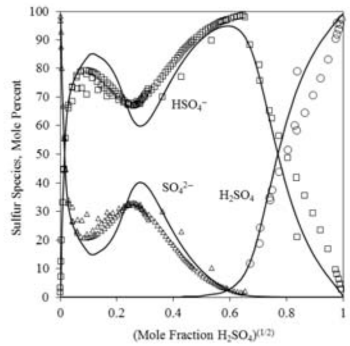
Introduction

Strong Electrolyte
Weak Electrolyte
Dissociation depends on concentration, model as reaction



18.2 Colligative properties
Electrolyte dissociation changes concentration more than non-electrolyte (large 'dilution' effect).
Freezing pt. 5 g each
NaCl 58.44g/mol, EG 62.07 g/mol, glucose 180 g/mol.

Tf = 270.0 K	271.7 K	272.7K

0.1 mole of each

Tf = 269.6 K	271.3 K	271.3 K

Osmotic pressure, 0.1 mole of each

Π = 4.89 MPa	2.5 MPa	2.5 MPa

Boiling pt elevation, 0.1 mole each

Tb = 101 C	100.5 C	100.5C

18.3 Speciation

$$H_2O_{(l)} \rightleftarrows H^+_{(aq)} + OH^-_{(aq)} \qquad 18.4$$

$$K_{a,\,298} = [H^+][OH^-] = 10^{-14}$$

$$K_{a,\,298} = \exp(-\Delta G^o_{298}/RT) = \frac{a_{H^+}\,a_{OH^-}}{a_{H_2O}}$$

18.4 Concentration Scales and Standard States
entity, superficial, apparent, nominal --

true --

molal - m_i mol/(kg solvent)
molarity - M_i mol/L
Standard States for electrolytes

Standard State for water.

$$K_{a,\,298} = (m_{H^+}\gamma^{\square}_{H^+}m_{OH^-}\gamma^{\square}_{OH^-})/(m^o_{H^+}m^o_{OH^-}a_{H_2O})$$
$$\approx m_{H^+}m_{OH^-} \approx [H^+][OH^-]$$

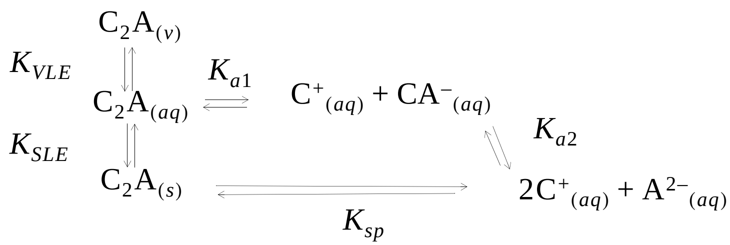
18.5 Definition of pH

$$\boxed{pH \equiv -\log_{10}(a_{H^+})} \qquad 18.7$$

$$pH \approx -\log_{10}[H^+] \qquad 18.8$$

Solvent is important.

18.6 Thermodynamic Network



18.7 Perspectives on Speciation

$2H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + OH^-_{(aq)}$

$AcOH_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + AcO^-_{(aq)}$

Charge Balance

18.8 Acids and Bases

Strong/Weak -

Leveling effect -

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Strong Acids - completely dissociate, superficial C_A

