_{surroundings} > 0$ or < 0?

So, how can one recast the 2nd law of thermodynamics…
… to indicate the amount of "energy" (although not an energy)…
… that is "free" to do work?

$$\Delta S_{universe} = \Delta S_{system} - (\Delta H_{system}/T) \geq 0$$

Free Energy, a bit more rigorous approach

Internal energy, E, is the energy of the system… and related terms are defined as **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 $dG = dH - TdS - SdT$

Are these state functions?

Well, it stems from the laws of thermodynamics:

(1) Conservation of Energy: $\Delta E_{universe} = 0$; $dE_{system} = dQ + dw$… where ***Q* is heat** and ***w* is work**
(2) Increase of Entropy: $\Delta S_{universe} \geq 0$, $\Delta G_{system} \leq 0$, and $dQ \leq TdS_{system}$
(3) Lower Limit to Entropy and Temperature: $S_{system} \geq 0$, $T \geq 0$

… where $dw = dw' + -pdV$

Many chemists are 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 work with systems at constant pressure (ambient) and temperature (also ambient)

… 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:** $\boldsymbol{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}}$

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

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

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

$$G_\mathrm{R} = \sum_r \mu_r n_r \qquad\qquad G_\mathrm{P} = \sum_p \mu_p n_P$$

So, ΔG for converting reactants to products is then $\Delta G = \sum_p \mu_p n_p - \sum_r \mu_r n_r$

… 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.

Chemical Potential

So, let’s take a deeper look at this for $\mathrm{A} \rightleftarrows \mathrm{B}$

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

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

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

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

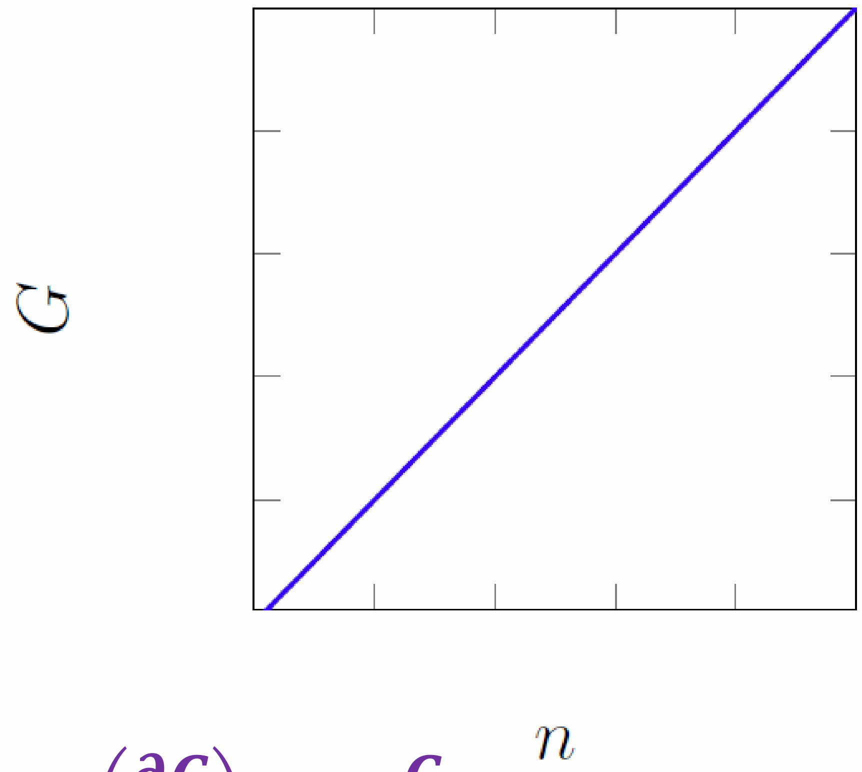
But hold on... at equilibrium, what is dG? **0** Yet based on the equation, won’t all A turn into B?

