



Lecture #4 of 15

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

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

1 1A																	18 8A
1 H Hydrogen 1.01																	2 He Helium 4.00
2 Li Lithium 6.94	3 Be Beryllium 9.01																
3 Na Sodium 22.99	4 Mg Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A Al Aluminum 26.98	14 4A Si Silicon 28.09	15 5A P Phosphorus 30.97	16 6A S Sulfur 32.07	17 7A Cl Chlorine 35.45	18 8A Ar Argon 39.95
4 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
5 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
6 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)									
			58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97	
			90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)	

Key

- 11 — Atomic number
- Na** — Element symbol
- Sodium — Element name
- 22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

... What does the atomic number tell you?...

... And why is the “average” atomic mass indicated?...

... for example, recall that there are 15 isotopes of carbon: ¹¹C, ¹²C, ¹³C, ¹⁴C



Chemical Properties

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

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

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 $dG = dH - TdS - SdT$

Well, it stems from the laws of thermodynamics:

Are these state functions?

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

(2) Increase of Entropy: $\Delta S_{\text{universe}} \geq 0$, $\Delta G_{\text{system}} \leq 0$, and $dQ \leq TdS_{\text{system}}$

(3) Lower Limit to Entropy and Temperature: $S_{\text{system}} \geq 0$, $T \geq 0$

... where $dw = dw' + -pdV$

Many chemists are interested in non- pdV work, dw' , and so using total differentials...

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

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

Q flow possible from internal energy

necessary Q flow

At constant T and p , **$(dG_{\text{sys}})_{T,p} = dw'$** ... **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**: $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$
 ... 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

$$G_R = \sum_r \mu_r n_r \quad G_P = \sum_p \mu_p n_p$$

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.

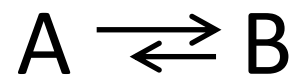
(Electro)Chemical Potential

So, let's take a deeper look at this for $A \rightleftharpoons B$

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

$$dG = \left(\frac{\partial G}{\partial n_A} \right) \partial n_A + \left(\frac{\partial G}{\partial n_B} \right) \partial n_B = \mu_A \partial n_A + \mu_B \partial n_B \dots \text{but since every loss of A has a gain of B}$$

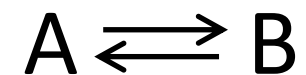
$$dG = (\mu_B - \mu_A) \partial n_B \dots \text{and so this is a detailed thermodynamic version of an ICE table!}$$



(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 $\mu_B^\alpha = \mu_A^\alpha$, at equilibrium

... as seen (next) by its definition: $\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i q \phi^\alpha = \mu_i^{0,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$ in phase α ...

(Electro)Chemical Potential

So where does the fundamental equation, $\bar{\mu}_i^\alpha = \bar{\mu}_i^{0,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$, come from?

... recall that, by definition, $d\mathbf{w}' = d\mathbf{G}_{\text{sys}} + \mathbf{S}_{\text{sys}} dT - \mathbf{V} d\mathbf{p}$ 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 and $p_{(\text{total})}$... one has $d\mathbf{w}'/dn_i = d\bar{\mu}_i - \mathbf{V}_i d\mathbf{p}_i$

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

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

... integration from $\bar{\mu}_i^{0,\alpha}$ to $\bar{\mu}_i^\alpha$ results in $\bar{\mu}_i^\alpha = \bar{\mu}_i^{0,\alpha} + RT \ln(p_i^\alpha/p_i^{0,\alpha}) + \mathbf{w}'_i$

... and when species i is non-ideal, $a_i^\alpha = \gamma_i^\alpha (p_i^\alpha/p_i^{0,\alpha})$ is more accurate in the natural log term

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

(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 $\bar{\mu}_i^\alpha = \bar{\mu}_i^{0,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$

$$\bar{\mu}_A^\alpha = \bar{\mu}_A^{0,\alpha} + RT \ln a_A^\alpha + (0)q\phi^\alpha$$

$$\bar{\mu}_B^\alpha = \bar{\mu}_B^{0,\alpha} + RT \ln a_B^\alpha + (0)q\phi^\alpha$$

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

Defining the free energy change upon mixing is facile as

$$G_{\text{initial}} = \bar{\mu}_A^\alpha n_A + \bar{\mu}_B^\alpha n_B \quad G_{\text{final}} = \bar{\mu}_{A,\text{eq}}^\alpha n_A + \bar{\mu}_{B,\text{eq}}^\alpha n_B$$

$$\Delta G_{\text{mix}} = n_A \left(RT \ln \frac{a_{A,\text{eq}}^\alpha}{a_A^\alpha} \right) + n_B \left(RT \ln \frac{a_{B,\text{eq}}^\alpha}{a_B^\alpha} \right)$$

... with total number, $n = n_A + n_B$, and mole fraction, $x_i = \frac{n_i}{n}$...