$[Cl^-] = C_A$ material balance for complete dissociation

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

$[H^+] = [Cl^-] + [OH^-]$ charge balance

Proton Condition -

$[H^+] = C_A + [OH^-]$ **proton condition**

Condition becomes $[H^+] = C_A + K_{a,w}/[H^+]$

Strong Bases - e.g. NaOH

$[Na^+] = C_B$ material balance for dissociation

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

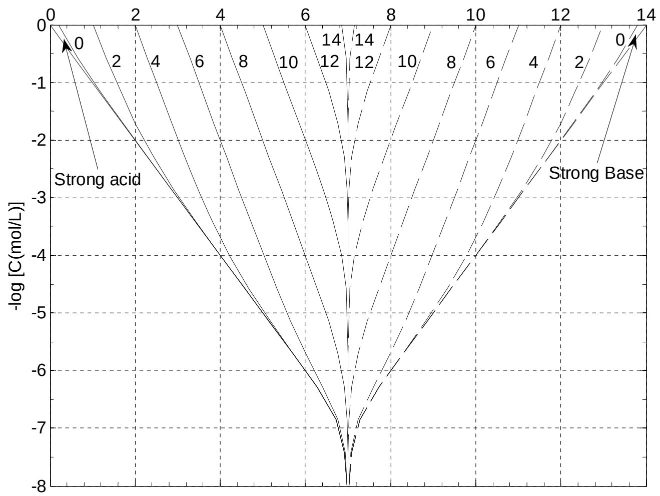
$[H^+] + [Na^+] = [OH^-]$ charge balance

Proton Condition

$[H^+] + C_B = [OH^-]$ **proton condition**

Condition becomes $[H^+] + C_B = K_{a,w}/[H^+]$

Flood diagram



Weak monoprotic acid -

$[A^-] + [HA] = C_A$ material balance

$K_{a,A} = [H^+][A^-]/[HA]$ equilibrium

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

$[H^+] = [A^-] + [OH^-]$ charge balance

$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})}$ undissociated acid (18.30)

$\boxed{[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})}$ conjugate base (18.31)

Weak monoprotic base -

$[Na^+] = [HA] + [A^-] = C_B$ material balance

$K_{a,B} = [HA][OH^-]/[A^-]$ equilibrium

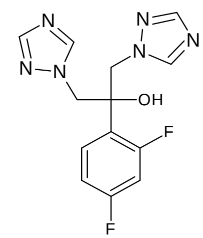
$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

$[H^+] + [Na^+] = [A^-] + [OH^-]$ charge balance

$\boxed{pK_{a,A} + pK_{a,B} = pK_{a,w} \quad \text{or} \quad K_{a,A}K_{a,B} = K_{a,w}}$

Use $pK_{a,A}$ to plot

Fluconazole + $H_2O \rightleftarrows$ Fluconazole$^+$ + OH^-



$\ln(K_a) = -1.28 - 8000/T$

18.9 Sillen Diagrams - seven steps

1. coordinates, strong acid/base lines.
2. material balance. 3. equil in acid form.
5. sketch acid and base equations.
6. proton condition to find intersection. 7. Check

Example 18.5 C_B = 1E-2 mol/L NaOAc

Step 1: The lines for $[H^+]$ and $[OH^-]$ have been drawn and labeled in the figure.

Step 2: $[Na^+] = [HOAc] + [OAc^-] = C_B$ material balance

Step 3: $K_a = [OAc^-][H^+]/[HOAc]$ equilibrium

$K_w = [H^+][OH^-] = 10^{-14}$ equilibrium

Step 4: $[H^+] + [Na^+] = [OAc^-] + [OH^-]$ charge balance

Proton Condition - eliminate large terms from charge balance

Polyprotic Acids (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-})

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} = \frac{K_{a1}}{[H^+]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[HPO_4^{2-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}}{[H^+]^2}$$

$$\frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{K_{a3}}{[H^+]} \text{ or } \frac{[PO_4^{3-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}$$

The material balance on phosphorous is

$$C = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$\frac{1}{\alpha_3} = \frac{C}{[H_3PO_4]} = 1 + \frac{[H_2PO_4^-]}{[H_3PO_4]} + \frac{[HPO_4^{2-}]}{[H_3PO_4]} + \frac{[PO_4^{3-}]}{[H_3PO_4]}$$

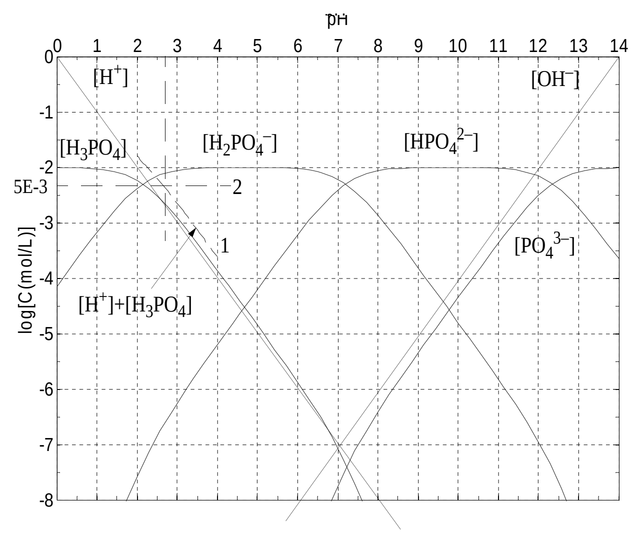
$$= 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}$$