... the answer is that μ_i are not constants with ∂n_i... and ultimately $\mu_{\mathrm{B}}^{\alpha} = \mu_{\mathrm{A}}^{\alpha}$, at equilibrium

... as seen from the definition of $\boldsymbol{\bar{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i q \phi^{\alpha} = \mu_i^{\mathrm{o},\alpha} + RT \ln a_i^{\alpha} + z_i q \phi^{\alpha}}$ in phase α

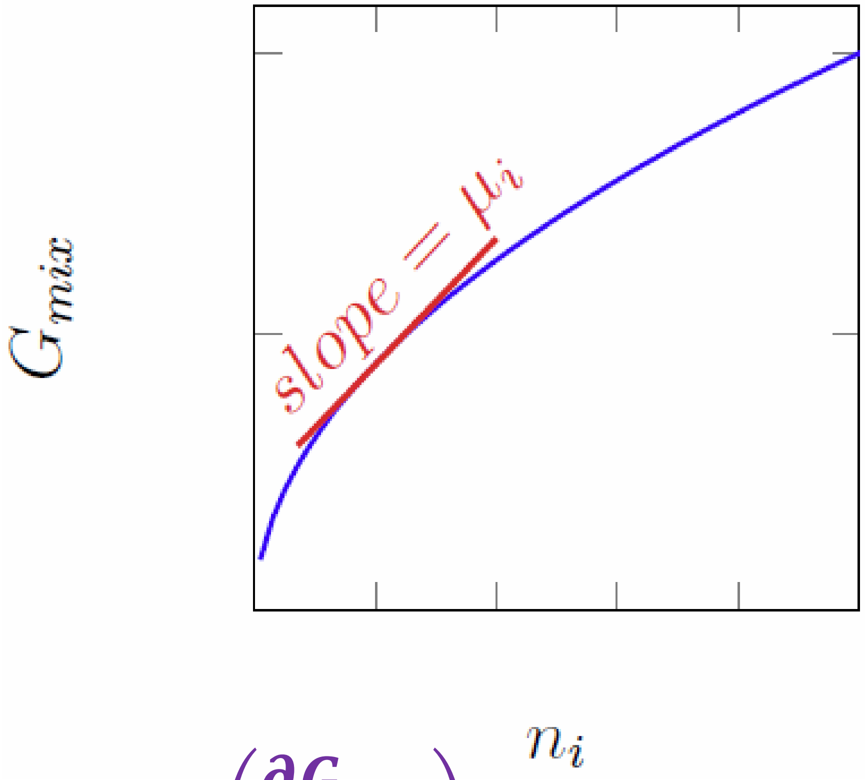
Chemical Potential

Pure substance



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

Mixture or Solution



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

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

Electro-Chemical Potential

So in the previous example, imagine that A and B are ideal gases…
… so they cannot react… n_A and n_B are independent and constant

