# Chapter 18 Electrolytes

Strong Electrolyte NaCl in water (strong dielectric, ions completely formed)
Weak Electrolyte Acetic Acid in water (use dissociation constant)

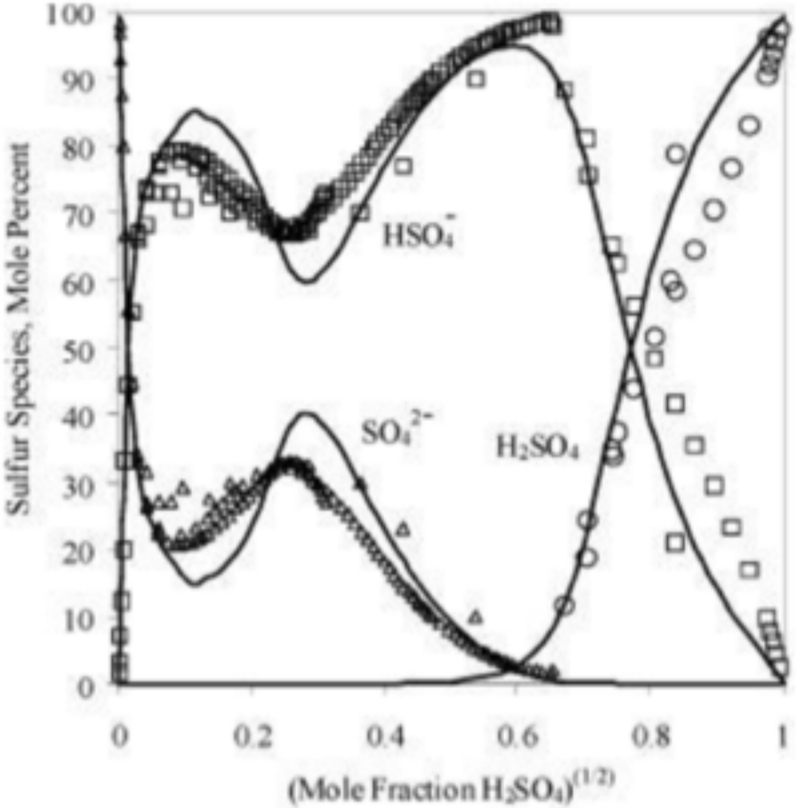
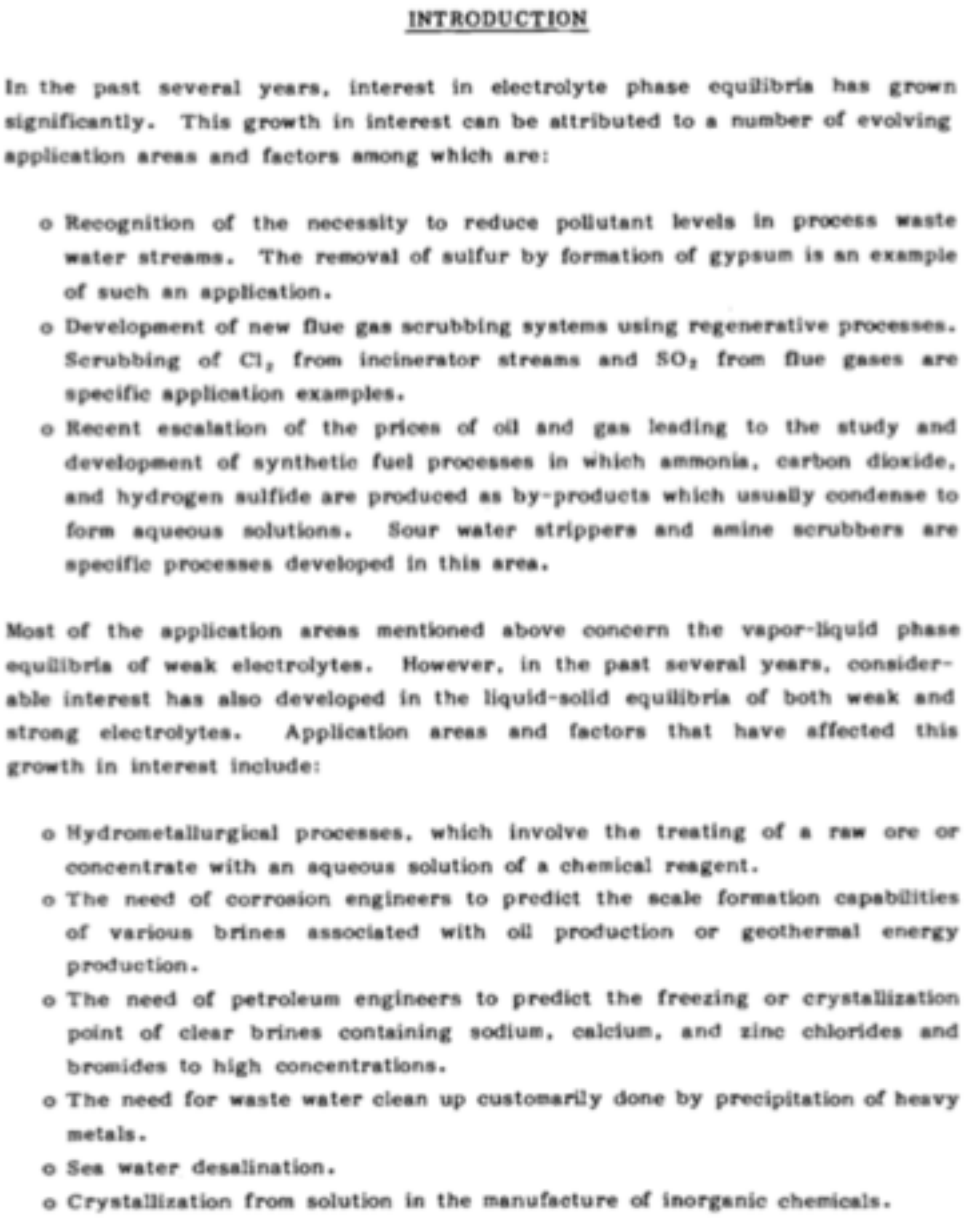


**Figure 18.1. Speciation of sulfuric acid in aqueous solutions as measured by experiments[1] and modeled by OLI Systems, Inc.[2] Note the square root scale to emphasize the dilute region.**

# Chapter 18 Electrolytes

Handbook of Aqueous Electrolyte Thermodynamics



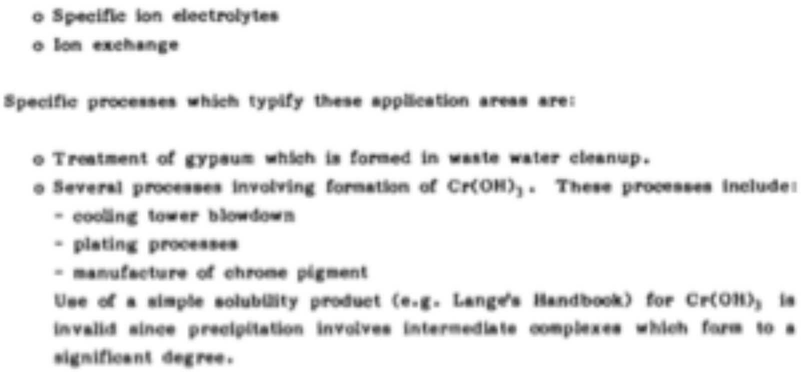
## INTRODUCTION

In the past several years, interest in electrolyte phase equilibria has grown significantly. This growth in interest can be attributed to a number of evolving application areas and factors among which are:

- Recognition of the necessity to reduce pollutant levels in process waste water streams. The removal of sulfur by formation of gypsum is an example of such an application.
- Development of new flue gas scrubbing systems using regenerative processes. Scrubbing of $Cl_2$ from incinerator streams and $SO_2$ from flue gases are specific application examples.
- Recent escalation of the prices of oil and gas leading to the study and development of synthetic fuel processes in which ammonia, carbon dioxide, and hydrogen sulfide are produced as by-products which usually condense to form aqueous solutions. Sour water strippers and amine scrubbers are specific processes developed in this area.

Most of the application areas mentioned above concern the vapor-liquid phase equilibria of weak electrolytes. However, in the past several years, considerable interest has also developed in the liquid-solid equilibria of both weak and strong electrolytes. Application areas and factors that have affected this growth in interest include:

- Hydrometallurgical processes, which involve the treating of a raw ore or concentrate with an aqueous solution of a chemical reagent.
- The need of corrosion engineers to predict the scale formation capabilities of various brines associated with oil production or geothermal energy production.
- The need of petroleum engineers to predict the freezing or crystallization point of clear brines containing sodium, calcium, and zinc chlorides and bromides to high concentrations.
- The need for waste water clean up customarily done by precipitation of heavy metals.
- Sea water desalination.
- Crystallization from solution in the manufacture of inorganic chemicals.



- Specific ion electrolytes
- Ion exchange

Specific processes which typify these application areas are:

- Treatment of gypsum which is formed in waste water cleanup.
- Several processes involving formation of $Cr(OH)_3$. These processes include:
  - cooling tower blowdown
  - plating processes
  - manufacture of chrome pigment

  Use of a simple solubility product (e.g. Lange's Handbook) for $Cr(OH)_3$ is invalid since precipitation involves intermediate complexes which form to a significant degree.

# Colligative (counting) Properties

$$\ln(x_i\gamma_i) = \frac{-\Delta H_i^{fus}}{R}\left(\frac{1}{T}-\frac{1}{T_{m,i}}\right)$$

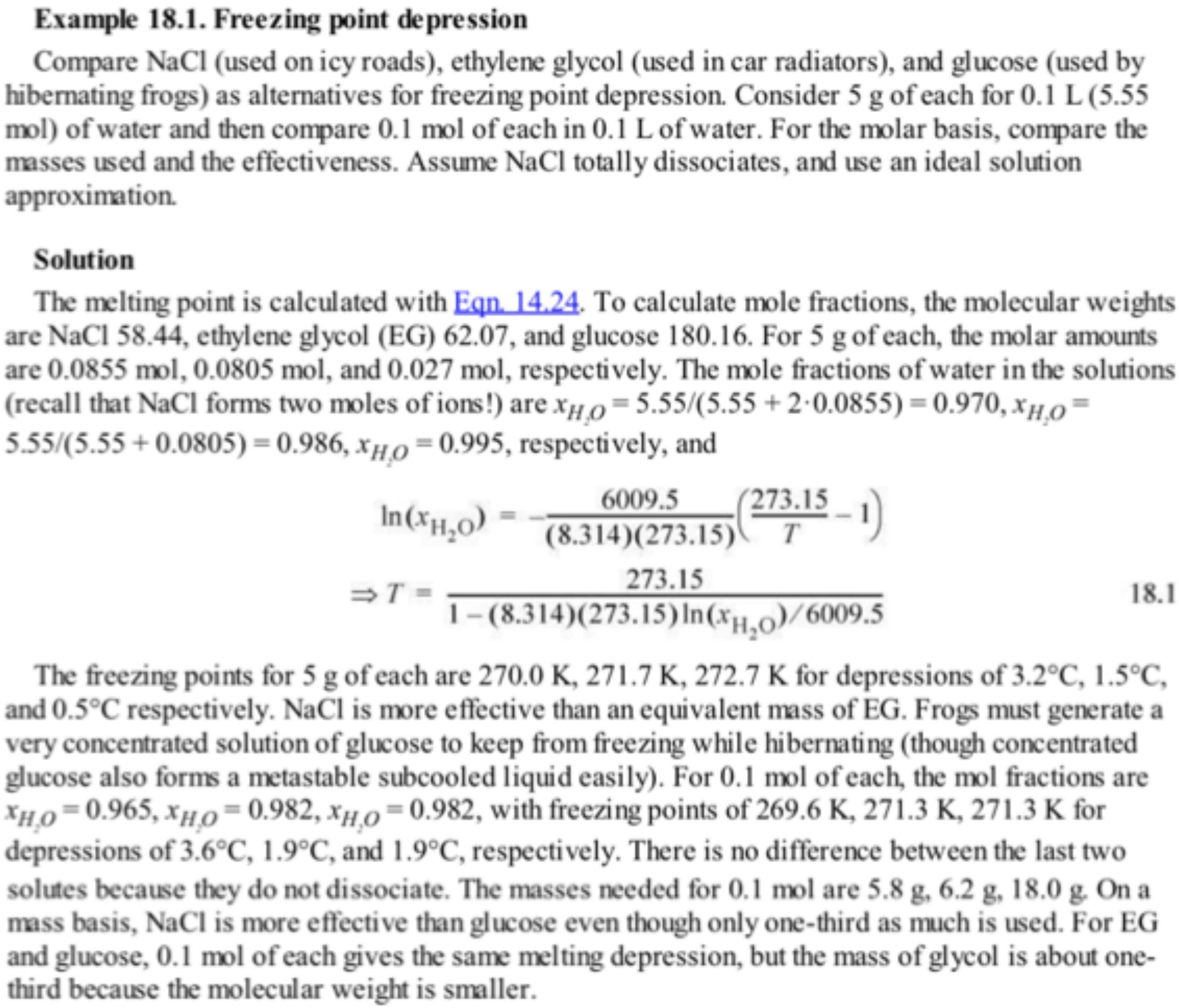
Melting Point Depression

$$\Pi = -\frac{RT}{V_W}\ln a_W$$

Osmotic Pressure $\Pi/RT = (c/M_w)\,(1 + B_2\,c + \ldots)$

$$y_{H2O}\,P = P = x_{H2O}P_{H20}^{Sat}$$

Boiling Point Elevation (for non-volatile solute)



**Example 18.1. Freezing point depression**

Compare NaCl (used on icy roads), ethylene glycol (used in car radiators), and glucose (used by hibernating frogs) as alternatives for freezing point depression. Consider 5 g of each for 0.1 L (5.55 mol) of water and then compare 0.1 mol of each in 0.1 L of water. For the molar basis, compare the masses used and the effectiveness. Assume NaCl totally dissociates, and use an ideal solution approximation.

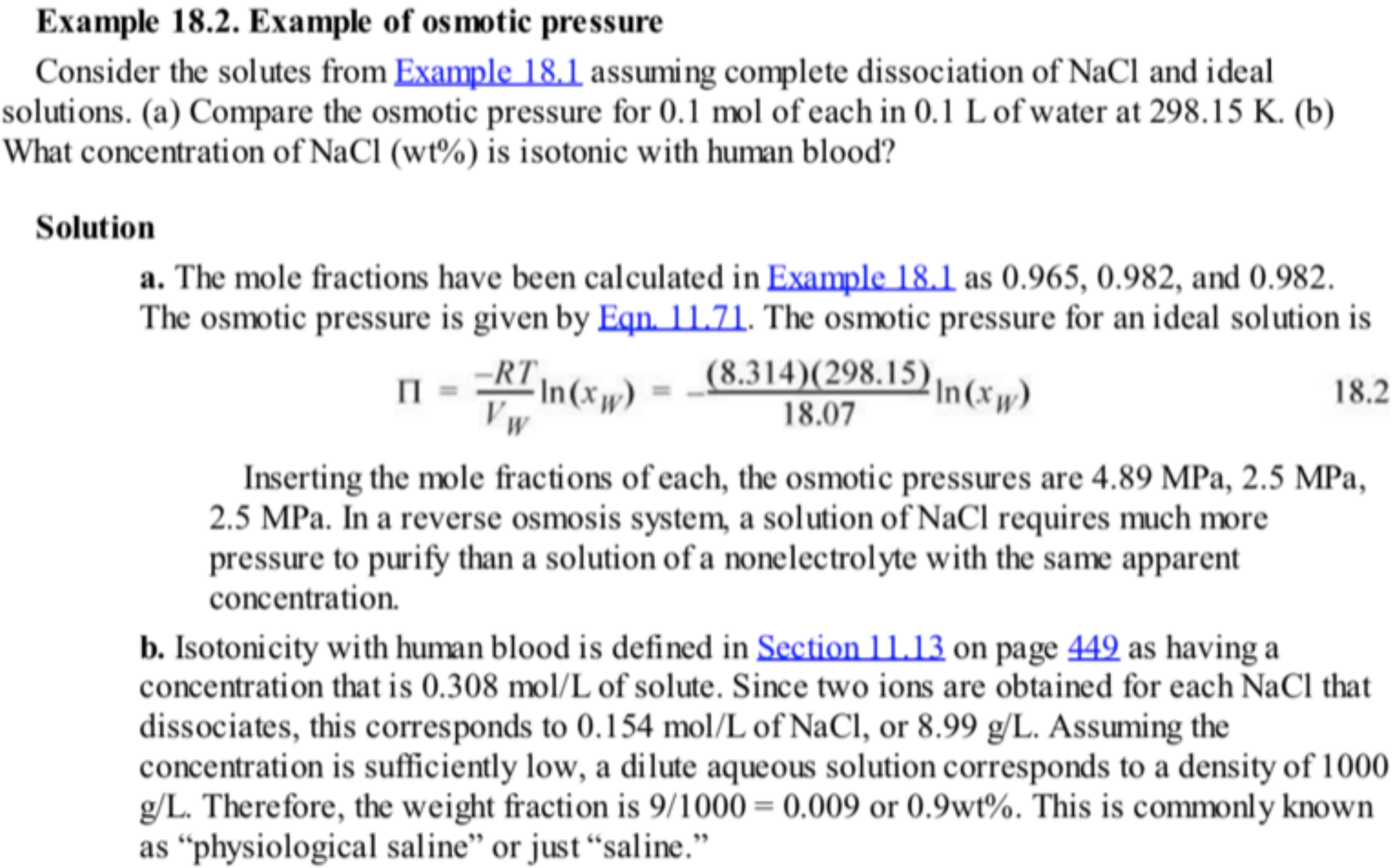
**Solution**

The melting point is calculated with Eqn. 14.24. To calculate mole fractions, the molecular weights are NaCl 58.44, ethylene glycol (EG) 62.07, and glucose 180.16. For 5 g of each, the molar amounts are 0.0855 mol, 0.0805 mol, and 0.027 mol, respectively. The mole fractions of water in the solutions (recall that NaCl forms two moles of ions!) are $x_{H_2O} = 5.55/(5.55 + 2\cdot 0.0855) = 0.970$, $x_{H_2O} = 5.55/(5.55 + 0.0805) = 0.986$, $x_{H_2O} = 0.995$, respectively, and

$$\ln(x_{\mathrm{H_2O}}) = -\frac{6009.5}{(8.314)(273.15)}\left(\frac{273.15}{T} - 1\right)$$

$$\Rightarrow T = \frac{273.15}{1 - (8.314)(273.15)\ln(x_{\mathrm{H_2O}})/6009.5} \qquad 18.1$$