$$\alpha_3 = \frac{[H_3PO_4]}{C}$$

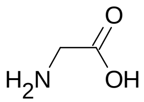
$$= \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

$$\alpha_2 = \frac{[H_2PO_4^-]}{C} = \frac{[H_3PO_4]}{C}\frac{[H_2PO_4^-]}{[H_3PO_4]} = \alpha_3\frac{K_{a1}}{[H^+]}$$

NaH_2PO_4, 1E-2 M, HCl, 5E-3 M



Amino Acids,



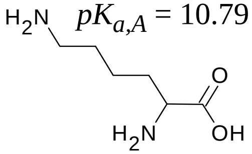
COOH, $pK_{a,A} = 2.35$
NH_2, $pK_{a,A} = 9.78$

glycinium	glycine	glycinate
H_2Gly^+	HGly	Gly^-
pH < 2.35	*2.35 < pH < 9.78*	*pH > 9.78*

$$^+H_3NCH_2COOH \rightleftarrows {}^+H_3NCH_2COO^- \rightleftarrows H_2NCH_2COO^-$$

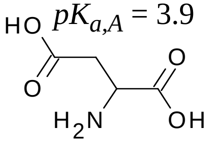
$pK_a = 2.35$ $\qquad$ $pK_a = 9.78$

$pK_{a,A} = 10.79$

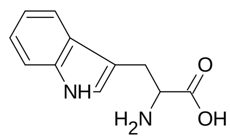


Lysine (Lys, K)

$pK_{a,A} = 3.9$

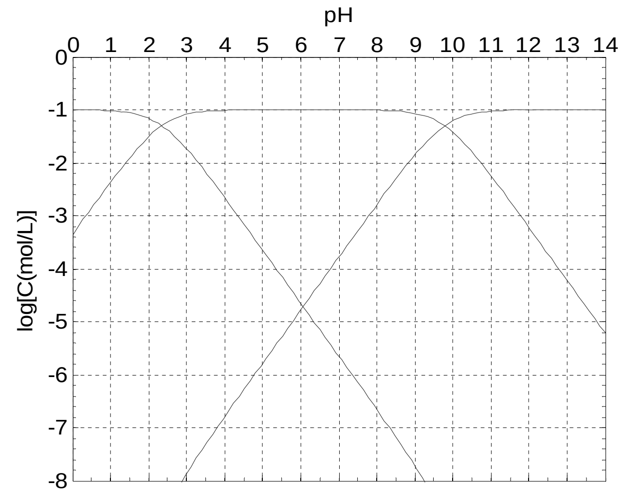


Aspartic Acid (Asp, D)



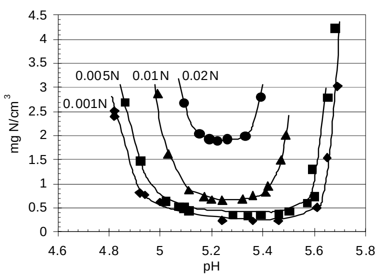
Tryptophan (Trp, W)

0.1 M Glycine



Buffers

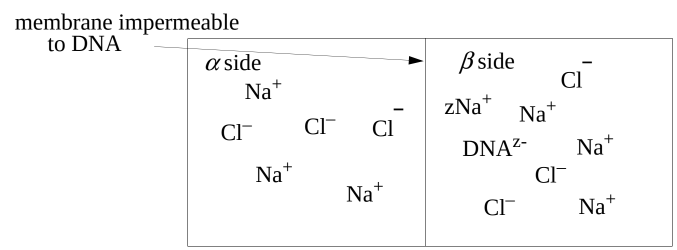
Isoelectric point



Salting In

Salting Out

Donnan Equilibria



Solubility and Ksp

Fluconazole, Example 18.8

$K_{SLE} = a_{\text{fluc}(aq)}$ and $\ln(K_{SLE}) = 8.474 - 3721.9/T$

$K_{a,A} = [\text{fluc}][H^+]/([\text{fluc}^+]a_{H2O})$

Common Ion Effect

$KCl_{(s)} \rightleftarrows K^+_{(aq)} + Cl^-_{(aq)} \quad K_{sp} = a_{K^+}a_{Cl^-}$