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

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

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

Defining the free energy change upon mixing is facile as

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

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

… and with mole fraction, x_i…

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

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

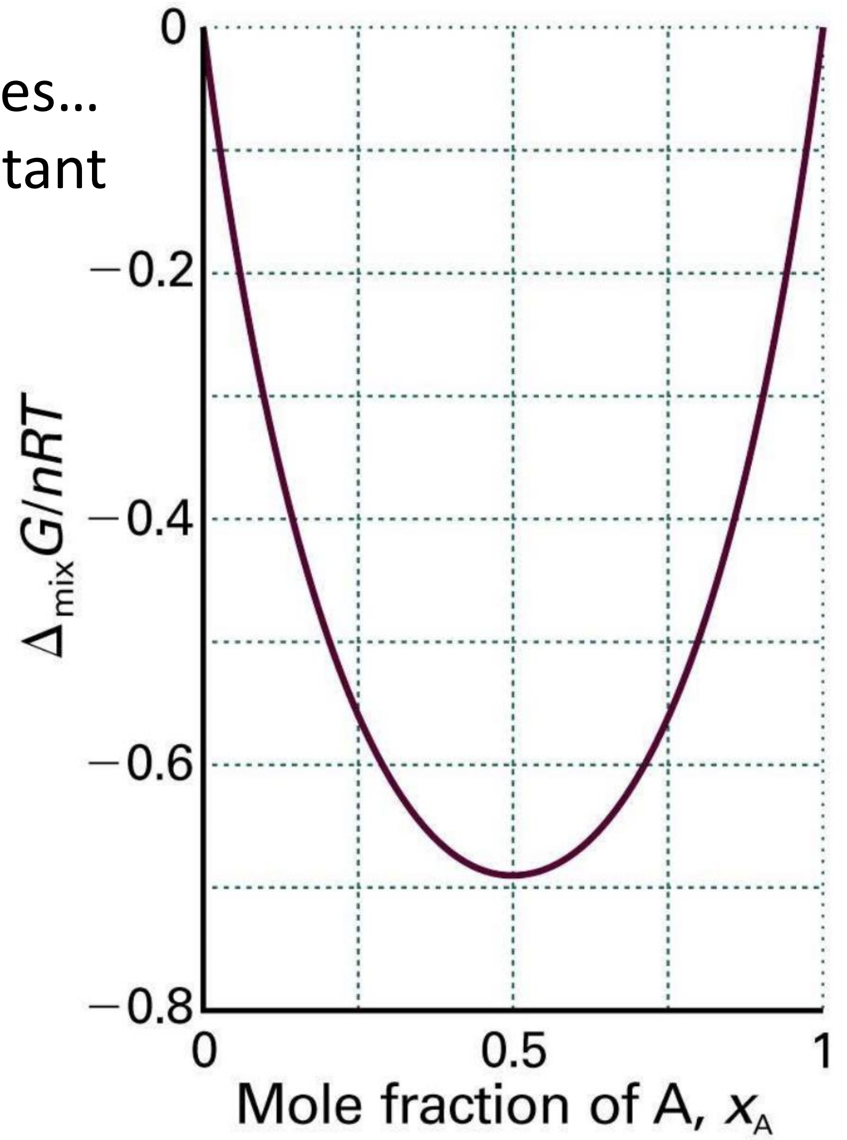


Figure 5-7
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Electrochemical Potential

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

... recall that, by definition, $\mathrm{d}w' = \mathrm{d}G_{\mathrm{sys}} + S_{\mathrm{sys}}\mathrm{d}T - V\mathrm{d}p$ and $\bar{\mu}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$

... and thus for species i, at constant T... one has $\mathrm{d}w'/\mathrm{d}n_i = \mathrm{d}\bar{\mu}_i - V_i\,\mathrm{d}p_i$

... where V_i is partial molar volume, $\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}}$

... then assuming ideal gas law behavior, $V_i = RT/p_i$... and so one has $\mathrm{d}\bar{\mu}_i = RT\,(1/p_i)\,\mathrm{d}p_i + \mathrm{d}w''$

... integration from $\bar{\mu}_i^{\mathrm{o},\alpha}$ to $\bar{\mu}_i^{\alpha}$ results in $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\mathrm{o},\alpha} + RT \ln\left(p_i^{\alpha}/p_i^{\mathrm{o},\alpha}\right) + w''$

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

... and/or when species i is charged, $z_i \neq 0$, then spatial effects due to ϕ^{α} are important

Equilibrium

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

And, in summary, as it relates to the fundamental equation, $\bar{\boldsymbol{\mu}}_{i}^{\alpha} = \bar{\boldsymbol{\mu}}_{i}^{\mathbf{o},\alpha} + \boldsymbol{RT}\ \mathbf{ln}\ \boldsymbol{a}_{i}^{\alpha} + \boldsymbol{z}_{i}\boldsymbol{q}\boldsymbol{\phi}^{\alpha}$