The freezing points for 5 g of each are 270.0 K, 271.7 K, 272.7 K for depressions of 3.2°C, 1.5°C, and 0.5°C respectively. NaCl is more effective than an equivalent mass of EG. Frogs must generate a very concentrated solution of glucose to keep from freezing while hibernating (though concentrated glucose also forms a metastable subcooled liquid easily). For 0.1 mol of each, the mol fractions are $x_{H_2O} = 0.965$, $x_{H_2O} = 0.982$, $x_{H_2O} = 0.982$, with freezing points of 269.6 K, 271.3 K, 271.3 K for depressions of 3.6°C, 1.9°C, and 1.9°C, respectively. There is no difference between the last two solutes because they do not dissociate. The masses needed for 0.1 mol are 5.8 g, 6.2 g, 18.0 g. On a mass basis, NaCl is more effective than glucose even though only one-third as much is used. For EG and glucose, 0.1 mol of each gives the same melting depression, but the mass of glycol is about one-third because the molecular weight is smaller.



**Example 18.2. Example of osmotic pressure**

Consider the solutes from Example 18.1 assuming complete dissociation of NaCl and ideal solutions. (a) Compare the osmotic pressure for 0.1 mol of each in 0.1 L of water at 298.15 K. (b) What concentration of NaCl (wt%) is isotonic with human blood?

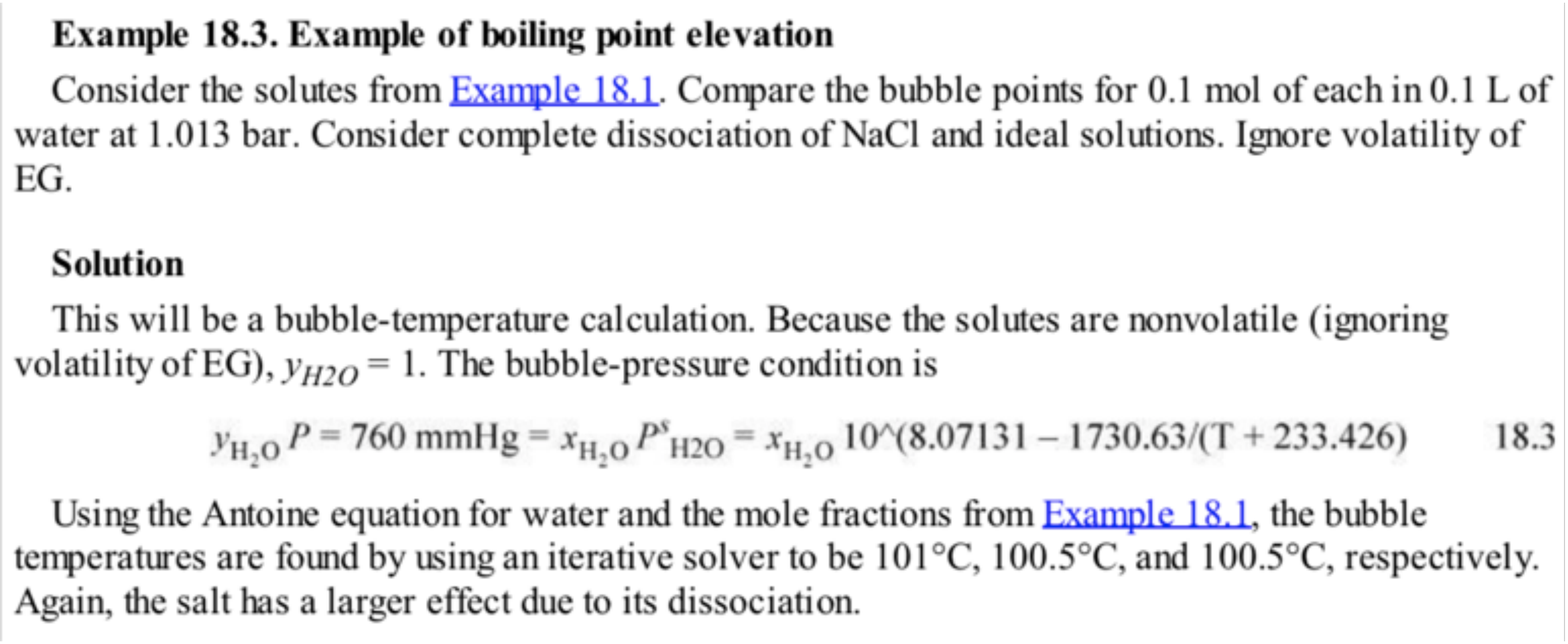
**Solution**

**a.** The mole fractions have been calculated in Example 18.1 as 0.965, 0.982, and 0.982. The osmotic pressure is given by Eqn. 11.71. The osmotic pressure for an ideal solution is

$$\Pi = \frac{-RT}{V_W}\ln(x_W) = -\frac{(8.314)(298.15)}{18.07}\ln(x_W) \tag{18.2}$$

Inserting the mole fractions of each, the osmotic pressures are 4.89 MPa, 2.5 MPa, 2.5 MPa. In a reverse osmosis system, a solution of NaCl requires much more pressure to purify than a solution of a nonelectrolyte with the same apparent concentration.

**b.** Isotonicity with human blood is defined in Section 11.13 on page 449 as having a concentration that is 0.308 mol/L of solute. Since two ions are obtained for each NaCl that dissociates, this corresponds to 0.154 mol/L of NaCl, or 8.99 g/L. Assuming the concentration is sufficiently low, a dilute aqueous solution corresponds to a density of 1000 g/L. Therefore, the weight fraction is 9/1000 = 0.009 or 0.9wt%. This is commonly known as “physiological saline” or just “saline.”



**Example 18.3. Example of boiling point elevation**

Consider the solutes from Example 18.1. Compare the bubble points for 0.1 mol of each in 0.1 L of water at 1.013 bar. Consider complete dissociation of NaCl and ideal solutions. Ignore volatility of EG.

**Solution**

This will be a bubble-temperature calculation. Because the solutes are nonvolatile (ignoring volatility of EG), $y_{H2O} = 1$. The bubble-pressure condition is

$$y_{H_2O} P = 760 \text{ mmHg} = x_{H_2O} P^s{}_{H2O} = x_{H_2O} \, 10\text{^}(8.07131 - 1730.63/(T + 233.426)) \qquad 18.3$$

Using the Antoine equation for water and the mole fractions from Example 18.1, the bubble temperatures are found by using an iterative solver to be 101°C, 100.5°C, and 100.5°C, respectively. Again, the salt has a larger effect due to its dissociation.

# Speciation and dissociation constant $K_{a,298}$, charge balance

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

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

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

$a_{H+}$ is dimensionless, $[H^+]$ is moles/liter (molarity, $M_{H+}$)
A neutral solution is pure water so $a_{H2O} = 1$
With temperature changes $[H^+]$ changes due to thermal expansion
Molality, number of moles of $H^+$ per kg of $H_2O$ is used, $m_{H+}$

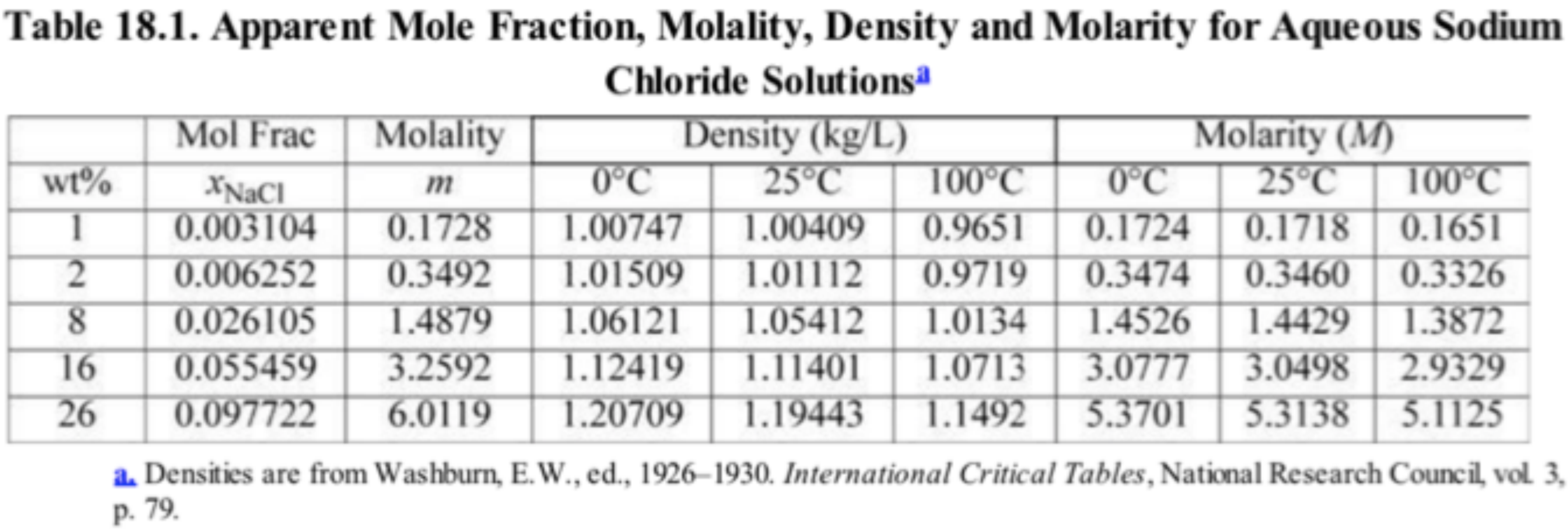


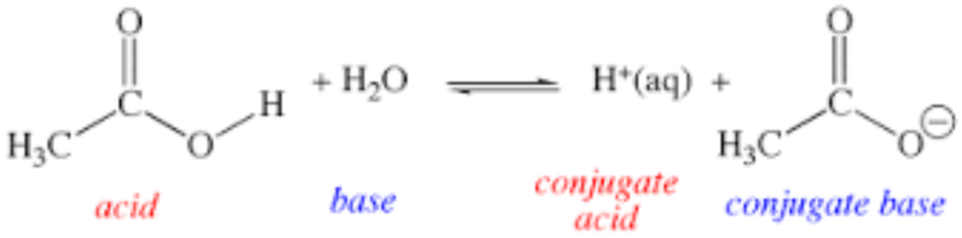
**Table 18.1. Apparent Mole Fraction, Molality, Density and Molarity for Aqueous Sodium Chloride Solutions**[a]

| | Mol Frac | Molality | Density (kg/L) | | | Molarity ($M$) | | |
|---|---|---|---|---|---|---|---|---|
| wt% | $x_{NaCl}$ | $m$ | 0°C | 25°C | 100°C | 0°C | 25°C | 100°C |
| 1 | 0.003104 | 0.1728 | 1.00747 | 1.00409 | 0.9651 | 0.1724 | 0.1718 | 0.1651 |
| 2 | 0.006252 | 0.3492 | 1.01509 | 1.01112 | 0.9719 | 0.3474 | 0.3460 | 0.3326 |
| 8 | 0.026105 | 1.4879 | 1.06121 | 1.05412 | 1.0134 | 1.4526 | 1.4429 | 1.3872 |
| 16 | 0.055459 | 3.2592 | 1.12419 | 1.11401 | 1.0713 | 3.0777 | 3.0498 | 2.9329 |
| 26 | 0.097722 | 6.0119 | 1.20709 | 1.19443 | 1.1492 | 5.3701 | 5.3138 | 5.1125 |

[a] Densities are from Washburn, E.W., ed., 1926–1930. *International Critical Tables*, National Research Council, vol. 3, p. 79.

# Concentration with speciation

Acetic Acid in water



$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-4.8}$$

Apparent concentration:  g/liter you put in of $C_2H_4O_2$
True concentration has to do with the dissociation species (based on a model)
VLE is based on the true concentration of undissociated species

## *pH*

$$pH = -\log_{10}(a_{H+})$$

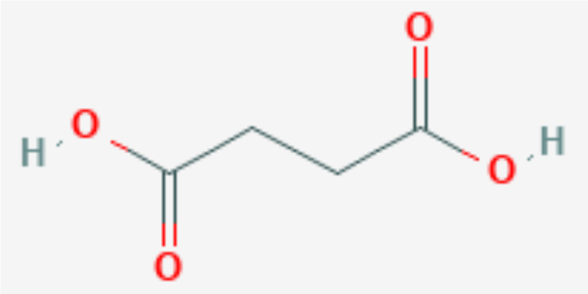
$a_{H+}$ is molal (molar as an approximation)

$$K_{a,w} = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = 10^{-14}$$

$$-\log(a_{H^+}a_{OH^-}) = -\log(a_{H^+}) = -\log(a_{OH^-}) = -\log K_{a,w}$$

$$pH + pOH = pK_{a,w}$$

# Electrolyte Equilibrium Constant



Succinic Acid

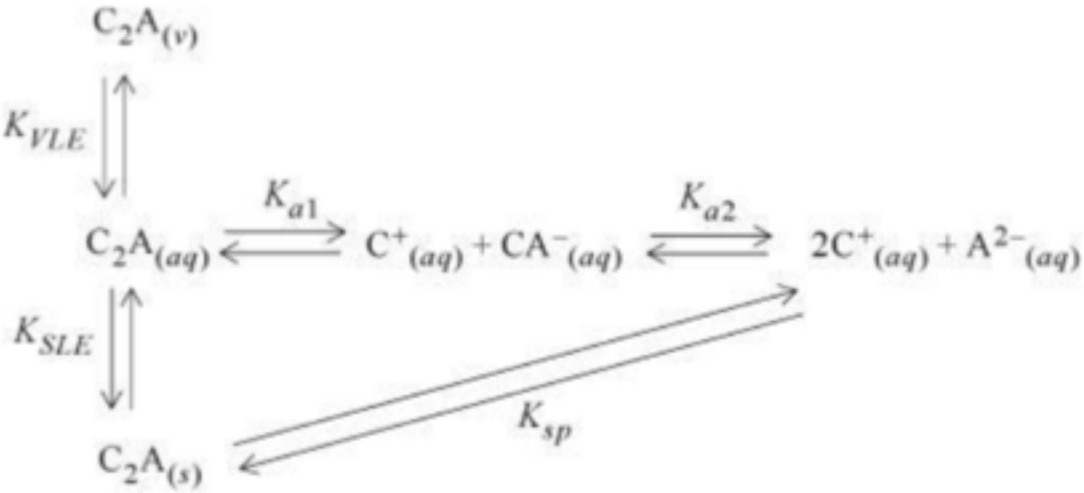


**Figure 18.2. Reaction network for an example electrolyte where C is a monovalent cation and A is a divalent cation. The equilibrium constants are related as explained in the text.**

$$\mu_i^L = \mu_{i(aq)}$$

$$K_{sp} = K_{SLE}K_{a1}K_{a2}$$

$$C_2A_{(s)} \overset{K_{sp}}{\rightleftarrows} 2C^+_{(aq)} + A^{2-}_{(aq)}$$

Water of hydration and hydronium ion

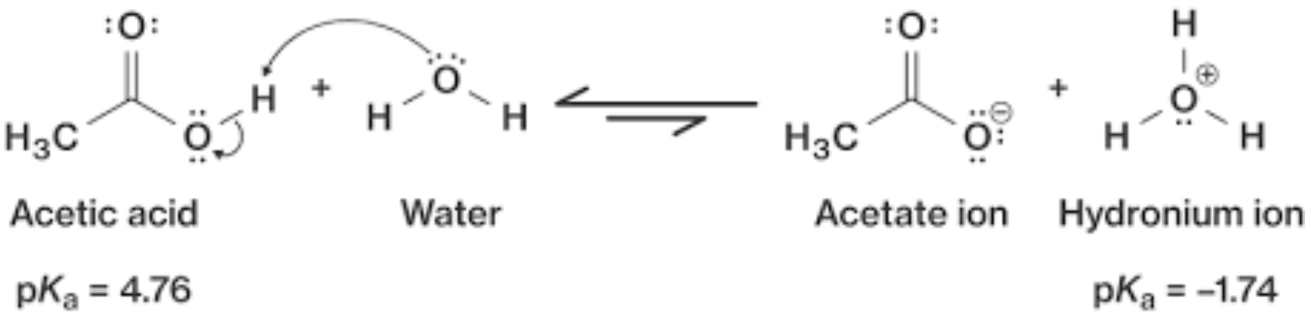
Cations have water of hydration associated with the ion