Redox reactions -

OILRIG

Methane combustion -

Li-Ion battery - $LiC_6 \rightleftarrows C_6 + Li^+ + e^-$,

$CoO_2 + Li^+ + e^- \rightleftarrows LiCoO_2$, $LiC_6 + CoO_2 \rightleftarrows C_6 + LiCoO_2$

Half-cell rxns, relative to $2H^+ + 2e^- \rightleftarrows H_{2(g)}$

$E° = E°_{\text{red}} - E°_{\text{ox}}$

Potential per electron!

Voltage and Gibbs Energy $\boxed{\Delta G° = -n_eFE° = -RT\ln K_a}$

Faraday constant - 96,485 J/V.

$\Delta G° = -n_eFE°_{\text{red}} + n_eFE°_{\text{ox}}$

(equilibrium condition - dead when K_a is reached.

$\Delta G = \Delta G° + RT\ln\prod a_i^{v_i}$ or $n_eFE = n_eFE° - RT\ln\prod a_i^{v_i}$

$\boxed{E = E° - \frac{RT}{n_eF}\ln\prod a_i^{v_i} = E° - \frac{0.05916}{n_e}\log\prod a_i^{v_i}}$ Nernst Eq.

Balancing, including non-redox.

Alkaline Battery

$Zn_{(s)}$ and γ-$MnO_{2(s)}$ $\qquad ZnO_{(s)}$, α-$MnOOH_{(s)}$.

$$E = E^\circ - \frac{0.05916}{2}\log\frac{a_{ZnO}a_{MnOOH}}{a_{Zn}a_{MnO_2}a_{H_2O}}$$

Fuel Cell

Biological Reactions

Degree of reduction $\quad C_dH_aO_bN_c \; \gamma_{red} = (4d + a - 2b)/d$

Glucose --> Ethanol

Binding polynomials

PO_4^{3-} binding receptor for H^+ ‘ligands’

$$K_{a1}^{bind} = 1/K_{a3}$$

$$C = [PO_4^{3-}]\left(1 + \frac{[H^+]}{K_{a3}} + \frac{[H^+]^2}{K_{a3}K_{a2}} + \frac{[H^+]^3}{K_{a3}K_{a2}K_{a1}}\right)$$

$$= [PO_4^{3-}](1 + K_{a1}^{bind}[H^+] + K_{a1}^{bind}K_{a2}^{bind}[H^+]^2 + K_{a1}^{bind}K_{a2}^{bind}K_{a3}^{bind}[H^+]^3)$$

$$\langle i\rangle = \frac{(0(1) + 1K_1[H^+] + 2K_2[H^+]^2 + 3K_3[H^+]^3)}{P_{bind}}$$

$$= P_{bind}^{-1}\sum_{i=0}^{t} iK_i[x]^i = \frac{[x]}{P_{bind}}\frac{dP_{bind}}{d[x]} = \frac{d\ln P_{bind}}{d\ln[x]}$$

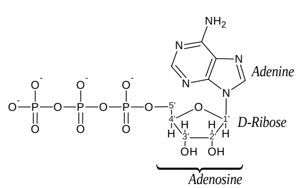
Energy Carriers

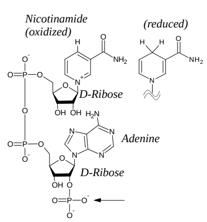
catabolic - $\qquad\qquad$ anabolic

exergonic - $\qquad\qquad$ energonic

coupling -

ATP $\qquad\qquad$ $NADP^+$





ATP^{4-}, $HATP^{3-}$, H_2ATP^{2-}, H_3ATP^-, H_4ATP, H_5ATP^+

Standard State

Transformed Gibbs Energy

(1) Constant pH, pMg

(2) Use apparent concentrations

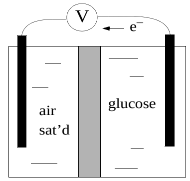
[ATP] = sum of all ATP species

$$\boxed{\Delta G' = \Delta G'^\circ + RT\ln\prod_i [i]^{\nu_i} \qquad \Delta G'^\circ = -RT\ln K_c'}$$