Recall that for species in solution, $\boldsymbol{a}_{i}^{\alpha} = \boldsymbol{\gamma}_{i}^{\alpha}\frac{\boldsymbol{c}_{i}^{\alpha}}{\boldsymbol{c}_{i}^{\mathbf{o},\alpha}}$,

where $\boldsymbol{\gamma}_{i}^{\alpha}$ are activity coefficients

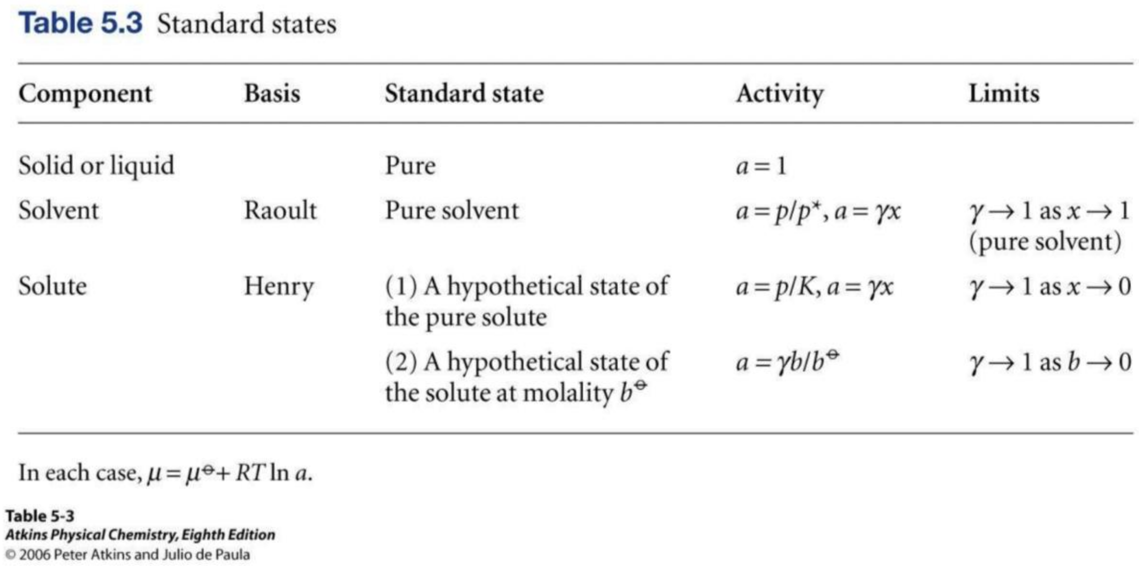

Table 5.3 Standard states

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

And back to $dG = (\bar{\mu}_{\mathrm{B}}^{\alpha} - \bar{\mu}_{\mathrm{A}}^{\alpha})\partial n_{\mathrm{B}}$… where ∂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 <u>exoergic/exergonic</u>, and net proceeds as written
… when $\Delta G > 0$ the reaction is <u>endoergic/endergonic</u>, and net proceeds opposite of as written
… when $\Delta G = 0$ the reaction is at <u>equilibrium</u> and proceeds equally in both directions (net is 0)

Chemical and Thermal Equilibrium

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

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

$$\Delta G = \bar{\mu}_{\mathrm{B}}^{\mathrm{o},\alpha} + RT\ln a_{\mathrm{B}}^{\alpha} + z_{\mathrm{B}} q\phi^{\alpha} - \bar{\mu}_{\mathrm{A}}^{\mathrm{o},\alpha} + RT\ln a_{\mathrm{A}}^{\alpha} + z_{\mathrm{A}} q\phi^{\alpha}$$

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: $\bar{\mu}_i^{\alpha} = \bar{\mu}_i^{\beta}$