Degree of hydration changes with concentration

At high concentrations ion pairs with the counter ion form

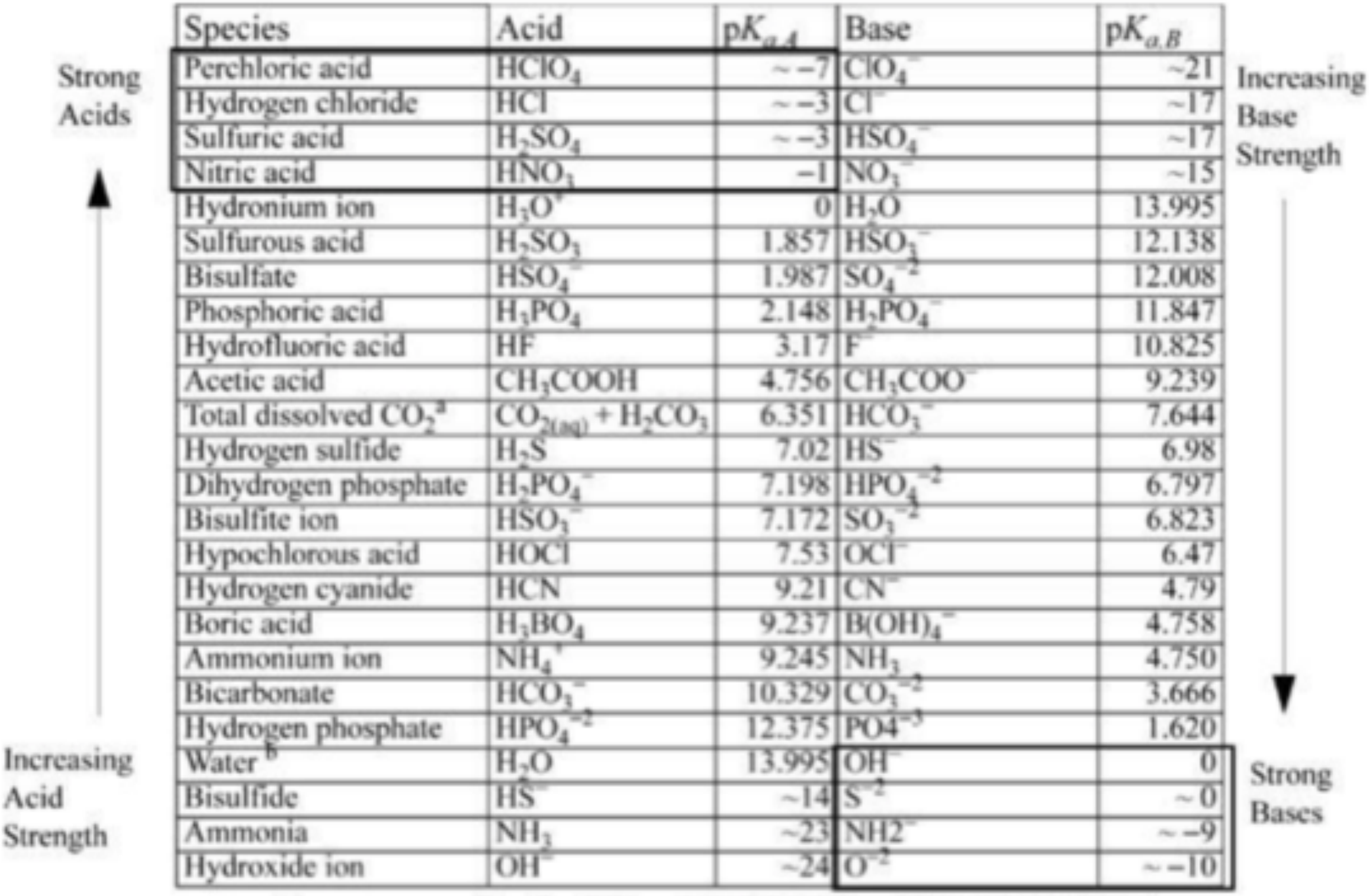
$$2H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + OH^-_{(aq)}$$

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



# Acids and conjugate bases

**Table 18.2. Reference Table for Relative Acid and Base Strengths at 25°C Based on $pK_{a,water} = -13.995$. $pK_b = 13.995 - pK_a$**



| Species | Acid | $pK_{a,A}$ | Base | $pK_{a,B}$ |
|---|---|---|---|---|
| Perchloric acid | $HClO_4$ | ~ −7 | $ClO_4^-$ | ~21 |
| Hydrogen chloride | $HCl$ | ~ −3 | $Cl^-$ | ~17 |
| Sulfuric acid | $H_2SO_4$ | ~ −3 | $HSO_4^-$ | ~17 |
| Nitric acid | $HNO_3$ | −1 | $NO_3^-$ | ~15 |
| Hydronium ion | $H_3O^+$ | 0 | $H_2O$ | 13.995 |
| Sulfurous acid | $H_2SO_3$ | 1.857 | $HSO_3^-$ | 12.138 |
| Bisulfate | $HSO_4^-$ | 1.987 | $SO_4^{-2}$ | 12.008 |
| Phosphoric acid | $H_3PO_4$ | 2.148 | $H_2PO_4^-$ | 11.847 |
| Hydrofluoric acid | $HF$ | 3.17 | $F^-$ | 10.825 |
| Acetic acid | $CH_3COOH$ | 4.756 | $CH_3COO^-$ | 9.239 |
| Total dissolved $CO_2$[a] | $CO_{2(aq)} + H_2CO_3$ | 6.351 | $HCO_3^-$ | 7.644 |
| Hydrogen sulfide | $H_2S$ | 7.02 | $HS^-$ | 6.98 |
| Dihydrogen phosphate | $H_2PO_4^-$ | 7.198 | $HPO_4^{-2}$ | 6.797 |
| Bisulfite ion | $HSO_3^-$ | 7.172 | $SO_3^{-2}$ | 6.823 |
| Hypochlorous acid | $HOCl$ | 7.53 | $OCl^-$ | 6.47 |
| Hydrogen cyanide | $HCN$ | 9.21 | $CN^-$ | 4.79 |
| Boric acid | $H_3BO_4$ | 9.237 | $B(OH)_4^-$ | 4.758 |
| Ammonium ion | $NH_4^+$ | 9.245 | $NH_3$ | 4.750 |
| Bicarbonate | $HCO_3^-$ | 10.329 | $CO_3^{-2}$ | 3.666 |
| Hydrogen phosphate | $HPO_4^{-2}$ | 12.375 | $PO4^{-3}$ | 1.620 |
| Water[b] | $H_2O$ | 13.995 | $OH^-$ | 0 |
| Bisulfide | $HS^-$ | ~14 | $S^{-2}$ | ~ 0 |
| Ammonia | $NH_3$ | ~23 | $NH2^-$ | ~ −9 |
| Hydroxide ion | $OH^-$ | ~24 | $O^{-2}$ | ~ −10 |

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of $H_2O$ is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

# Strong Acid

$[Cl^-] = C_A$ material balance for complete dissociation 18.17

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium 18.18

$[H^+] = [Cl^-] + [OH^-]$ charge balance 18.19

$[H^+] = C_A + [OH^-]$ proton condition 18.20

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

$[H^+]$ is large so $[OH^-]$ is very small, can be ignored

$pH \sim pC_A$

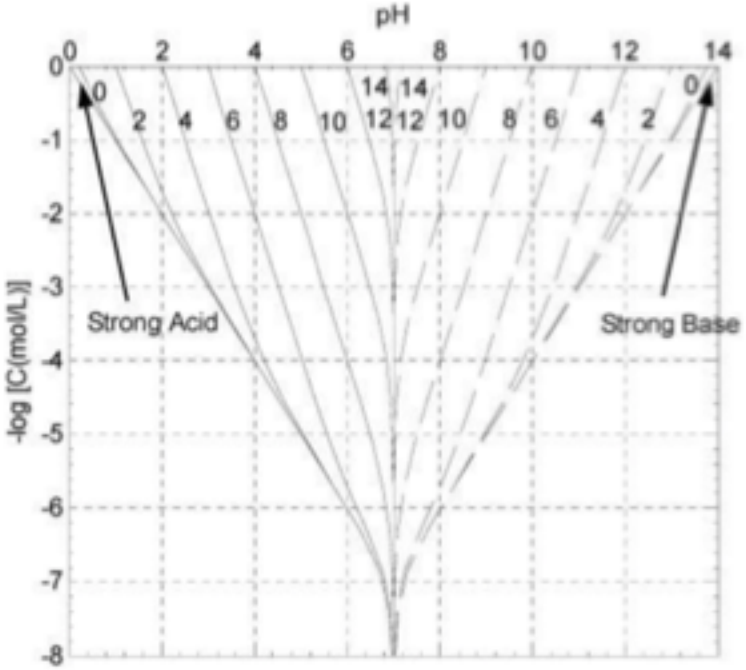


**Figure 18.3. Flood diagram showing the behavior of strong monoprotic acids, weak monoprotic acids, salts of weak monoprotic bases, and strong monovalent bases.**

# Strong Base

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

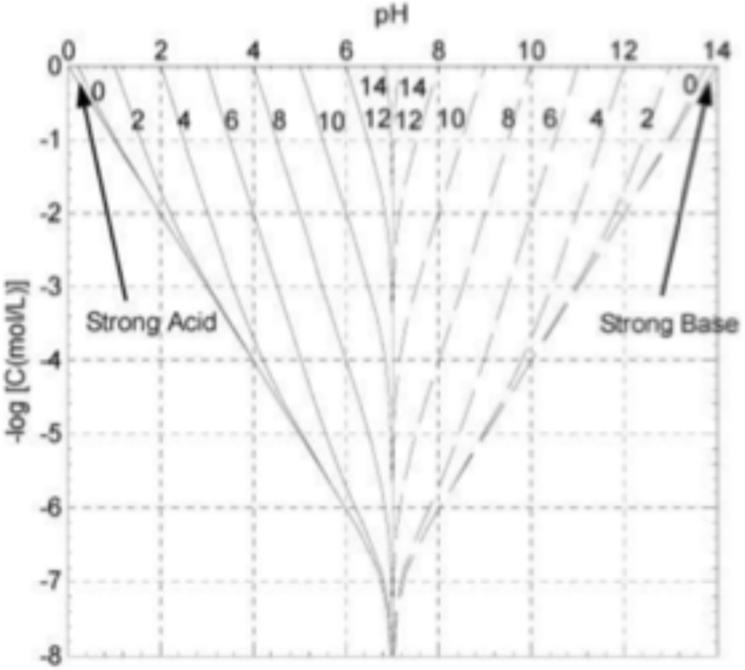
$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium

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

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

$[OH^-]$ is large so $[H^+]$ is very small, can be ignored

$pOH \sim pC_B$



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# Weak monoprotic Acid (Acetic Acid $pK_{a,A} = 4.7$)

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

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

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

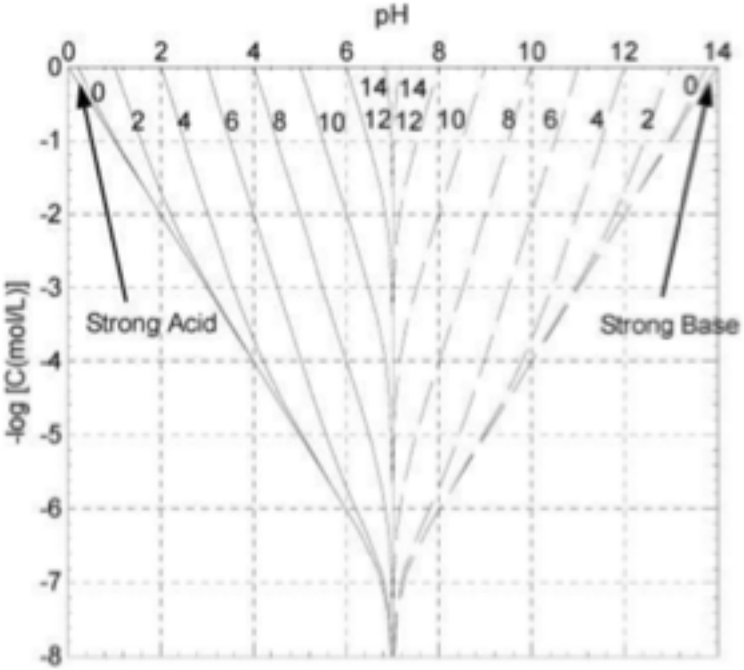
$[H^+] = [A^-] + [OH^-]$ charge balance

$[H^+]^3 + K_{a,A}[H^+]^2 - (C_A K_{a,A} + K_{a,w})[H^+] - K_{a,A}K_{a,w} = 0$ (Hint: limited utility)

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

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

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



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# Weak monoprotic Based (Acetate ion $p\mathrm{K}_{a,B} = 9.3$)

$$A^- + H_2O \rightleftarrows HA + OH^-.$$

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

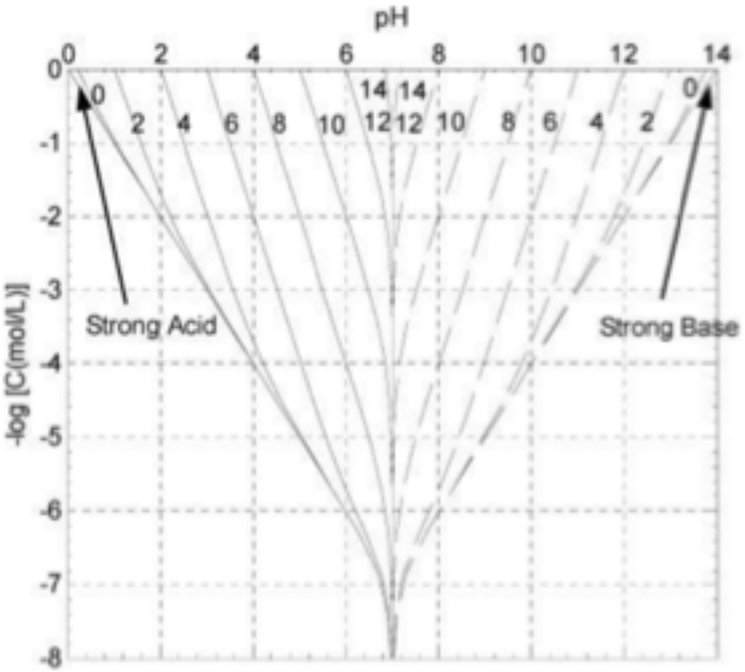
$K_{a,B} = [HA][OH^-]/[A^-]$ equilibrium

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

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

Start with sodium acetate which is a strong electrolyte, the resulting acetate ion is a weak base

$K_{a,B}[H^+]^3 + (C_B K_{a,B} + K_{a,w})[H^+]^2 - K_{a,B}K_{a,w}[H^+] - K_{a,w}^2 = 0$ limited use



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# Acid or Base Added to water

$$\boxed{pK_{a,A} + pK_{a,B} = pK_{a,w} \quad \text{or} \quad K_{a,A}K_{a,B} = K_{a,w}} \qquad 18.37$$

# Example 18.4. Dissociation of fluconazole

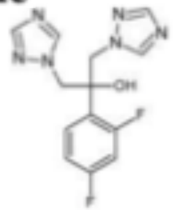


Figure 18.4. Structure of Fluconazole.