$ATP + H_2O \rightleftarrows ADP + H_3PO_4 \qquad$ or $\qquad ATP + H_2O \rightleftarrows ADP + P_i$

$$K_c' = \frac{[ADP][P_i]}{[ATP]} = \exp\left(\frac{\Delta G'^\circ_{f,\,ADP} + \Delta G'^\circ_{f,\,P_i} - \Delta G'^\circ_{f,\,ATP} - \Delta G'^\circ_{f,\,H_2O}}{RT}\right)$$

Biological Fuel Cells
Glucose --> Gluconolactone
O_2 --> H_2O_2



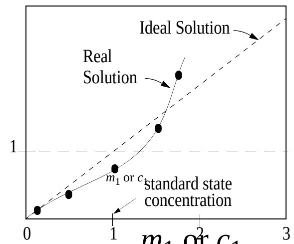
Non-ideal Solutions

$$\mu_i = \mu_i^{\square} + RT\ln(m_i\gamma_i^{\square})$$

For biology, usually

$$a_1 = m_1\gamma_1^{\square}$$
or
$$a_1 = c_1\gamma_1^{\emptyset}$$

$a_1^{\emptyset}$



$a_1^{\square}$

m_1 or c_1

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\Phi}{\partial r}\right] = \frac{-\rho_{\pm}(r)}{\varepsilon}$$

r is radial position, Φ is electric potential, $\rho_{\pm}(r)$ is charge distribution as a function of radial distance, $\varepsilon = \varepsilon_o D$, where ε_o is the permittivity of a vacuum and D is the dielectric constant

$g(r) \sim \exp(-u_{Coul}/kT)$

$$\log_{10}\gamma_i^{\square} = \frac{-z_i^2 A_\gamma\sqrt{I}}{1 + Ba\sqrt{I}} \text{ up to } I = 0.1 \text{ m}$$

$$\log_{10}\gamma_s = \frac{2A_\gamma M_{w,s}}{1000(Ba)^3}\left\{1 + Ba\sqrt{I} - \frac{1}{1 + Ba\sqrt{I}} - 2\ln(1 + Ba\sqrt{I})\right\}$$

$$\Phi = \frac{-1000}{M_{w,s}\sum\limits_{electrolytes} m_i}\ln a_s \text{ osmotic coefficient}$$

$$\Pi = \frac{RT}{V_s}\,\frac{M_{w,s}\sum\limits_{electrolytes} m_i}{1000}\Phi \text{ osmotic pressure}$$

Gibbs energies for electrolytes

$$\frac{\Delta G_T}{RT} = \frac{\Delta G_T^{\circ}}{RT} + \ln\left[\prod_{i=1}^{NC}[a_i]^{\nu_i}\right]$$

$$\Delta G_{298}^{o} = \Delta G_{f,298}^{\square}(H^+) + \Delta G_{f,298}^{\square}(OH^-) - \Delta G_{f,298}^{o}(H_2O_{(l)})$$

$$= \Delta G_{f,298}^{\square}(H^+) + \Delta G_{f,298}^{\square}(OH^-) + 237.18 = 79.908 \text{ kJ/mol}$$