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

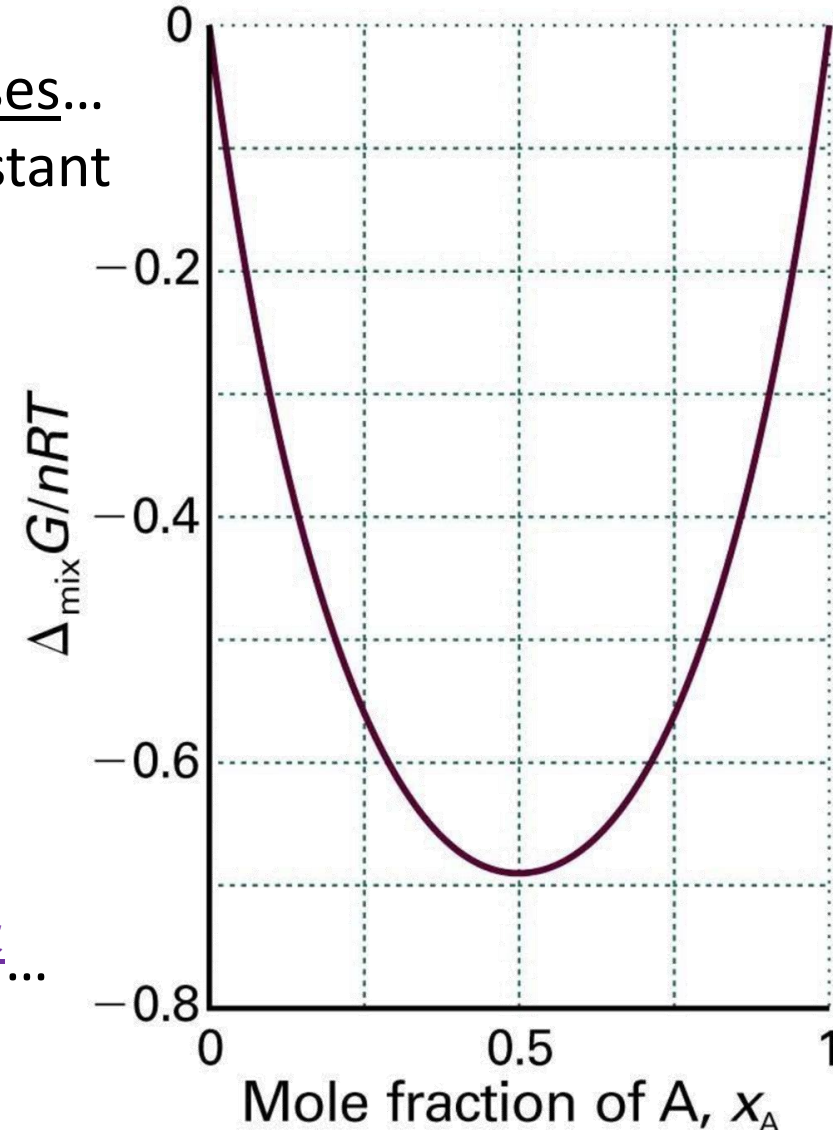
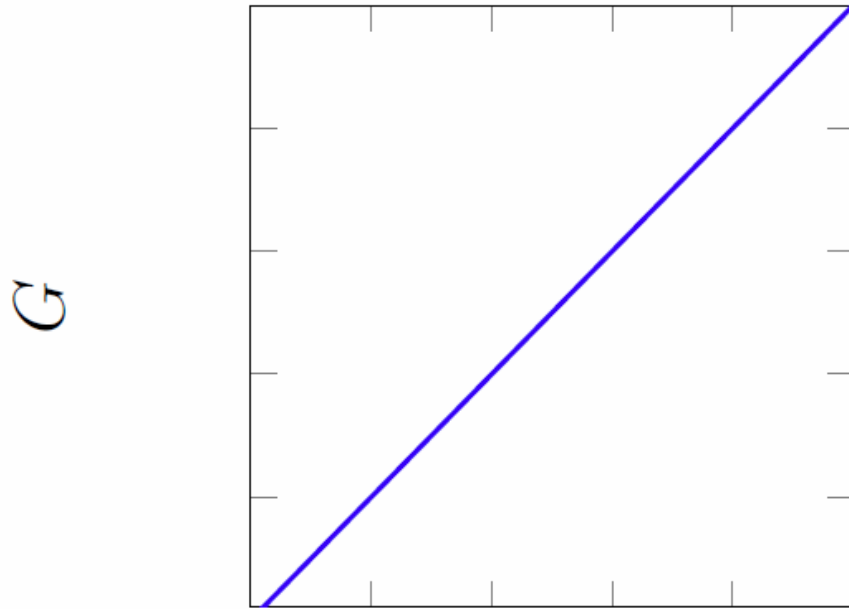