**Base** **Acid**

$$\text{Fluconazole} + H_2O \rightleftarrows \text{Fluconazole}^+ + OH^- \qquad 18.38$$

$$\ln(K_a) = -1.28 - 8000/T \qquad 18.39$$

Eqn. 18.39 represents $K_{a,B}$.

fluconazole and its ion and the hydroxyl are on the molality scale

Randall scale. Determine the percentage of fluconazole dissociated at pH 7 and pH 1.5 when the apparent amount of fluconazole in aqueous solution is 1.5E-3m. The molecular weight of fluconazole is 306.27. Assume ideal solutions.

Standard acid form of eqn. 18.39

$$\text{Fluconazole}^+ + H_2O \rightleftarrows \text{Fluconazole} + H_3O^+$$

At 298K, $K_{a,B}$ = 6.18 e-13 from eqn. 18.39

$K_{a,A}$ = 1e-14/6.18 e-13 = 0.0162 or p$K_{a,A}$ = 1.79

Fluconazole is protonated below p$H$ = 1.8 and neutral (undissociated) above

p$H$ = 7

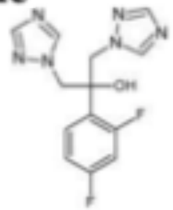
$\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})}$ useful for undissociated acid 18.30

$[\text{Fluc}^+] = C_{fluc}[H^+] / ([H^+] + K_{a,A}) = 1.5\text{E-}3\text{m}(10^{-7})/(10^{-7} + 0.01617) = 9.27\text{E-}9\text{m}$.

None is dissociated so:

[Fluc] = 1.5E-3m, and the fraction protonated is 9.27E-9/(1.5E-3)· 100% = 0% (trace).

# Example 18.4. Dissociation of fluconazole



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p$H$ = 1.5 $\boxed{[HA] = C_A[H^+]/([H^+] + K_{a,A})}$ useful for undissociated acid 18.30

$[\text{Fluc}^+] = C_{fluc}[H^+] / ([H^+] + K_{a,A}) =$ 1.5E-3m$(10^{-1.5})/(10^{-1.5} + 0.01617)$ = 9.9E-4m.

About half is dissociated:

[Fluc] = 1.5E-3m – 9.9E-4m = 5.1E-4m. protonated is 9.9E-4/(1.5E-3)·100% = 66%.

# Sillén Diagram or Bjerrum Plot or Hägg Diagram

$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$

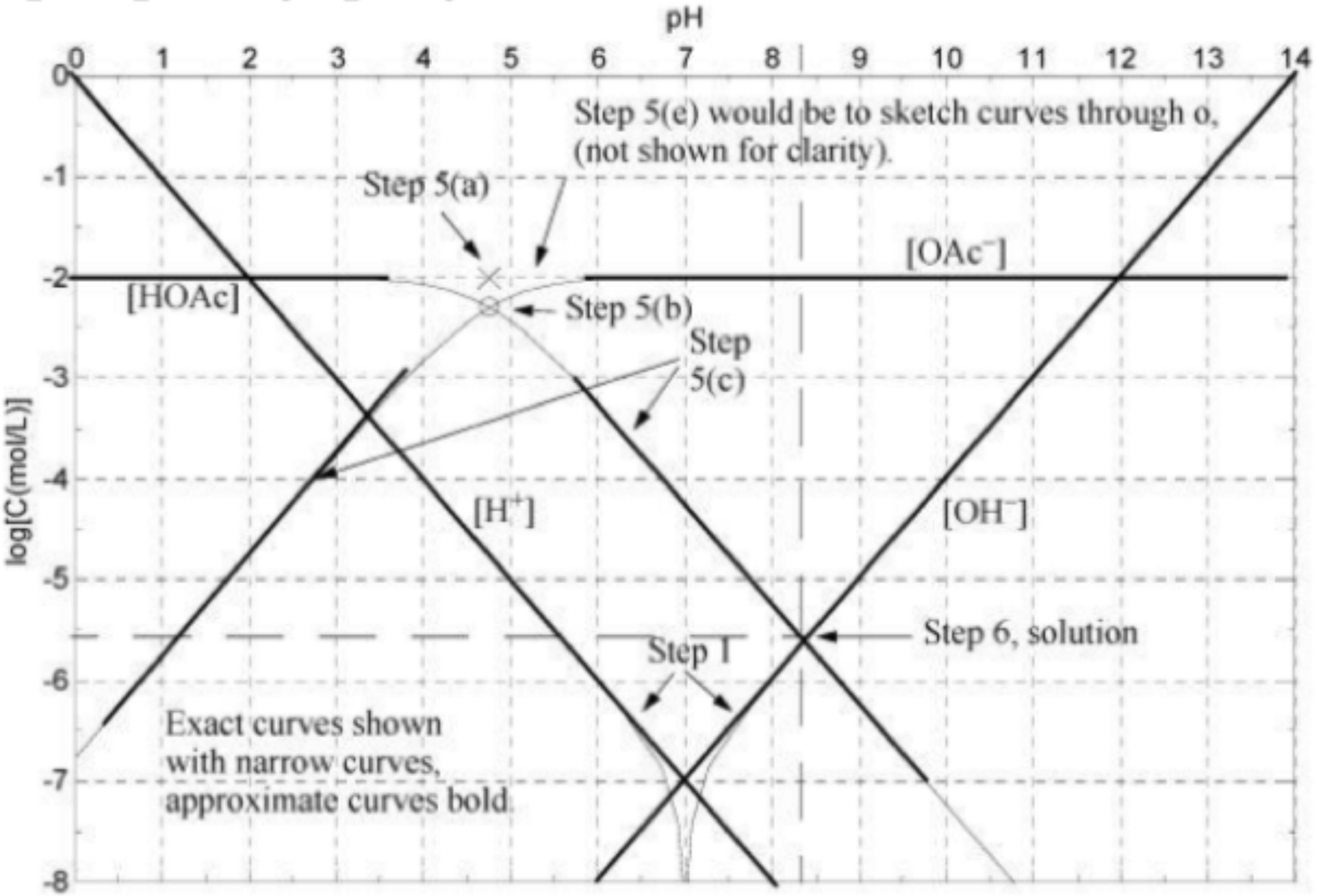
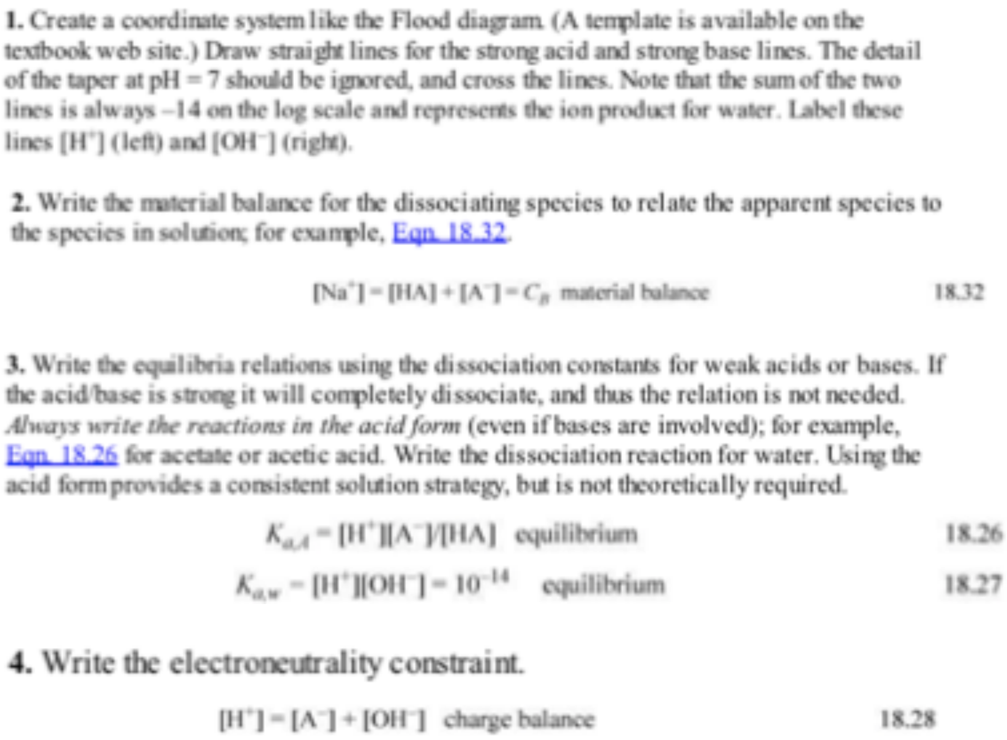


**Figure 18.5. Sillèn plot for Example 18.5, acetate with an overall concentration 0.01 M.**

# Sillén Diagram



**1.** Create a coordinate system like the Flood diagram. (A template is available on the textbook web site.) Draw straight lines for the strong acid and strong base lines. The detail of the taper at pH = 7 should be ignored, and cross the lines. Note that the sum of the two lines is always −14 on the log scale and represents the ion product for water. Label these lines $[H^+]$ (left) and $[OH^-]$ (right).

**2.** Write the material balance for the dissociating species to relate the apparent species to the species in solution; for example, Eqn. 18.32.

$$[Na^+] = [HA] + [A^-] = C_B \quad \text{material balance} \qquad 18.32$$

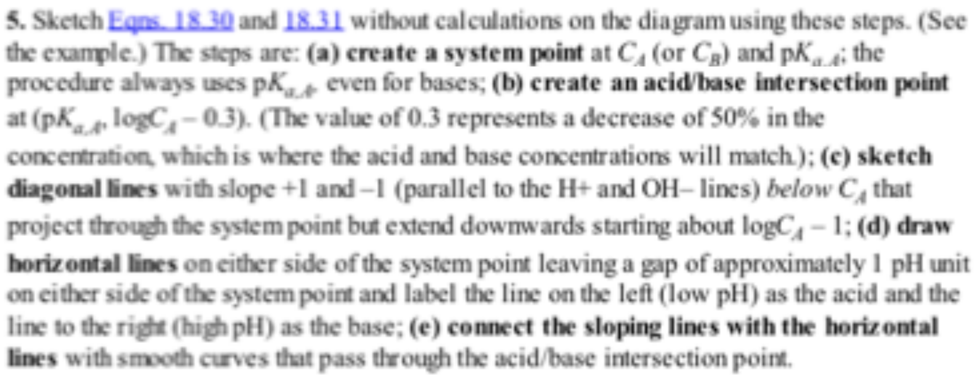
**3.** Write the equilibria relations using the dissociation constants for weak acids or bases. If the acid/base is strong it will completely dissociate, and thus the relation is not needed. *Always write the reactions in the acid form* (even if bases are involved); for example, Eqn. 18.26 for acetate or acetic acid. Write the dissociation reaction for water. Using the acid form provides a consistent solution strategy, but is not theoretically required.

$$K_{a,A} = [H^+][A^-]/[HA] \quad \text{equilibrium} \qquad 18.26$$

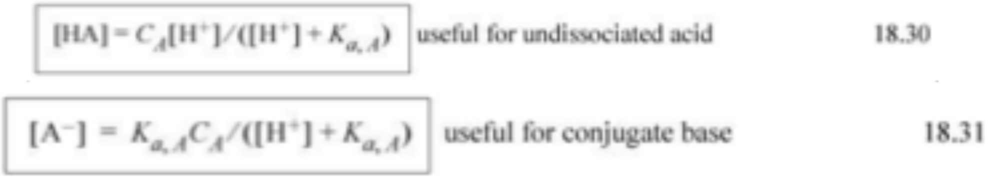
$$K_{a,w} = [H^+][OH^-] = 10^{-14} \quad \text{equilibrium} \qquad 18.27$$

**4.** Write the electroneutrality constraint.

$$[H^+] = [A^-] + [OH^-] \quad \text{charge balance} \qquad 18.28$$



**5.** Sketch Eqns. 18.30 and 18.31 without calculations on the diagram using these steps. (See the example.) The steps are: **(a) create a system point** at $C_A$ (or $C_B$) and p$K_{a,A}$; the procedure always uses p$K_{a,A}$, even for bases; **(b) create an acid/base intersection point** at (p$K_{a,A}$, log$C_A$ − 0.3). (The value of 0.3 represents a decrease of 50% in the concentration, which is where the acid and base concentrations will match.); **(c) sketch diagonal lines** with slope +1 and −1 (parallel to the H+ and OH− lines) *below* $C_A$ that project through the system point but extend downwards starting about log$C_A$ − 1; **(d) draw horizontal lines** on either side of the system point leaving a gap of approximately 1 pH unit on either side of the system point and label the line on the left (low pH) as the acid and the line to the right (high pH) as the base; **(e) connect the sloping lines with the horizontal lines** with smooth curves that pass through the acid/base intersection point.



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

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

**6.** Decide which concentrations are largest and which are least significant. Let $C_i$ be the apparent concentration. The goal is to simplify the balances and provide a good guess for true concentrations. This is almost always done by converting the charge balance to a proton condition by inserting the mass balance to eliminate terms that are largest and leave smaller terms that are more similar in magnitude. Use the diagram as a guide to decide which concentrations are insignificant in the pH range expected. The goal is to use the proton condition to identify the intersection of the positive and negative charges of the proton condition. Unless some of the diagonal curves are very close to each other this will be easy. There can be various proton conditions that are equally valid when many ions are present at similar concentrations. Hints: Remember that each unit on the log scale is an order of magnitude. Acids by themselves result in $pH < 7$; bases alone result in $pH > 7$; salts of a strong acid and weak base (e.g., $NH_4^+Cl^-$) are acidic; salts of a weak acid and strong base (e.g., NaOAc) are basic.

**7.** Check the result. The results can be checked by iterating on charge balance pH by inserting Eqns. 18.30 and 18.31 or the analogs.

**Table 18.2. Reference Table for Relative Acid and Base Strengths at 25°C Based on $pK_{a,water}$ = $-13.995$. $pK_b = 13.995 - pK_a$**

Strong Acids

Increasing Base Strength

| Species | Acid | $pK_{a,A}$ | Base | $pK_{a,B}$ |
|---|---|---|---|---|
| Perchloric acid | $HClO_4$ | ~ −7 | $ClO_4^-$ | ~21 |
| Hydrogen chloride | $HCl$ | ~ −3 | $Cl^-$ | ~17 |
| Sulfuric acid | $H_2SO_4$ | ~ −3 | $HSO_4^-$ | ~17 |
| Nitric acid | $HNO_3$ | −1 | $NO_3^-$ | ~15 |
| Hydronium ion | $H_3O^+$ | 0 | $H_2O$ | 13.995 |
| Sulfurous acid | $H_2SO_3$ | 1.857 | $HSO_3^-$ | 12.138 |
| Bisulfate | $HSO_4^-$ | 1.987 | $SO_4^{-2}$ | 12.008 |
| Phosphoric acid | $H_3PO_4$ | 2.148 | $H_2PO_4^-$ | 11.847 |
| Hydrofluoric acid | $HF$ | 3.17 | $F^-$ | 10.825 |
| Acetic acid | $CH_3COOH$ | 4.756 | $CH_3COO^-$ | 9.239 |
| Total dissolved $CO_2$[a] | $CO_{2(aq)} + H_2CO_3$ | 6.351 | $HCO_3^-$ | 7.644 |
| Hydrogen sulfide | $H_2S$ | 7.02 | $HS^-$ | 6.98 |
| Dihydrogen phosphate | $H_2PO_4^-$ | 7.198 | $HPO_4^{-2}$ | 6.797 |
| Bisulfite ion | $HSO_3^-$ | 7.172 | $SO_3^{-2}$ | 6.823 |
| Hypochlorous acid | $HOCl$ | 7.53 | $OCl^-$ | 6.47 |
| Hydrogen cyanide | $HCN$ | 9.21 | $CN^-$ | 4.79 |
| Boric acid | $H_3BO_4$ | 9.237 | $B(OH)_4^-$ | 4.758 |
| Ammonium ion | $NH_4^+$ | 9.245 | $NH_3$ | 4.750 |
| Bicarbonate | $HCO_3^-$ | 10.329 | $CO_3^{-2}$ | 3.666 |
| Hydrogen phosphate | $HPO_4^{-2}$ | 12.375 | $PO4^{-3}$ | 1.620 |
| Water[b] | $H_2O$ | 13.995 | $OH^-$ | 0 |
| Bisulfide | $HS^-$ | ~14 | $S^{-2}$ | ~ 0 |
| Ammonia | $NH_3$ | ~23 | $NH2^-$ | ~ −9 |
| Hydroxide ion | $OH^-$ | ~24 | $O^{-2}$ | ~ −10 |

Increasing Acid Strength

Strong Bases

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of $H_2O$ is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

## Example 18.5. Sillèn diagram for HOAc and NaOAc

Sodium acetate, NaOAc, is dissolved in water at an apparent concentration of $C_B = 10^{-2}$ mol/L. Construct a Sillèn diagram and estimate the pH. For acetic acid, $pK_{a,A} = 4.76$ at room temperature in dilute solutions.