Transformed Gibbs Energies

$G' = U - TS + PV - N_H\mu_{H^+} - N_{Mg}\mu_{Mg^{2+}}$

$$\boxed{\begin{aligned}\Delta G'^{\circ}_{f,T,i}(I, \text{pH}, p\text{Mg}) &= \Delta G^{\circ}_{f,T,i}(I) \\ &- N_{H,i}\{\Delta G^{\circ}_{f,T,H^+}(I) - RT\text{pH}_c\ln(10)\} \\ &- N_{Mg,i}\{\Delta G^{\circ}_{f,T,Mg^{2+}}(I) - RT\text{pMg}\ln(10)\}\end{aligned}}$$

$$\boxed{\Delta G^{\circ}_{f,T,j}(I) = \Delta G^{\circ}_{f,T,j}(I{=}0) - RT\ln(10)z_j^2 A_\gamma(\sqrt{I}/(1 + Ba\sqrt{I}))}$$

$$\boxed{\begin{aligned}\Delta G^{\circ}_{f,j}(I{=}0) &= \left(\frac{T}{298.15}\right)\Delta G^{\circ}_{f,298.15,j}(I{=}0) \\ &+ \left(1 - \frac{T}{298.15}\right)\Delta H^{\circ}_{f,298.15,j}(I{=}0)\end{aligned}}$$

Gibbs Energies of Pseudoisomers

$$\boxed{\Delta G'^{\circ}_{f,\,T,\,i}(I,\, \text{pH}_c,\, \text{pMg}) = \Delta G'^{\circ}_{f,\,T,\,i(1)}(I,\, \text{pH}_c,\, \text{pMg}) - RT\ln P_{\text{bind}}}$$

$$P_{\text{bind}} = \left(1 + \exp\left(\frac{\Delta G'^{\circ}_{f,\,i(1)} - \Delta G'^{\circ}_{f,\,i(2)}}{RT}\right) + \exp\left(\frac{\Delta G'^{\circ}_{f,\,i(1)} - \Delta G'^{\circ}_{f,\,i(3)}}{RT}\right) + \ldots\right)$$

$$P_{\text{bind}} = \left(1 + \frac{1}{K'_{a3}} + \frac{1}{K'_{a3}K'_{a2}} + \frac{1}{K'_{a3}K'_{a2}K'_{a1}}\right)$$

$$= (1 + K'^{\text{bind}}_{a1} + K'^{\text{bind}}_{a1}K'^{\text{bind}}_{a2} + K'^{\text{bind}}_{a1}K'^{\text{bind}}_{a2}K'^{\text{bind}}_{a3})$$

$$r_j = \frac{1}{P_{\text{bind}}}\exp\left(\frac{\Delta G'^{\circ}_{f,\,i(1)} - \Delta G'^{\circ}_{f,\,i(j)}}{RT}\right) = \exp\left(\frac{\Delta G'^{\circ}_{f,\,T,\,i} - \Delta G'^{\circ}_{f,\,i(j)}}{(RT)}\right)$$

Example, $\text{pH}_c = 7$, $\text{pMg}_c = 3$, $I = 0.25$ mol/kg

$$\frac{[\text{ATP}^{4-}]}{\text{P}_i} = \frac{1}{P_{\text{bind}}} = \frac{1}{9.7452} = 0.10$$

$$\frac{[\text{HATP}^{3-}]}{\text{P}_i} = \frac{[\text{MgATP}]}{\text{P}_i} = \frac{0.2863}{9.7452} = 0.03$$

$$\frac{[\text{MgATP}^{2-}]}{\text{P}_i} = \frac{8.148}{9.7452} = 0.84$$

$$\Delta G'^{\circ}_{f,\,\text{P}_i} = \Delta G'^{\circ}_{f,\,\text{P}_i(1)} - RT\ln P_{\text{bind}}$$

$$= -2291.9 - 0.008314(298.15)\ln 9.7452$$

$$= -2297.5 \text{ kJ/mol}$$

Coupled Reaction and Phase Equilibria (Ideal Solutions only)

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)}$$

$$K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} = 1\text{E-}3.348$$

$$HClO_{(aq)} = H^+ + ClO^- \qquad K_{a2} = \frac{a_{H^+}\,a_{ClO^-}}{a_{HClO_{(aq)}}} = 1\text{E}{-}7.555$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = 1\text{E-}14$$

Write the VLE as “reactions”

$$H_2O_{(v)} \rightleftarrows H_2O_{(l)} \quad K_W = a_W/(y_W P) = 1/(P_W^{sat})$$

$Cl_{2(v)} \rightleftarrows Cl_{2(aq)}$ $\quad K_H = [Cl_{2(aq)}]/(y_{Cl2}P)$, Henry’s Law