Figure 5-7
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

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

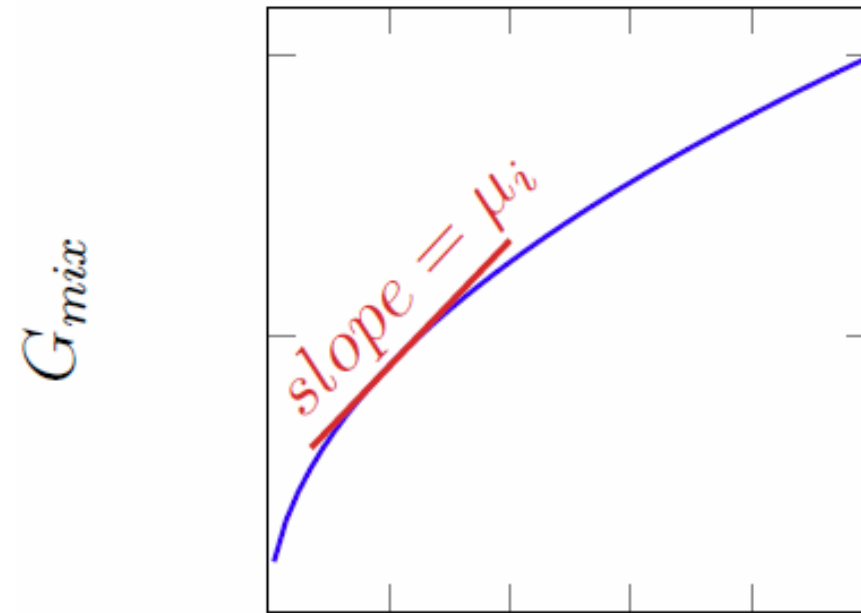
Chemical Potential

Pure substance




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

Mixture or Solution



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

Equilibrium

(REVIEW) 84
 classical version of \bar{V} for effects outside of the Hamiltonian "box" 

And, in summary, as it relates to the fundamental equation, $\bar{\mu}_i^\alpha = \bar{\mu}_i^{0,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$

Recall that for species in solution, $a_i^\alpha = \gamma_i^\alpha \frac{c_i^\alpha}{c_i^{0,\alpha}}$

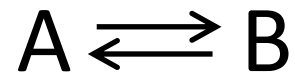
... where γ_i^α are activity coefficients (*more in a bit*)

Table 5.3 Standard states

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

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

Table 5-3
 Atkins Physical Chemistry, Eighth Edition
 © 2006 Peter Atkins and Julio de Paula



And back to $dG = (\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha) \partial n_B$... where ∂n_B is termed the **progress of the reaction**, and so...

$$\Delta G = \left(\bar{\mu}_B^\alpha - \frac{v_A}{v_B} \bar{\mu}_A^\alpha \right) \dots \text{with } v_A \text{ (stoichiometric number)}$$

... 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)

Chemical (and Thermal) Equilibrium

Given $\Delta G = (\bar{\mu}_B^\alpha - \bar{\mu}_A^\alpha)$... which could have ν_i too...

and using $\bar{\mu}_i^\alpha = \bar{\mu}_i^{0,\alpha} + RT \ln a_i^\alpha + z_i q \phi^\alpha$

$$\Delta G = \bar{\mu}_B^{0,\alpha} + RT \ln a_B^\alpha + z_B q \phi^\alpha - \bar{\mu}_A^{0,\alpha} + RT \ln a_A^\alpha + z_A q \phi^\alpha$$

Which means that

$$\Delta G = (\bar{\mu}_B^{0,\alpha} - \bar{\mu}_A^{0,\alpha}) + RT \ln \frac{a_B^\alpha}{a_A^\alpha} + zq(0)$$

$$\Delta G = \Delta G^{0,\alpha} + RT \ln Q \dots \text{where } Q = \frac{a_B^\alpha}{a_A^\alpha}, \text{ and} \dots$$

$$\Delta G = \Delta G^{0',\alpha} + RT \ln Q' \dots \text{where } Q' = \frac{c_B^\alpha / c_B^{0,\alpha}}{c_A^\alpha / c_A^{0,\alpha}}$$

... where $\Delta G^{0',\alpha}$ contains the activity coefficients, γ_i^α

At equilibrium $\bar{\mu}_B - \bar{\mu}_A = 0 = \Delta G^{0',\alpha} + RT \ln Q'_{\text{eq}}$, so $\Delta G^{0',\alpha} = -RT \ln K'$ with $K' = \frac{c_{B,\text{eq}}^\alpha / c_B^{0,\alpha}}{c_{A,\text{eq}}^\alpha / c_A^{0,\alpha}}$