***$[OH^-][H^+]=10^{-14}$ so log $[OH^-]$+log$[H^+]$ = 14 (two lines as drawn)***

**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 18.40

***When one component is small the other is $C_B$***

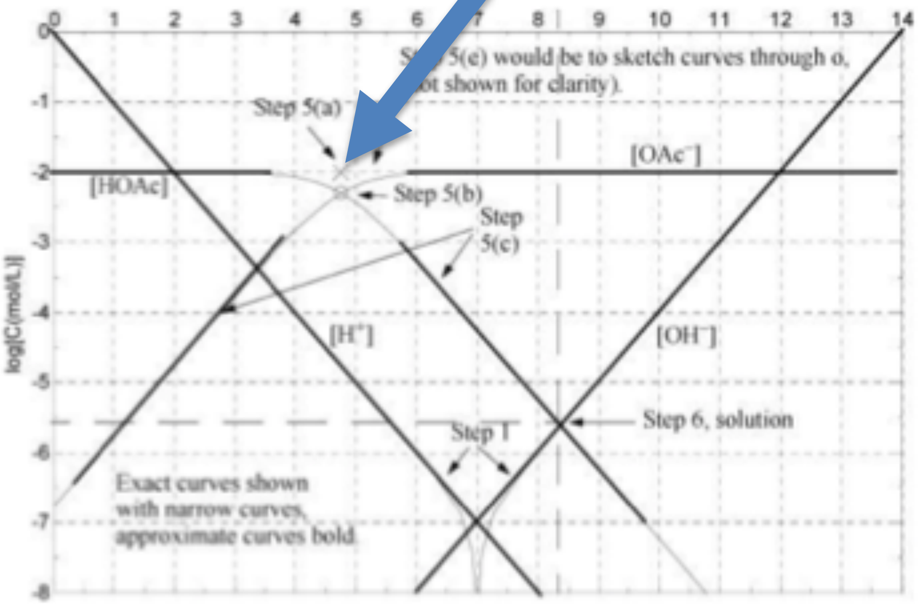
**Step 3:** $K_{a,A} = [OAc^-][H^+]/[HOAc]$ equilibrium 18.41

***When $[OAc^-] = [HOAc]$ then $K_{a,A} = [H^+]$***

$K_{a,w} = [H^+][OH^-] = 10^{-14}$ equilibrium 18.42

**Step 4:** $[H^+] + [Na^+] = [OAc^-] + [OH^-]$ charge balance 18.43

***When $[OAc^-] = [Na^+]$ then $[OH^-] = [HOAc]$ this gives the pH***



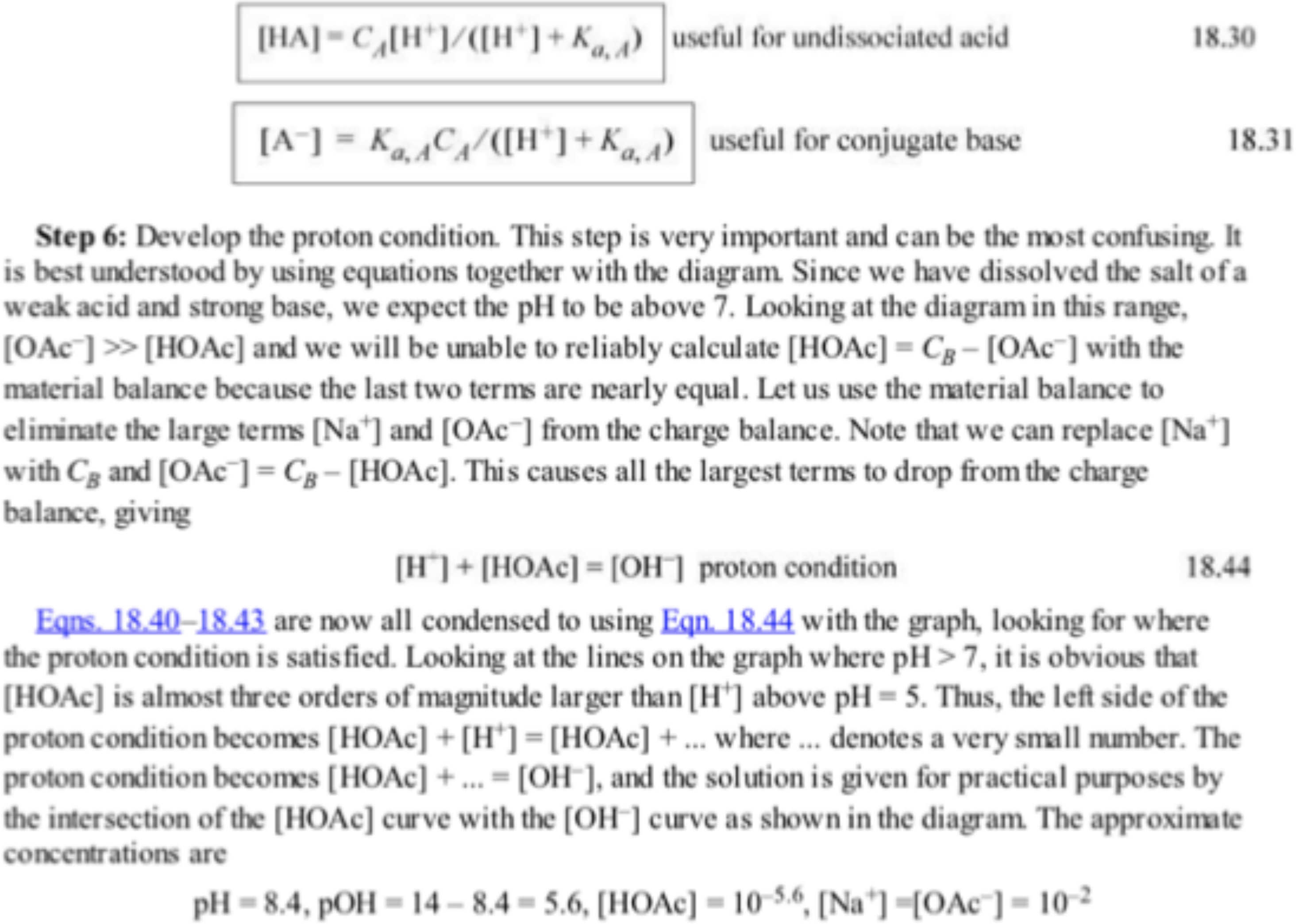
$[HA] = C_A[H^+]/([H^+] + K_{a,A})$

***[HOAc] is parallel to $[H^+]$ when $[H^+]$ is small***

$[A^-] = K_{a,A}C_A/([H^+] + K_{a,A})$

***$[H^+]=10^{-14}/[OH^-]$ so $[OAc^-]$ is parallel to $[OH^-]$ when $[OH^-]$ is small***

**Step 5:** See the diagram labels denoting steps 5(a) and 5(b). Referring to the procedure above indicates the system point (**x**) should be at $C_B$ and p$K_{a,A}$. On the diagram below, use a straight edge to verify that the lines for step 5(c) extrapolate through the **x** from step 5(a). Note that the curves for step 5(e) are not shaded for clarity, but it is obvious that the curves could be easily drawn through o. Recall that step 5 plots Eqns. 18.30 and 18.31 without calculations.



$$\boxed{[\mathrm{HA}] = C_A[\mathrm{H}^+]/([\mathrm{H}^+] + K_{a,A})} \quad \text{useful for undissociated acid} \qquad 18.30$$

$$\boxed{[\mathrm{A}^-] = K_{a,A}C_A/([\mathrm{H}^+] + K_{a,A})} \quad \text{useful for conjugate base} \qquad 18.31$$

**Step 6:** Develop the proton condition. This step is very important and can be the most confusing. It is best understood by using equations together with the diagram. Since we have dissolved the salt of a weak acid and strong base, we expect the pH to be above 7. Looking at the diagram in this range, $[\mathrm{OAc}^-] >> [\mathrm{HOAc}]$ and we will be unable to reliably calculate $[\mathrm{HOAc}] = C_B - [\mathrm{OAc}^-]$ with the material balance because the last two terms are nearly equal. Let us use the material balance to eliminate the large terms $[\mathrm{Na}^+]$ and $[\mathrm{OAc}^-]$ from the charge balance. Note that we can replace $[\mathrm{Na}^+]$ with $C_B$ and $[\mathrm{OAc}^-] = C_B - [\mathrm{HOAc}]$. This causes all the largest terms to drop from the charge balance, giving

$$[\mathrm{H}^+] + [\mathrm{HOAc}] = [\mathrm{OH}^-] \quad \text{proton condition} \qquad 18.44$$

Eqns. 18.40–18.43 are now all condensed to using Eqn. 18.44 with the graph, looking for where the proton condition is satisfied. Looking at the lines on the graph where pH > 7, it is obvious that [HOAc] is almost three orders of magnitude larger than $[\mathrm{H}^+]$ above pH = 5. Thus, the left side of the proton condition becomes $[\mathrm{HOAc}] + [\mathrm{H}^+] = [\mathrm{HOAc}] + \ldots$ where ... denotes a very small number. The proton condition becomes $[\mathrm{HOAc}] + \ldots = [\mathrm{OH}^-]$, and the solution is given for practical purposes by the intersection of the [HOAc] curve with the $[\mathrm{OH}^-]$ curve as shown in the diagram. The approximate concentrations are

$$\mathrm{pH} = 8.4,\ \mathrm{pOH} = 14 - 8.4 = 5.6,\ [\mathrm{HOAc}] = 10^{-5.6},\ [\mathrm{Na}^+] = [\mathrm{OAc}^-] = 10^{-2}$$

**Step 7:** The proton condition is in terms of Eqns. 18.27 and 18.30, and avoiding taking differences, $[OH^-] = 10^{-14}/[H^+] = [H^+] + [HOAc] = [H^+] + C_A[H^+] / ([H^+] + K_{a,A})$

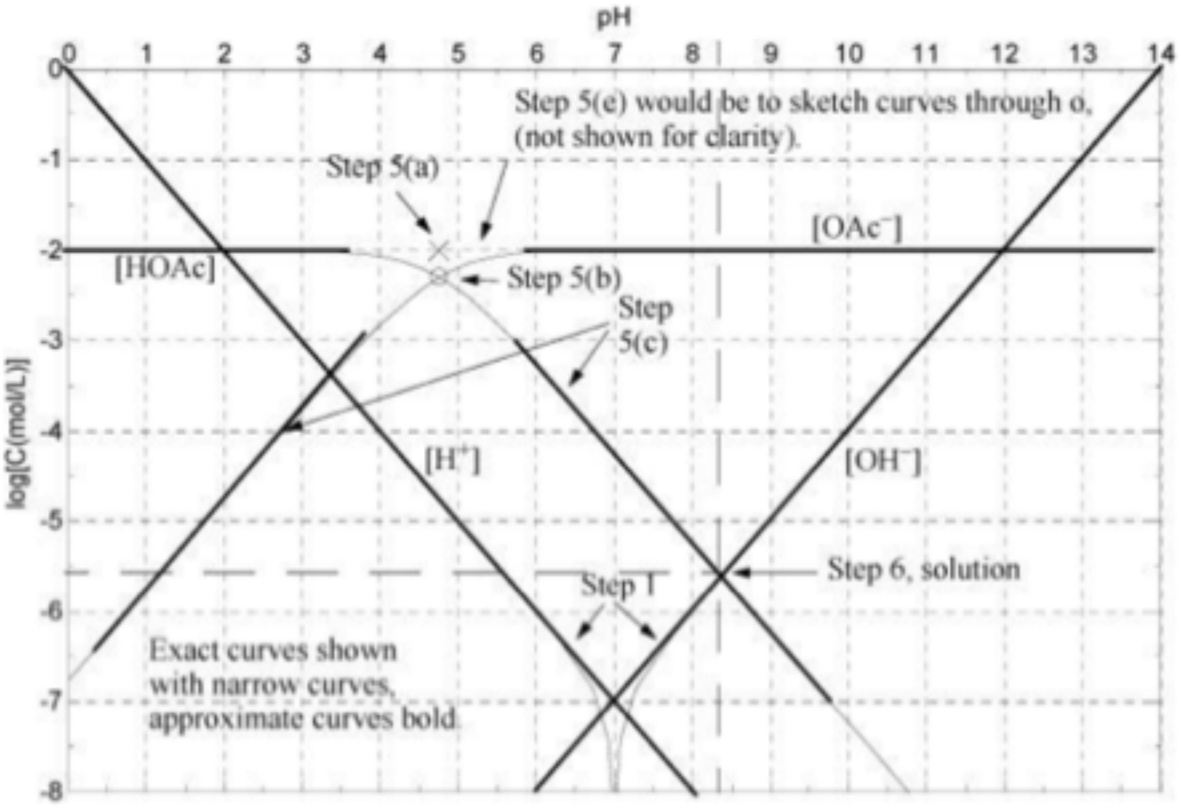
Rearranging for successive substitution on $[H^+]$, and inserting the initial guess of pH = 8.4, iterate on the highest power of $[H^+]$,

$$[H^+]^2 = 10^{-14}/ (1 + C_A / ([H^+] + K_{a,A})) = 10^{-8.4} + (10^{-2})(10^{-8.4})/(10^{-8.4} + 10^{-4.76})$$

$$[H^+] = \sqrt{10^{-14}/(1 + C_A/([H^+] + K_{a,A}))} = \sqrt{10^{-14}/(1 + 10^{-2}/(10^{-8.4} + 10^{-4.76}))}$$

$$= 4.165E\text{-}9$$

pH = 8.38. Plugging this back in results in no further changes. Recall that if successive substitution results in divergence rather than convergence, that the equation needs to be rearranged. See Appendix A, Section A.4.



## Polyprotic Acids and Bases

The phosphoric system ($H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$, $PO_4^{3-}$) and the $CO_2$ ($CO_2$, $HCO_3^-$, $CO_3^{2-}$) systems are important for both biology and environmental applications. Succinic acid, a dicarboxylic acid produced by fermentation, is expected to become more widely produced via fermentation in future years, typically as a salt. Amino acids, the building blocks for proteins, combine a basic amine and a carboxylic acid on the same molecule. Let us begin by considering the nonvolatile phosphate system.