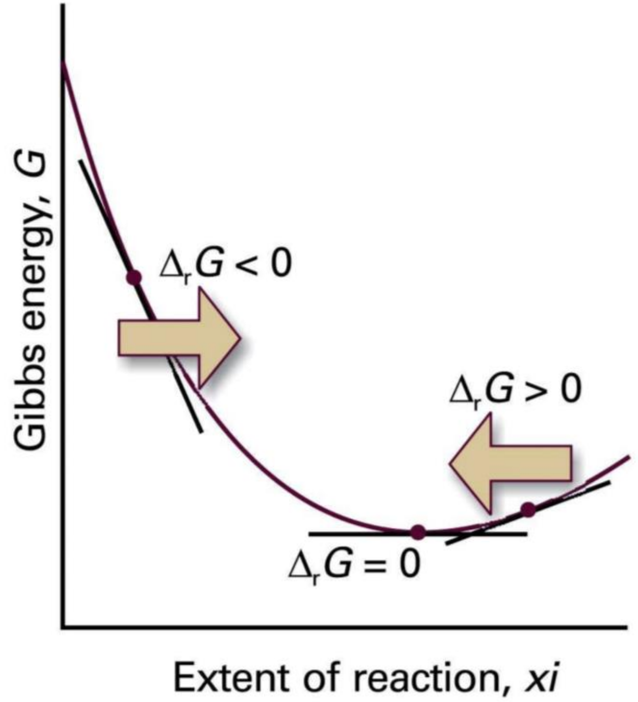
Which means that

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

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

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

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



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

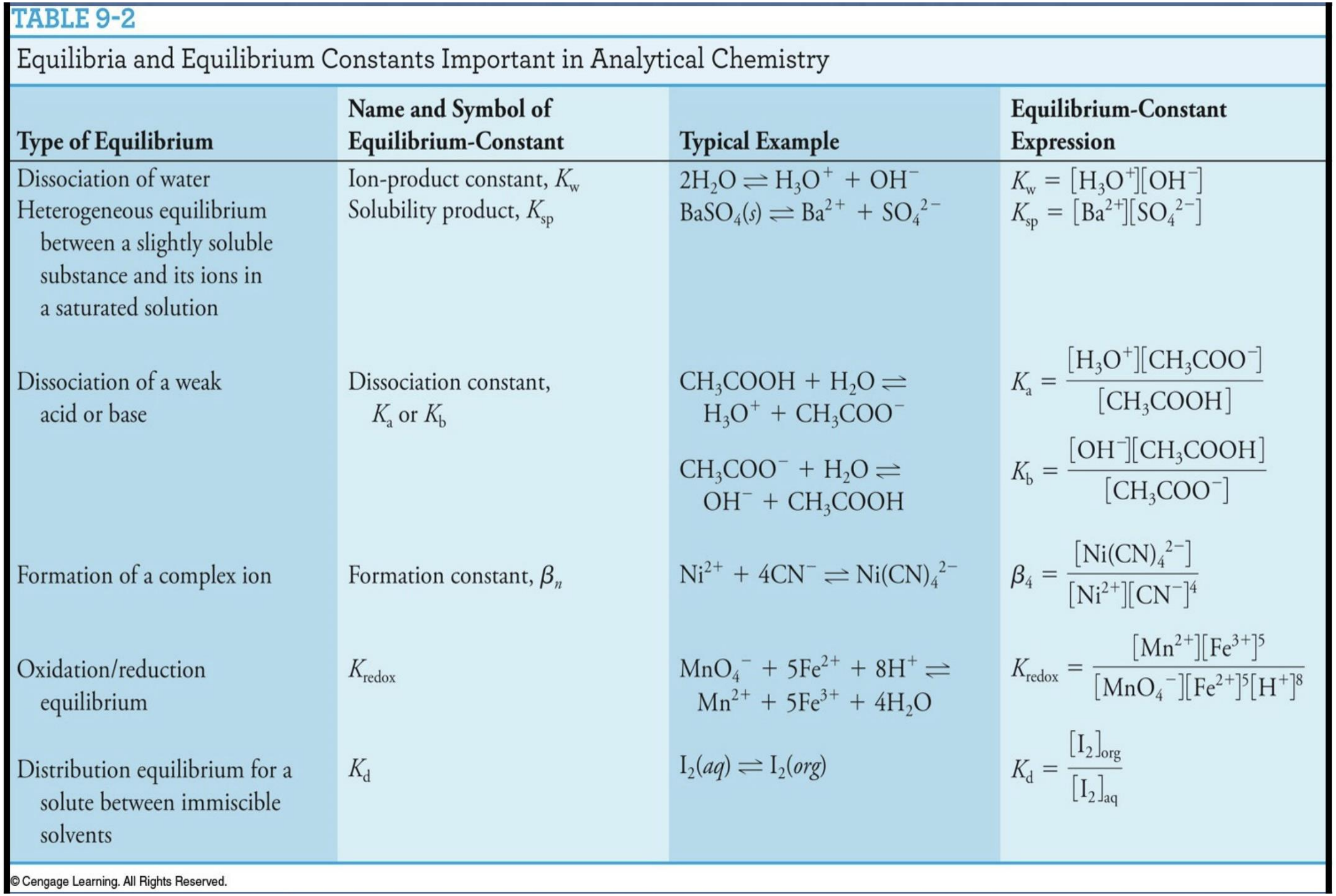


TABLE 9-2

Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ $K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

… so if you see a capital *K*… the letter after J in the alphabet… you should know what it means and what chemists are thinking about…

… but shouldn't these be *K′* values, and where are the standard states?… Um, yup!… Oh nomenclature; speaking of which… https://goldbook.iupac.org/

http://sites.usm.edu/electrochem/Analytical%20Chemistry/Lecture%20Notes/Chapter%209%20Chem%20Equilibria.pdf

Scientists & Engineers love to vary Temperature

$\Delta G^{\mathrm{o}\prime,\alpha} = -RT\ln K'$ indicates that *T* relates a measurable quantity, K', to $\Delta G^{\mathrm{o}\prime,\alpha}$…

… but an even more accurate analysis relies on $\Delta G^{\mathrm{o}\prime,\alpha} = \Delta H^{\mathrm{o}\prime,\alpha} - T\Delta S^{\mathrm{o}\prime,\alpha}$ for a given *T* and *p*,

… leading to the linearized **van't Hoff equation**: $\ln K' = -\frac{\Delta H^{\mathrm{o}\prime,\alpha}}{R}\frac{1}{T} + \frac{\Delta S^{\mathrm{o}\prime,\alpha}}{R}$

… but this is also an approximation that only holds over a rather small ranges of *T* due to the temperature dependence of $\Delta H^{o\prime,\alpha} = C_p\Delta T$, and C_p, and $\Delta S^{o\prime,\alpha}$

… nevertheless, many thermochemical properties that can be determined by varying *T*…

… and chemical kinetic properties too (stay tuned)…

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

Activity Coefficients

Debye–Hückel equation *(in water at 25 °C)*

$$-\log \gamma_x = \frac{0.51 z_x^2 \sqrt{I}}{1 + 3.3\alpha_x \sqrt{I}}$$

α = effective diameter of hydrated ion (nm)