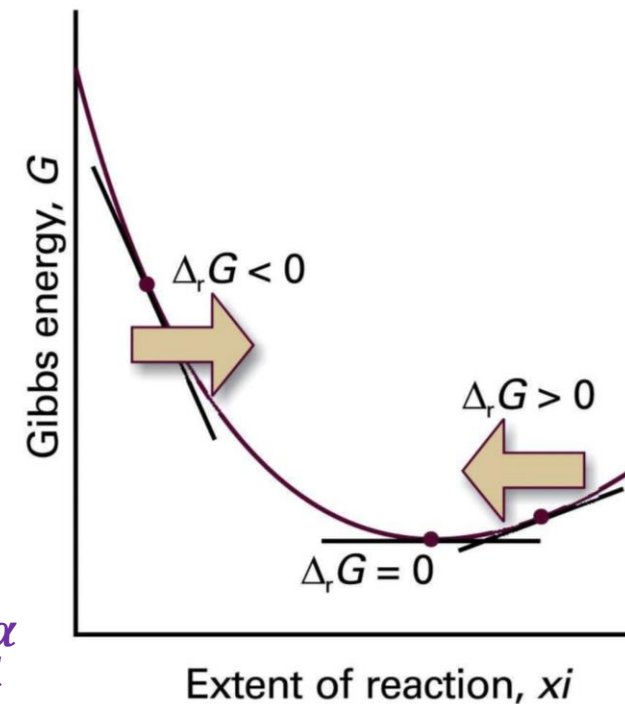
For an uncharged species: $\bar{\mu}_i^\alpha = \mu_i^\alpha$

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



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
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

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 Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Ion-product constant, K_w	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$
	Solubility product, K_{sp}	$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$
		$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$	$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$
Formation of a complex ion	Formation constant, β_n	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$\text{I}_2(aq) \rightleftharpoons \text{I}_2(org)$	$K_d = \frac{[\text{I}_2]_{org}}{[\text{I}_2]_{aq}}$

© Cengage Learning. All Rights Reserved.

... 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/>

Scientists & Engineers love to vary Temperature

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

... but an even more accurate analysis relies on $\Delta G^{o',\alpha} = \Delta H^{o',\alpha} - T\Delta S^{o',\alpha}$ for a given T and p ,

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

... but this is also an approximation that only holds over a rather small ranges of T due to the temperature dependence of $\Delta H^{o',\alpha} = C_p \Delta T$, and C_p , and $\Delta S^{o',\alpha}$

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

... and chemical kinetic properties too (*stay tuned*)...

At equilibrium $\bar{\mu}_B - \bar{\mu}_A = 0 = \Delta G^{o',\alpha} + RT \ln Q'_{\text{eq}}$, so $\Delta G^{o',\alpha} = -RT \ln K'$ with $K' = \frac{c_{B,\text{eq}}^\alpha / c_B^{o,\alpha}}{c_{A,\text{eq}}^\alpha / c_A^{o,\alpha}}$

Activity Coefficients

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

$$\log \gamma_X = -\frac{0.51z_X^2\sqrt{I}}{1 + 3.3\alpha_X\sqrt{I}}$$

TABLE 10-2

Activity Coefficients for Ions at 25 °C

Ion	α_X , nm	Activity Coefficient at Indicated Ionic Strength, I				
		0.001	0.005	0.01	0.05	0.1
H ₃ O ⁺	0.9	0.967	0.934	0.913	0.85	0.83
Li ⁺ , C ₆ H ₅ COO ⁻	0.6	0.966	0.930	0.907	0.83	0.80
Na ⁺ , IO ₃ ⁻ , HSO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , H ₂ AsO 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 ₂ O ₄ ²⁻	0.45	0.868	0.741	0.665	0.45	0.36
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O 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.

© 2004 Thomson - Brooks/Cole

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

α = effective diameter (nm) of hydrated ion, X

... 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)...

$$\log \gamma_X = -0.51z_X^2\sqrt{I}$$

Le Chatelier's Principle

Initial states equilibrate based on ICE, ICE Baby!



Reaction:	HA	A ⁻	H ₃ O ⁺
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



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



<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

$$K' = \frac{\left(c_{B,eq}^{\alpha} / c_B^{0,\alpha} \right) \left(c_{C,eq}^{\alpha} / c_C^{0,\alpha} \right)}{c_{A,eq}^{\alpha} / c_A^{0,\alpha}}$$

Le Chatelier's Principle

... Le Chatelier's Principle indicates that the reaction will continue...



... but for how long? ...



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

"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

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!