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} = \frac{K_{a1}}{[H^+]} \tag{18.45}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[HPO_4^{2-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}}{[H^+]^2} \tag{18.46}$$

$$\frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{K_{a3}}{[H^+]} \text{ or } \frac{[PO_4^{3-}]}{[H_3PO_4]} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \tag{18.47}$$

$$C = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{18.48}$$

$$\alpha_3 = \frac{[H_3PO_4]}{C}, \alpha_2 = \frac{[H_2PO_4^-]}{C}, \alpha_1 = \frac{[HPO_4^{2-}]}{C}, \alpha_0 = \frac{[PO_4^{3-}]}{C} \tag{18.49}$$

$$\frac{1}{\alpha_3} = \frac{C}{[H_3PO_4]} = 1 + \frac{[H_2PO_4^-]}{[H_3PO_4]} + \frac{[HPO_4^{2-}]}{[H_3PO_4]} + \frac{[PO_4^{3-}]}{[H_3PO_4]} = 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \tag{18.50}$$

$$\alpha_3 = \frac{[H_3PO_4]}{C} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \tag{18.51}$$

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

$$\alpha_2 = \frac{[H_2PO_4^-]}{C} = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \tag{18.52}$$

$$\alpha_1 = \frac{[HPO_4^{2-}]}{C} = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \tag{18.53}$$

$$\alpha_0 = \frac{[PO_4^{3-}]}{C} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} \tag{18.54}$$

## Table 18.2. Reference Table for Relative Acid and Base Strengths at 25°C Based on $pK_{a,water} = -13.995$. $pK_b = 13.995 - pK_a$

Strong Acids

Increasing Base Strength

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| Nitric acid | $HNO_3$ | −1 | $NO_3^-$ | ~15 |
| Hydronium ion | $H_3O^+$ | 0 | $H_2O$ | 13.995 |
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| Hydrogen cyanide | $HCN$ | 9.21 | $CN^-$ | 4.79 |
| Boric acid | $H_3BO_4$ | 9.237 | $B(OH)_4^-$ | 4.758 |
| Ammonium ion | $NH_4^+$ | 9.245 | $NH_3$ | 4.750 |
| Bicarbonate | $HCO_3^-$ | 10.329 | $CO_3^{-2}$ | 3.666 |
| Hydrogen phosphate | $HPO_4^{-2}$ | 12.375 | $PO4^{-3}$ | 1.620 |
| Water[b] | $H_2O$ | 13.995 | $OH^-$ | 0 |
| Bisulfide | $HS^-$ | ~14 | $S^{-2}$ | ~ 0 |
| Ammonia | $NH_3$ | ~23 | $NH2^-$ | ~ −9 |
| Hydroxide ion | $OH^-$ | ~24 | $O^{-2}$ | ~ −10 |

Increasing Acid Strength

Strong Bases

a. By common use. Based on $([CO_{2(aq)}] + [H_2CO_3])K_a = [HCO_3^-][H^+]$. $[H_2CO_3] \approx 0.002[CO_{2(aq)}]$ at 298.15 K. Thus, $(1.002[CO_{2(aq)}])K_a = [HCO_3^-][H^+]$ at 298.15 K.

b. If water is acting as a solute rather than a solvent, as it must if the acid strength of $H_2O$ is being compared with that of other very weak acids, then $pK_{a,A} \sim 16$ should be used. See 1990. *J. Chem. Ed.* 67(5):386–388.

The Sillèn diagram for the phosphate system is slightly more complicated than a monoprotic system, but can still be quickly drawn by hand. The concentration of each species *i* can rigorously be calculated at each pH by $\alpha_i C$ where $\alpha_i$ is calculated from Eqns. 18.51–18.54. The exact

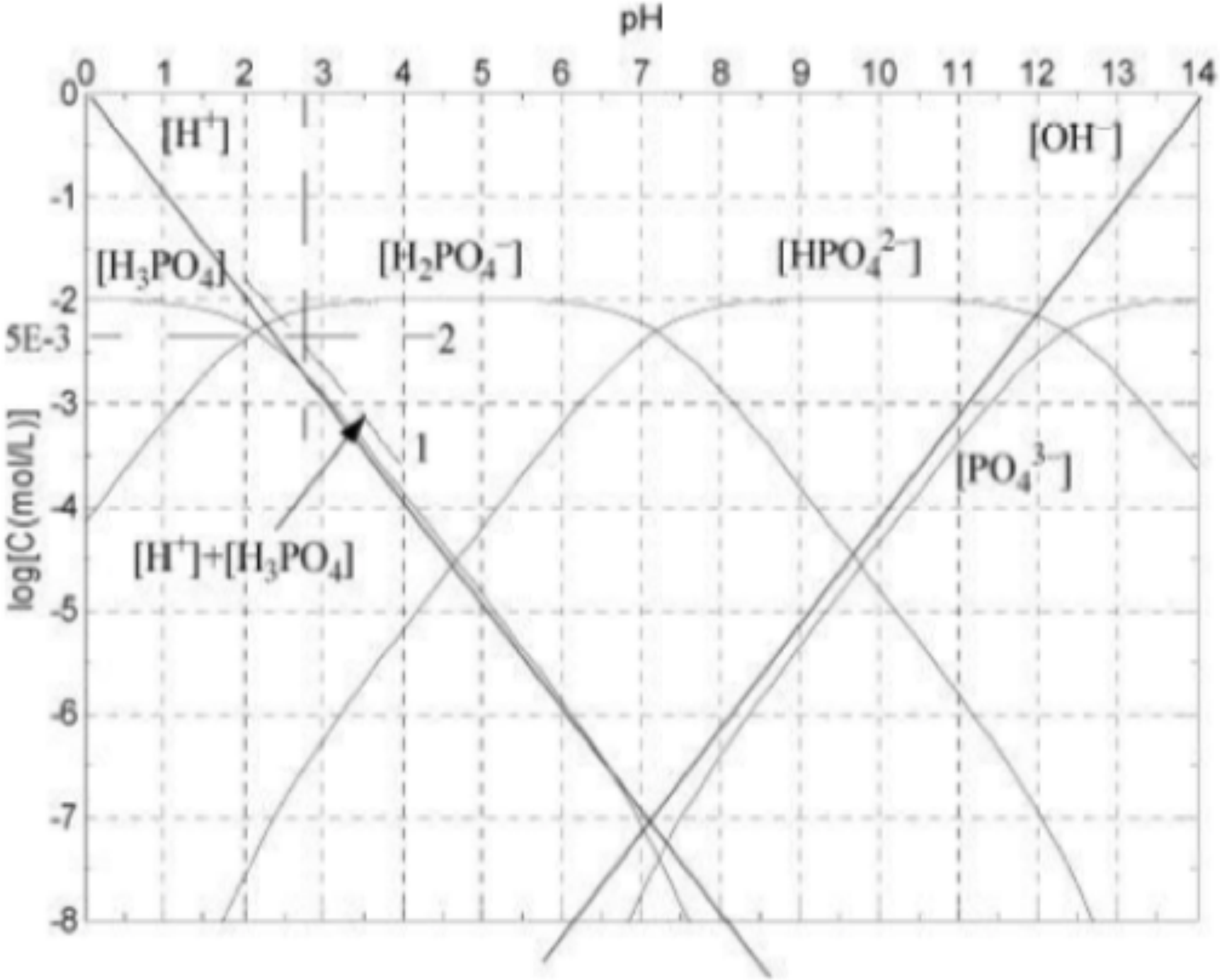


**Figure 18.6. Phosphoric system at $C = 10^{-2}$ mol/L discussed in Example 18.6.**

## Example 18.6. Phosphate salt and strong acid

A solution of $NaH_2PO_4$ and HCl is prepared such that the total phosphorous concentration is 1E-2 M and the total Cl concentration is 5E-3M. Calculate the pH and concentrations of species present.

$$1\times10^{-2}\text{M} = [H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}] = [Na^+] \qquad 18.55$$

$$[Cl^-] = 5\times10^{-3}\text{M} \qquad 18.56$$

$$[H^+]+[Na^+] = [H_2PO_4^-]+2[HPO_4^{2-}]+3[PO_4^{3-}]+[OH^-]+[Cl^-] \text{ charge balance} \qquad 18.57$$

**Step 6.** The proton condition is developed by eliminating $[Na^+]$ and $[Cl^-]$ using the material balances since they are both known constants. The material balance for phosphate is also inserted, resulting in

$$[H^+]+10^{-2} = 10^{-2}-[H_3PO_4]+[HPO_4^{2-}]+2[PO_4^{3-}]+[OH^-]+5\cdot10^{-3} \qquad 18.58$$

which becomes

$$[H^+]+[H_3PO_4] = [HPO_4^{2-}]+2[PO_4^{3-}]+[OH^-]+5\cdot10^{-3} \text{ proton condition} \qquad 18.59$$

Understanding where to find the solution requires some thought and reasoning rather than a direct numerical manipulation. Both terms on the left side of the proton condition are almost equal at $2.5 < \text{pH} < 7$. The values are added on the short dashed line marked "1" (since they are virtually equal in most of the range, the sum is double, or about 0.3 units higher on the $\log_{10}$ scale). Note that $[H_2PO_4^-]$ does not appear in the proton condition. On the right-hand side, the term 5E-3 dominates at pH < 6. Solutions at high pH are impossible because the decreasing right-hand side is too small to balance the value of 5E-3 plus increasing concentrations of the negative phosphate and hydroxide ions in the proton condition. Therefore, the solution must be a low pH where the concentration of negative phosphate and hydroxide ions in the proton condition are small. The solution occurs where $[H^+]+[H_3PO_4]$ = 5E-3 (the line marked "2"), and pH = 2.6. The approximate concentrations from the diagram are $[H^+] = [H_3PO_4]$ = 2.5E-3. Eqn. 18.45 simplifies to $[H_2PO_4^-] = K_{a1} = 10^{-2.15}$, $[HPO_4^{2-}] = 10^{-6.5}$, $[Na^+]$ = 1E-2, $[Cl^-]$ = 5E-3.

$$\frac{[H_2PO_4^-]}{[H_3PO_4]} = \frac{K_{a1}}{[H^+]} \qquad 18.45$$

**Step 7.** The detailed calculations are often tedious. Inserting Eqn. 18.51 into the proton condition, where the first three terms on the right side are negligible,

$$[\mathrm{H^+}] + \frac{C[\mathrm{H^+}]^3}{[\mathrm{H^+}]^3 + K_{a1}[\mathrm{H^+}]^2 + K_{a1}K_{a2}[\mathrm{H^+}] + K_{a1}K_{a2}K_{a3}} = 5\text{E-3} + \ldots \tag{18.60}$$

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

$$[\mathrm{H^+}]\left(1 + \frac{C/[\mathrm{H^+}]}{1 + K_{a1}/[\mathrm{H^+}] + (K_{a1}K_{a2})/[\mathrm{H^+}]^2 + (K_{a1}K_{a2}K_{a3})/[\mathrm{H^+}]^3}\right) = 5\text{E-3} \tag{18.61}$$

Inserting the initial guess,

$$[\mathrm{H^+}] = (5\text{E-3})/\left[1 + \frac{C/[\mathrm{H^+}]}{1 + K_{a1}/[\mathrm{H^+}] + (K_{a1}K_{a2})/[\mathrm{H^+}]^2 + (K_{a1}K_{a2}K_{a3})/[\mathrm{H^+}]^3}\right] \tag{18.62}$$

$$[\mathrm{H^+}] = (5\text{E-3})/\left[1 + \frac{10^{-2}/[\mathrm{H^+}]}{1 + 10^{-2.148}/[\mathrm{H^+}] + \ldots}\right]$$

$$= (5\text{E-3})/\left[1 + \frac{10^{-2}/10^{-2.6}}{1 + 10^{-2.148}/10^{-2.6} + \ldots}\right] = (5\text{E-3})/\left[1 + \frac{3.981}{1 + 2.8314 + \ldots}\right] \tag{18.63}$$

$$(5\text{E-3})/[2.039] = 2.45\text{E-3} = 10^{-2.611}$$

Repeating the iteration results in $[\mathrm{H^+}] = 2.44\text{E-3}$, pH = 2.613. Note how close we were with the graphical value of pH = 2.6.

# Amino Acids (Zwiterions)

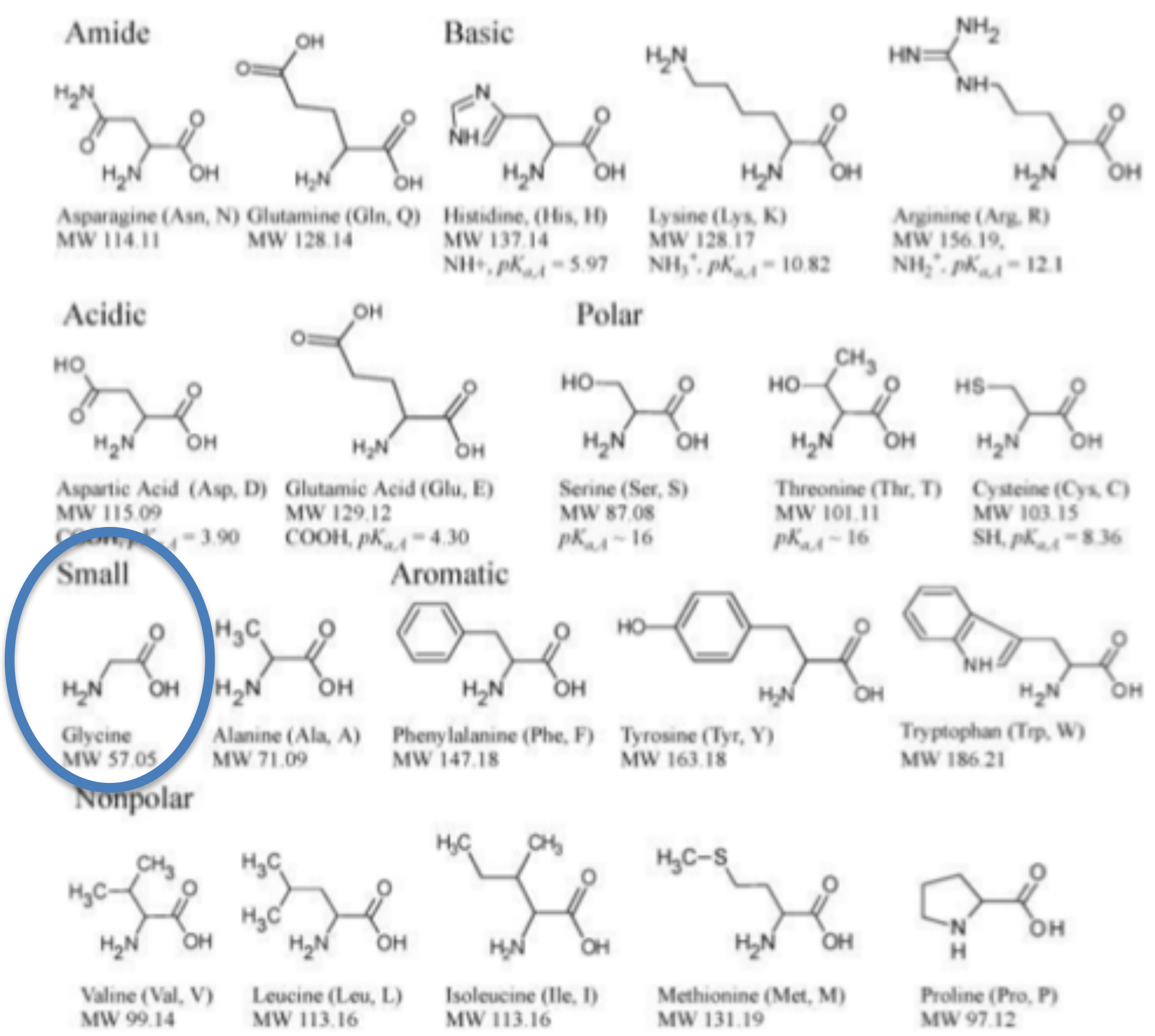
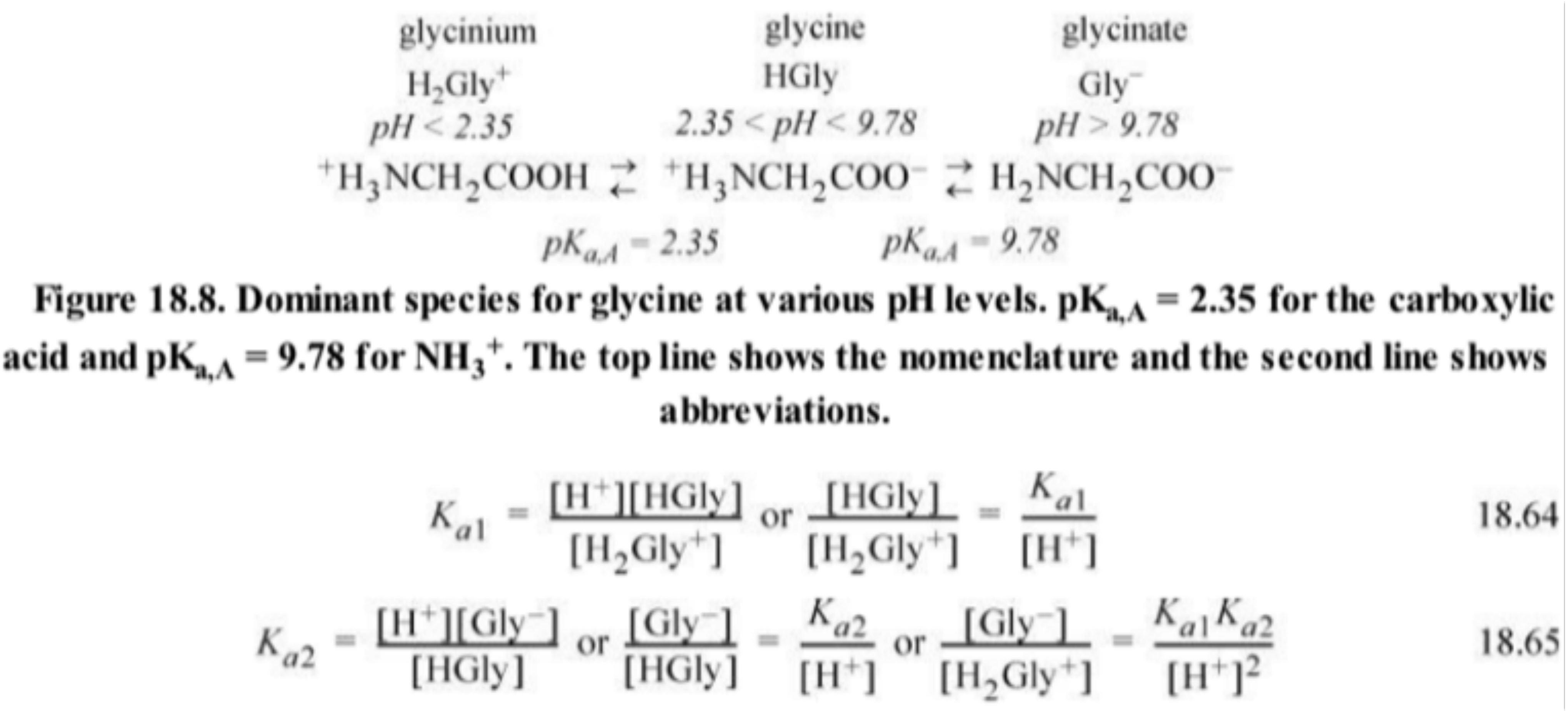