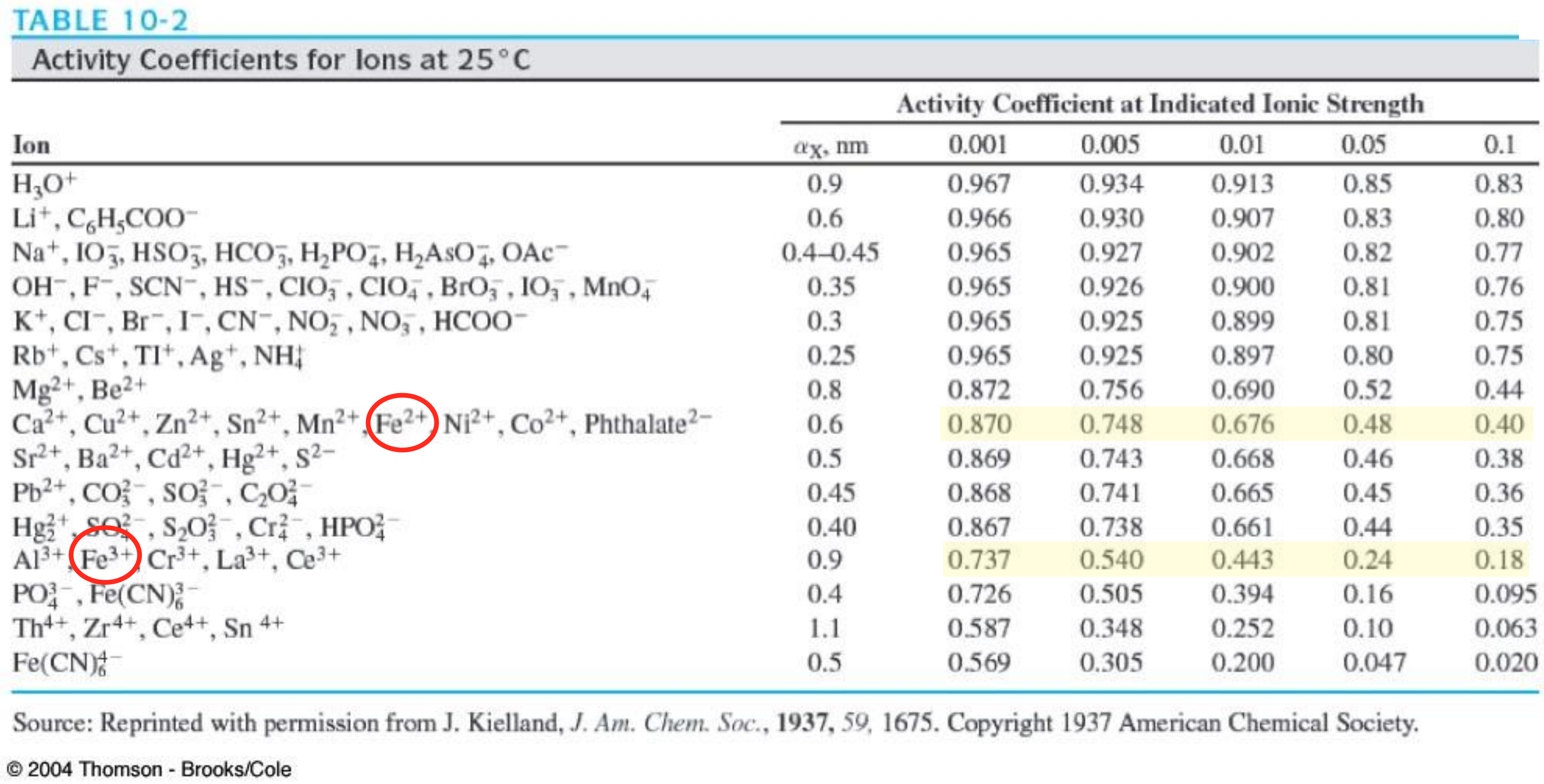


TABLE 10-2

Activity Coefficients for Ions at 25°C

Ion	α_X, nm	Activity Coefficient at Indicated Ionic Strength: 0.001	0.005	0.01	0.05	0.1
H_3O^+	0.9	0.967	0.934	0.913	0.85	0.83
Li^+, $C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, MnO_4^-	0.35	0.965	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.965	0.925	0.899	0.81	0.75
Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+	0.25	0.965	0.925	0.897	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.756	0.690	0.52	0.44
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Phthalate^{2-}	0.6	0.870	0.748	0.676	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.869	0.743	0.668	0.46	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, $C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, Cr_4^{2-}, HPO_4^{2-}	0.40	0.867	0.738	0.661	0.44	0.35
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.737	0.540	0.443	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.587	0.348	0.252	0.10	0.063
$Fe(CN)_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020

Source: Reprinted with permission from J. Kielland, *J. Am. Chem. Soc.*, 1937, *59*, 1675. Copyright 1937 American Chemical Society.

Table 10-2, p. 274 in Skoog & West

… the derivation is long…
… but the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/ Gauss)

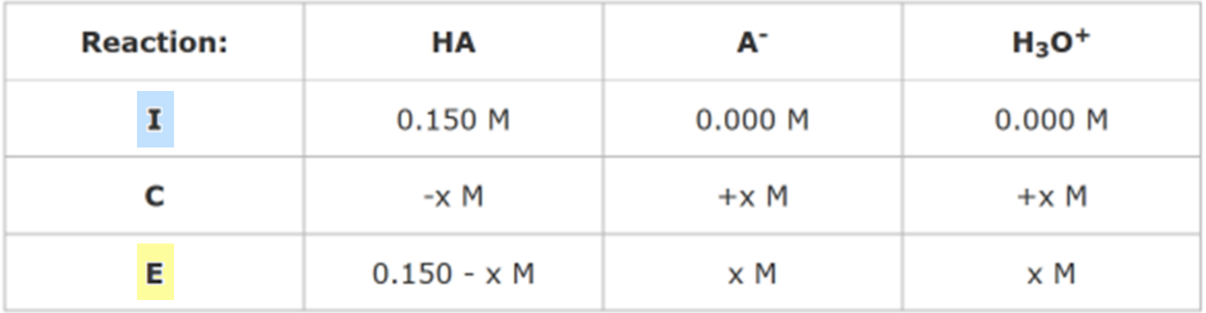
… the "limiting law" is when $I \rightarrow 0$ (< 10 mM)…

$$-\log \gamma_x = 0.51 z_x^2 \sqrt{I}$$

Le Chatelier’s Principle

Initial states equilibrate based on ICE, ICE Baby!

$$A \rightleftharpoons B + C$$



Reaction:	HA	A^-	H_3O^+
I	0.150 M	0.000 M	0.000 M
C	-x M	+x M	+x M
E	0.150 - x M	x M	x M

http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables

http://buzzworthy.mtv.com/2012/11/14/justin-bieber-vanilla-ice-photo/

Given K', and assuming typical standard-state conditions, use the following equation and plug in information from E (in ICE) to calculate *x*

$$A \rightleftharpoons B + C$$

$$K' = \frac{\left(c_{\mathrm{B,eq}}^{\alpha}/c_{\mathrm{B}}^{\mathrm{o},\alpha}\right)\left(c_{\mathrm{C,eq}}^{\alpha}/c_{\mathrm{C}}^{\mathrm{o},\alpha}\right)}{c_{\mathrm{A,eq}}^{\alpha}/c_{\mathrm{A}}^{\mathrm{o},\alpha}}$$

Vanilla Ice wants to know, “As the initial state progresses, what happens if you keep supplying A and pulling B and C away?” …

Le Chatelier’s Principle

… Le Chatelier’s Principle indicates that the reaction will continue…

$$\longrightarrow A \rightleftharpoons B + C \longrightarrow$$

… but for how long? …

$$M_1 \longrightarrow A \rightleftharpoons B + C \longrightarrow M_2$$

> "changes in the temperature, pressure, volume, or concentration of a system will result in predictable and opposing changes in the system in order to achieve a new equilibrium state."
> – Wiki, Le Chatelier’s principle

… as long as the rate of supply in and/or the rate of exit out are non-zero…

In an ideal world, i.e. under certain *rare* conditions, $\frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = \frac{\partial c_C}{\partial t} = 0$, and the system is in a ***steady-state*** where there is a net flux of species (generation of A, from the left, and loss of B & C, to the right) but the species concentrations in the cell do not change with time

Chemical Properties *(summary for today)*

- **Molecular nomenclature, Solutions, Balanced chemical reactions**
- **State functions, Standard states, Thermochemistry**
- **Non-ideal gases, Intermolecular forces, Physical properties, Phase changes, Colligative properties, Water activity**
- **Free energy, (X)Chemical potential, Chemical equilibrium, van't Hoff equation, Activity coefficients, Le Chatelier's principle**
- Schrödinger equation, Internal energy, Atomic orbitals, Hybridization
- Valence bond theory, Molecular orbital theory, Band diagrams
- Crystal field theory, Ligand field theory

Paper(s) Time!