**Figure 18.7. Summary of 20 amino acids encoded by the universal genetic code. The amine and carboxylic groups on the bottom of each molecule are where the amino acid is linked into the biomolecule. The acidic and basic side chains are shown uncharged.**

# Amino Acids (Zwiterions)



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

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

$pK_{a,A} = 2.35$ $\quad$ $pK_{a,A} = 9.78$

**Figure 18.8. Dominant species for glycine at various pH levels. $pK_{a,A} = 2.35$ for the carboxylic acid and $pK_{a,A} = 9.78$ for $NH_3^+$. The top line shows the nomenclature and the second line shows abbreviations.**

$$K_{a1} = \frac{[H^+][HGly]}{[H_2Gly^+]} \text{ or } \frac{[HGly]}{[H_2Gly^+]} = \frac{K_{a1}}{[H^+]} \qquad 18.64$$

$$K_{a2} = \frac{[H^+][Gly^-]}{[HGly]} \text{ or } \frac{[Gly^-]}{[HGly]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[Gly^-]}{[H_2Gly^+]} = \frac{K_{a1}K_{a2}}{[H^+]^2} \qquad 18.65$$

## Example 18.7. Distribution of species in glycine solution

**a.** Calculate the pH of a 0.1 M solution of glycine.

**b.** What is the distribution of species for glycine at a physiological pH of 7.4?

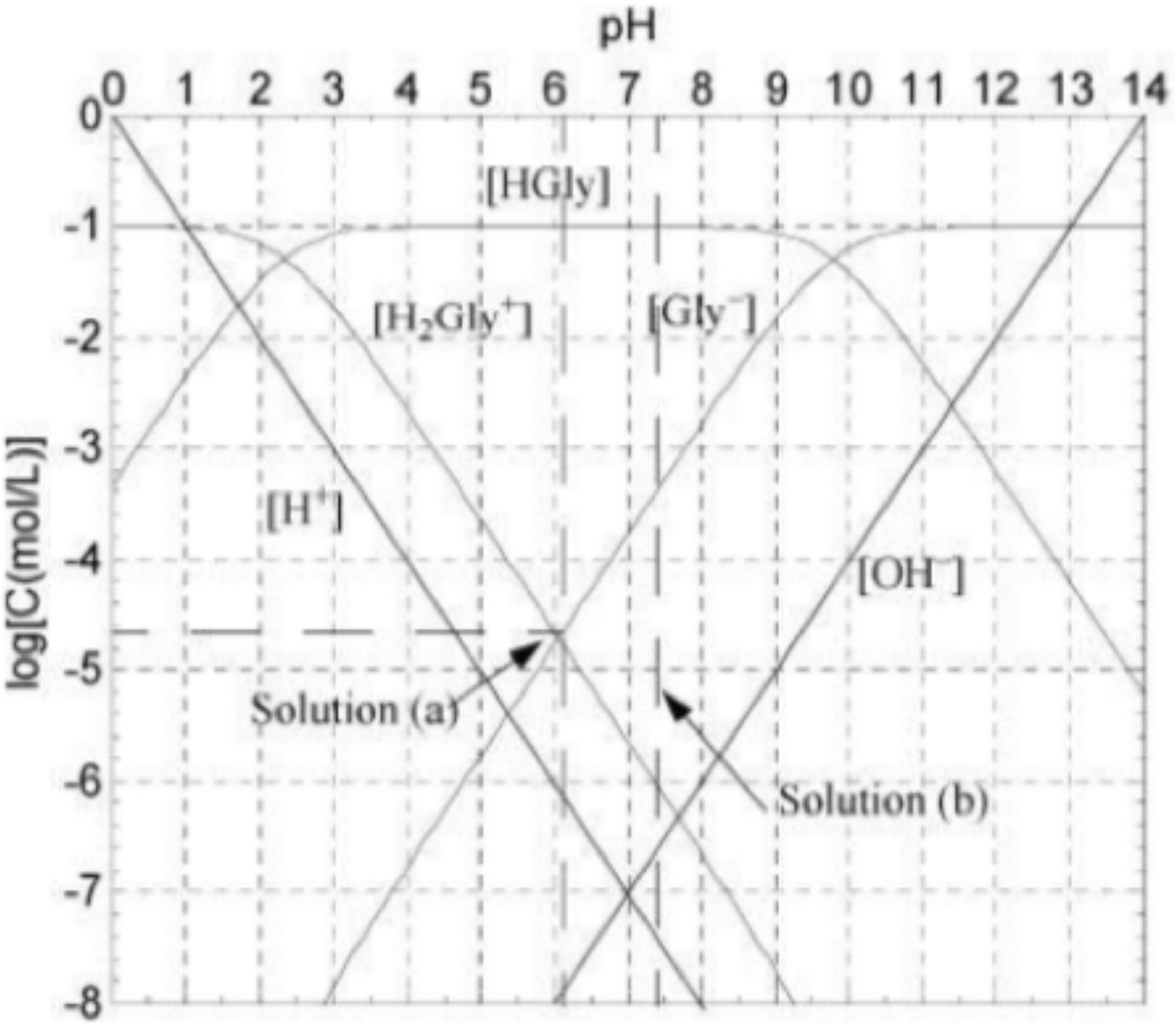


**Figure 18.9. Sillèn diagram for 0.1 M glycine discussed in Example 18.7.**

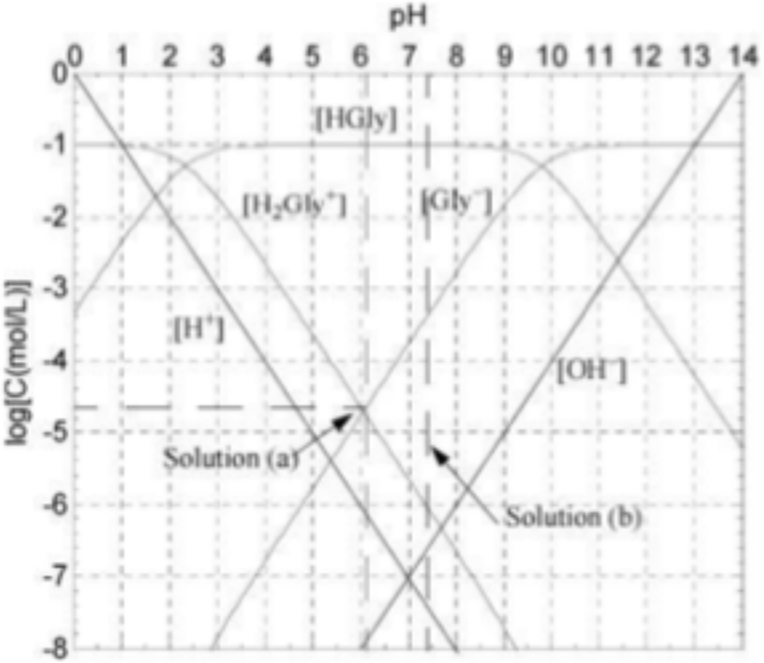
$$K_{a1} = \frac{[H^+][HGly]}{[H_2Gly^+]} \text{ or } \frac{[HGly]}{[H_2Gly^+]} = \frac{K_{a1}}{[H^+]} \qquad 18.64$$

$$K_{a2} = \frac{[H^+][Gly^-]}{[HGly]} \text{ or } \frac{[Gly^-]}{[HGly]} = \frac{K_{a2}}{[H^+]} \text{ or } \frac{[Gly^-]}{[H_2Gly^+]} = \frac{K_{a1}K_{a2}}{[H^+]^2} \qquad 18.65$$

$$C = [H_2Gly^+] + [HGly] + [Gly^-] = 0.1M \qquad 18.66$$

$$[H^+] + [H_2Gly^+] = [Gly^-] + [OH^-] \qquad 18.67$$

**Charge balance (18.67) is reached about where $1.1[H_2Gly^+] = [Gly^-]$, a little above p$H$ = 6**



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

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

# Buffer: a salt and an acid that share a common ion

Acetic Acid and Sodium Acetate

$$[\mathrm{HA}] + [\mathrm{A}^-] = C_A + C_B \text{ and } [\mathrm{Na}^+] = C_B \quad \text{material balances} \tag{18.69}$$

$$K_{a,A} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \quad \text{equilibrium} \tag{18.70}$$

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14} \quad \text{equilibrium} \tag{18.71}$$

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \quad \text{charge balance} \tag{18.72}$$

$$[\mathrm{A}^-] = C_B + [\mathrm{H}^+] - [\mathrm{OH}^-] \tag{18.73}$$

$$[\mathrm{HA}] = C_A - [\mathrm{H}^+] + [\mathrm{OH}^-] \tag{18.74}$$

$$[\mathrm{H}^+] = K_{a,A}\frac{C_A - [\mathrm{H}^+] + [\mathrm{OH}^-]}{C_B + [\mathrm{H}^+] - [\mathrm{OH}^-]} \tag{18.75}$$

Henderson-Hasselbalch Equation

$$[\mathrm{H}^+] \approx K_{a,A}\frac{C_A}{C_B} \text{ or } \mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A}{C_B} = \mathrm{p}K_{a,A} + \log\frac{C_B}{C_A}$$

# Buffer: a salt and an acid that share a common ion

Acetic Acid and Sodium Acetate

$$[\mathrm{HA}] + [\mathrm{A}^-] = C_A + C_B \text{ and } [\mathrm{Na}^+] = C_B \quad \text{material balances} \tag{18.69}$$

$$K_{a,A} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \quad \text{equilibrium} \tag{18.70}$$

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14} \quad \text{equilibrium} \tag{18.71}$$

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] \quad \text{charge balance} \tag{18.72}$$

$$[\mathrm{A}^-] = C_B + [\mathrm{H}^+] - [\mathrm{OH}^-] \tag{18.73}$$

$$[\mathrm{HA}] = C_A - [\mathrm{H}^+] + [\mathrm{OH}^-] \tag{18.74}$$

$$[\mathrm{H}^+] = K_{a,A}\frac{C_A - [\mathrm{H}^+] + [\mathrm{OH}^-]}{C_B + [\mathrm{H}^+] - [\mathrm{OH}^-]} \tag{18.75}$$

Better equation:

$$\mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A - [\mathrm{H}^+]}{C_B + [\mathrm{H}^+]} \text{ (acidic p}K_{a,A}\text{) or } \mathrm{pH} \approx \mathrm{p}K_{a,A} - \log\frac{C_A + [\mathrm{OH}^-]}{C_B - [\mathrm{OH}^-]} \text{ (basic p}K_{a,A}\text{)} \tag{18.77}$$

# Isoelectric Point

For a zwitterion like an amino acid amines protonate at neutral p*H* and carboxylic acids are deprotonated. When there is no net charge the p*H* = p*I* is the isoelectric point. Solubility is at a minimum at the isoelectric point.

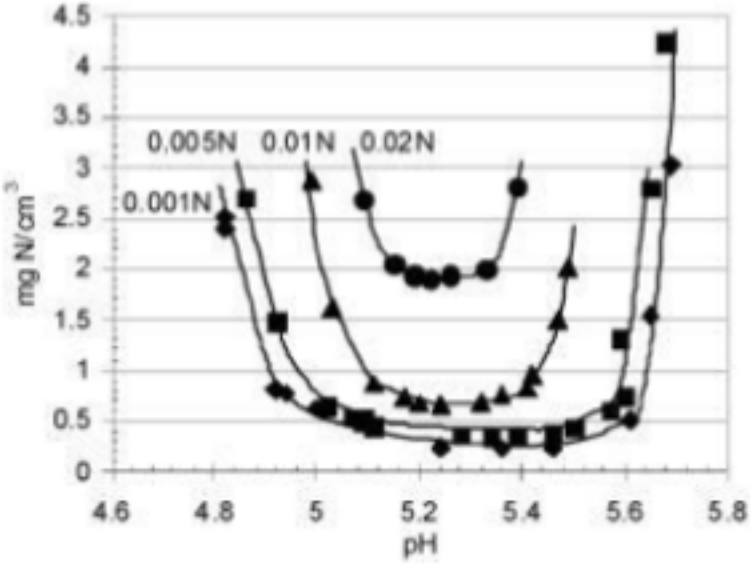
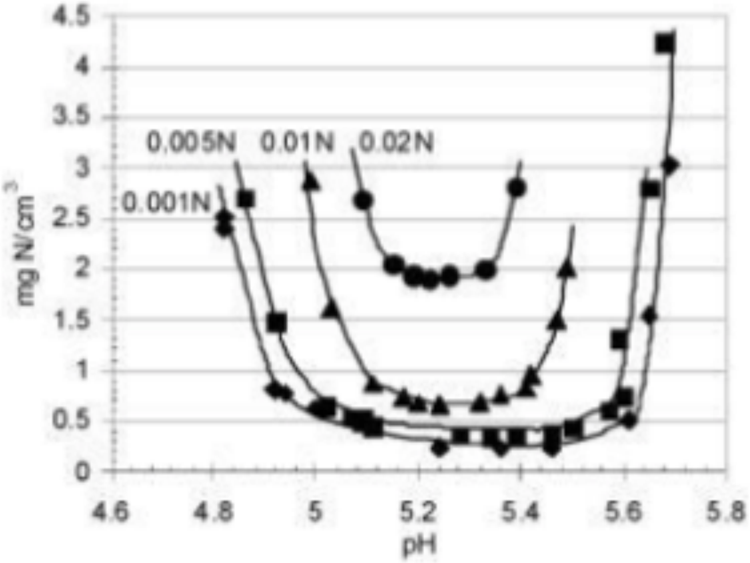


**Figure 18.10. Salting in and illustration of minimum solubility at the isoelectric point for milk protein β-lactoglobulin as a function of pH and ionic strength. Gronwall, A., 1942. C.R. Trav. Lab. Carlsberg, Ser. Chim. 24:185-200.**

# Ionic Strength (salt concentration)

For low ionic strength, as ionic strength increases, solubility increases (salting in).
For high ionic strength, as ionic strength increases, solubility decreases (salting out).
Maximum solubility at intermediate salt concentrations.



Salting in

**Figure 18.10. Salting in and illustration of minimum solubility at the isoelectric point for milk protein β-lactoglobulin as a function of pH and ionic strength. Gronwall, A., 1942. C.R. Trav. Lab. Carlsberg, Ser. Chim. 24:185-200.**

# Donnan Equilibria

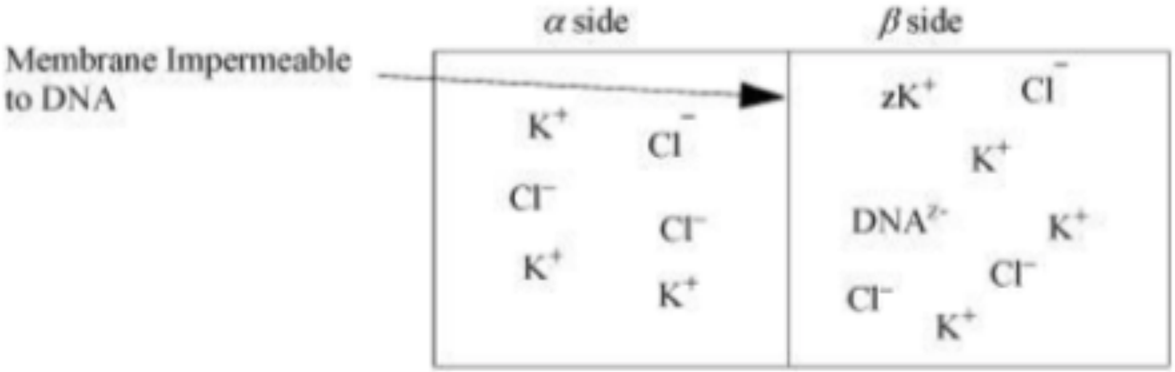


**Figure 18.11. Illustration of Donnan Equilibria for DNA. DNA cannot cross the membrane. A larger concentration of ions will exist on the β side, creating higher pressure on the β side due to osmotic pressure.**

$$(a_{K^+}a_{Cl^-})_\alpha = (a_{K^+}a_{Cl^-})_\beta \qquad 18.78$$

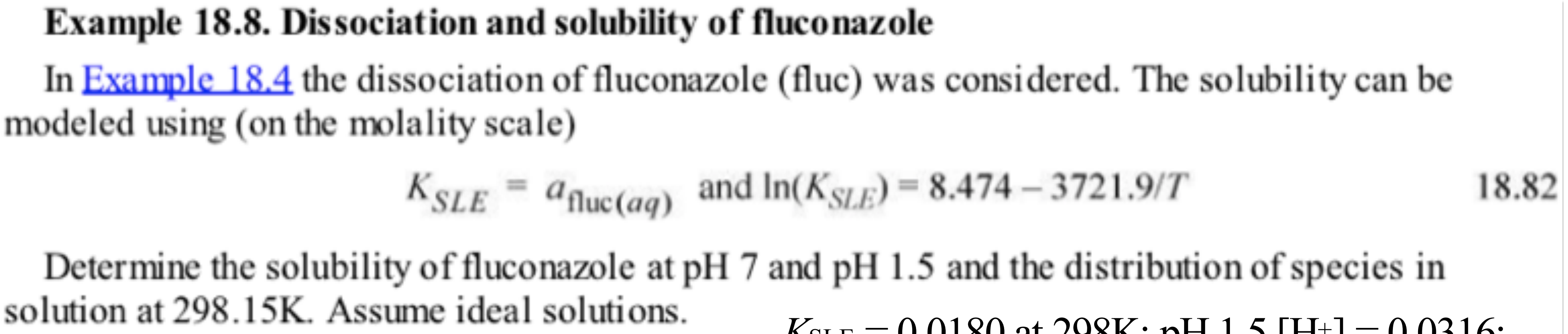
$$[K^+]_\alpha = [Cl^-]_\alpha \quad \text{and} \quad [K^+]_\beta = z[DNA^{z-}]_\beta + [Cl^-]_\beta \qquad 18.79$$

$$[K^+]_\alpha = [K^+]_\beta\left(1 - \frac{z[DNA^{z-}]}{[K^+]_\beta}\right)^{1/2} \qquad 18.80$$

$$[Cl^-]_\alpha = [Cl^-]_\beta\left(1 + \frac{z[DNA^{z-}]}{[Cl^-]_\beta}\right)^{1/2} \qquad 18.81$$

# Solubility

Solubility and vapor pressure rely on equilibria with the un-ionized species. So solubility depends on p*H*. *Remember, the activity of a solid is 1.*

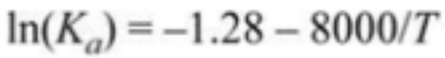


**Example 18.8. Dissociation and solubility of fluconazole**

In Example 18.4 the dissociation of fluconazole (fluc) was considered. The solubility can be modeled using (on the molality scale)

$$K_{SLE} = a_{\text{fluc}(aq)} \quad \text{and} \quad \ln(K_{SLE}) = 8.474 - 3721.9/T \qquad 18.82$$

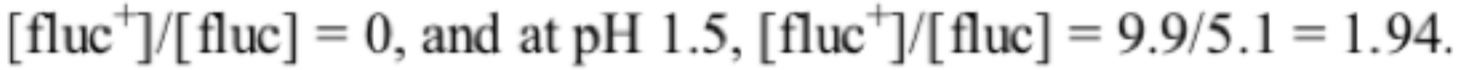
Determine the solubility of fluconazole at pH 7 and pH 1.5 and the distribution of species in solution at 298.15K. Assume ideal solutions.



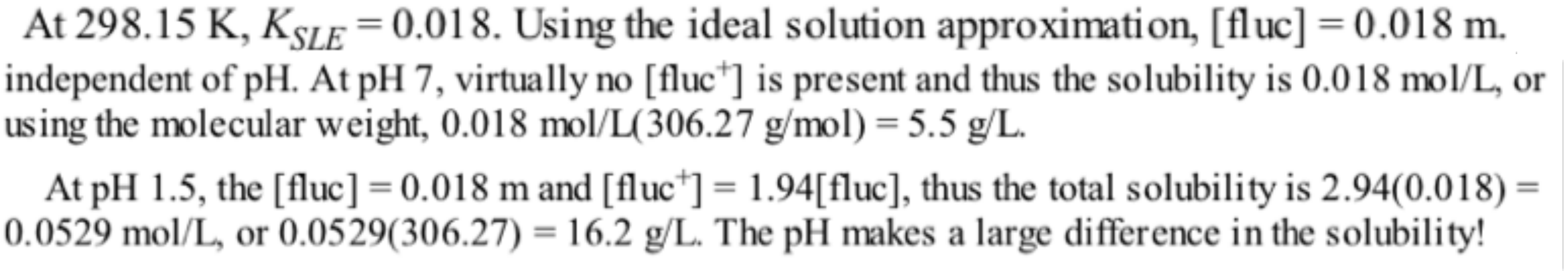
$$\ln(K_a) = -1.28 - 8000/T$$

$K_{SLE} = 0.0180$ at 298K; pH 1.5 $[H^+] = 0.0316$; pH 7 $[H^+] = 1e\text{-}7$; $K_a = 6.18\ e\text{-}13$; p$K_a = 1.8$ so protonated below pH 1.8 and undissociated above pH 7

*From slide 18 example 18.4*



$[\text{fluc}^+]/[\text{fluc}] = 0$, and at pH 1.5, $[\text{fluc}^+]/[\text{fluc}] = 9.9/5.1 = 1.94$.



At 298.15 K, $K_{SLE} = 0.018$. Using the ideal solution approximation, [fluc] = 0.018 m. independent of pH. At pH 7, virtually no $[\text{fluc}^+]$ is present and thus the solubility is 0.018 mol/L, or using the molecular weight, 0.018 mol/L(306.27 g/mol) = 5.5 g/L.

At pH 1.5, the [fluc] = 0.018 m and $[\text{fluc}^+]$ = 1.94[fluc], thus the total solubility is 2.94(0.018) = 0.0529 mol/L, or 0.0529(306.27) = 16.2 g/L. The pH makes a large difference in the solubility!

## Common ion effect

Add NaCl to a KCl saturated solution causes precipitation

$$KCl_{(s)} \rightleftarrows K^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \quad K_{sp} = a_{K^{+}} a_{Cl^{-}} \qquad 18.83$$

## **Redox Reactions** OILRIG

Lose or gain electrons

Electrochemical Cell (discharge)

Anode: $LiC_6 \rightleftarrows C_6 + Li^+ + e^-$ Oxidation (OIL)

Cathode: $CoO_2 + Li^+ + e^- \rightleftarrows LiCoO_2$ Reduction (RIG)

3.9 Volts

Reference voltage is platinum electrode:$H_2$(g) electrode at p*H* = 0; 298K; 1 bar

$2H^+ + 2e^- \rightleftarrows H_{2(g)}$ Reduction of $H^+$ Potential set to 0 as reference

$$\boxed{\Delta G^\circ = -n_e F E^\circ = -RT \ln K_a} \qquad 18.84$$

**Faraday's constant** 96,485 J/V, and $E^\circ = E^\circ_{red} - E^\circ_{ox}$

$$\Delta G^\circ = -n_e F E^\circ_{\text{red}} + n_e F E^\circ_{ox}$$

Standard Reduction Potentials at 25°C

| Half Reaction | E° (V) |
|---|---|
| $F_2 + 2e^- \rightarrow 2F^-$ | +2.87 |
| $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$ | +1.70 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | +1.51 |
| $Au^{3+} + 3e^- \rightarrow Au$ | +1.50 |
| $Cl_2 + 2e^- \rightarrow 2Cl^-$ | +1.36 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | +1.33 |
| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | +1.23 |
| $Br_2 + 2e^- \rightarrow 2Br^-$ | +1.07 |
| $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ | +0.96 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{\ 2+}$ | +0.92 |
| $Hg^{2+} + 2e^- \rightarrow Hg$ | +0.85 |
| $Ag^+ + e^- \rightarrow Ag$ | +0.80 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | +0.77 |
| $I_2 + 2e^- \rightarrow 2I^-$ | +0.53 |
| $Cu^+ + e^- \rightarrow Cu$ | +0.52 |
| $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | +0.40 |
| $Cu^{2+} + 2e^- \rightarrow Cu$ | +0.34 |
| $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ | +0.13 |
| $2H^+ + 2e^- \rightarrow H_2$ | 0.00 |
| $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13 |
| $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.14 |
| $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.25 |
| $Co^{2+} + 2e^- \rightarrow Co$ | −0.28 |
| $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | −0.31 |
| $Cd^{2+} + 2e^- \rightarrow Cd$ | −0.40 |
| $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.44 |
| $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.74 |
| $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.76 |
| $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ | −0.83 |
| $Mn^{2+} + 2e^- \rightarrow Mn$ | −1.18 |
| $Al^{3+} + 3e^- \rightarrow Al$ | −1.66 |
| $Be^{2+} + 2e^- \rightarrow Be$ | −1.70 |
| $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.37 |
| $Na^+ + e^- \rightarrow Na$ | −2.71 |
| $Ca^{2+} + 2e^- \rightarrow Ca$ | −2.87 |
| $Sr^{2+} + 2e^- \rightarrow Sr$ | −2.89 |
| $Ba^{2+} + 2e^- \rightarrow Ba$ | −2.90 |
| $Rb^+ + e^- \rightarrow Rb$ | −2.92 |
| $K^+ + e^- \rightarrow K$ | −2.92 |
| $Cs^+ + e^- \rightarrow Cs$ | −2.92 |
| $Li^+ + e^- \rightarrow Li$ | −3.05 |

# **Redox Reactions** OILRIG

$$\boxed{\Delta G^\circ = -n_e F E^\circ = -RT \ln K_a} \tag*{18.84}$$

$$\Delta G^\circ = -\, n_e F E^\circ{}_{\text{red}} + n_e F E^\circ{}_{ox}$$

$$\Delta G = \Delta G^\circ + RT \ln \prod a_i^{v_i} \quad \text{or} \quad n_e F E = n_e F E^\circ - RT \ln \prod a_i^{v_i} \tag*{18.85}$$

$$\boxed{E = E^\circ - \frac{RT}{n_e F} \ln \prod a_i^{v_i} = E^\circ - \frac{0.05916}{n_e} \log \prod a_i^{v_i}} \quad \text{Nernst equation} \tag*{18.86}$$

## Example 18.9. Alkaline dry-cell battery

Consumer portable electronics are commonly powered by ‘alkaline’ dry-cell batteries. These cells use an alkaline paste instead of an aqueous solution. The moisture content is low to minimize leakage, and the alkaline solution is used instead of acid because the degradation of the electrodes is slower in alkali compared to acid. The relevant species are $Zn_{(s)}$, $ZnO_{(s)}$, $\gamma$-$MnO_{2(s)}$, and $\alpha$-$MnOOH_{(s)}$. A new battery has $Zn_{(s)}$ and $\gamma$-$MnO_{2(s)}$ electrodes.

**a.** Determine the balanced reactions for $H^+$ and then transform them to use $OH^-$. Then provide the balanced overall reaction. (b) Determine the voltage generated by the cell when $[OH^-] = 1$ m and $[OH^-] = 1.1$ m, and the Gibbs energy of reaction.

| | |
|---|---|
| $\gamma$-$MnO_{2(s)} + H_2O + e^- \rightleftarrows \alpha$-$MnOOH_{(s)} + OH^-$ | 0.30 |

**a.** For Mn, the half-cell reduction reaction is found to be $\gamma$-$MnO_{2(s)} + H^+ + e^- \rightleftarrows \alpha$-$MnOOH_{(s)}$, through the following procedure. Start with the Mn species (MnO2 and MnOOH) on each side of the reaction (more reduced on the right). The reduction requires one electron to go from +4 to +3, so one electron is added to the left. At this point, the O is already balanced, and one $H^+$ is added to the left to balance hydrogen. The total charge is 0 on each side of the reaction. To convert to the base form, we add $H_2O \rightleftarrows H^+ + OH^-$, giving $\gamma$-$MnO_{2(s)} + H_2O + e^- \rightleftarrows \alpha$-$MnOOH_{(s)} + OH^-$ and the total charge is $-1$ on each side of the reaction.

| | |
|---|---|
| $ZnO_{(s)} + H_2O + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$ | −1.260 |

For the other electrode, the half-cell reduction reaction is found to be $ZnO_{(s)} + 2H^+ + 2e^- \rightleftarrows Zn_{(s)} + H_2O$ through the following procedure. After writing the Zn species on each side (more reduced on the right), we note that the reaction requires two electrons and add them to the left, water is added on the right side to balance oxygen, then $2H^+$ are added to the left side to balance H. The total charge is 0 on each side. To convert to the base form, we add $2H_2O \rightleftarrows 2H^+ + 2OH^-$, giving $ZnO_{(s)} + H_2O + 2e^- \rightleftarrows Zn_{(s)} + 2OH^-$.

For the overall reaction, to balance electrons, two Mn must be reduced for each Zn oxidized. Combining, $Zn_{(s)} + 2\gamma$-$MnO_{2(s)} + H_2O \rightleftarrows ZnO_{(s)} + 2\alpha$-$MnOOH_{(s)}$.

| Reaction[a] | E° (volts) | dE°/dT (mV/K) |
|---|---|---|
| **Copper** | | |
| $Cu^{+} + e^{-} \rightleftarrows Cu_{(s)}$ | 0.518 | –0.754 |
| $Cu^{2+} + 2e^{-} \rightleftarrows Cu_{(s)}$ | 0.339 | 0.011 |
| $Cu^{2+} + e^{-} \rightleftarrows Cu^{+}$ | 0.161 | 0.776 |
| $Cu(OH)_{2(s)} + 2e^{-} \rightleftarrows Cu_{(s)} + 2OH^{-}$ | –0.222 | |
| **Hydrogen** | | |
| $2H^{+} + 2e^{-} \rightleftarrows H_{2(g)}$ | 0.000 | 0 |
| $H_2O + e^{-} \rightleftarrows ½H_{2(g)} + OH^{-}$ | –0.8280 | –0.8360 |
| **Iron** | | |
| $FeO_4^{2-} + 3H_2O + 3e^{-} \rightleftarrows FeOOH_{(s)} + 5OH^{-}$ | 0.80 | –1.59 |
| $Fe^{3+} + e^{-} \rightleftarrows Fe^{2+}$ | 0.771 | 1.175 |
| $FeOOH_{(s)} + 3H^{+} + e^{-} \rightleftarrows Fe^{2+} + 2H_2O$ | 0.74 | –1.05 |
| $Fe(glutamate)^{3+} + e^{-} \rightleftarrows Fe(glutamate)^{2+}$ | 0.240 | |
| $FeOH^{+} + H^{+} + 2e^{-} \rightleftarrows Fe_{(s)} + H_2O$ | –0.16 | 0.07 |
| $Fe^{2+} + e^{-} \rightleftarrows Fe_{(s)}$ | –0.44 | 0.07 |
| $FeCO_{3(s)} + 2e^{-} \rightleftarrows Fe_{(s)} + CO_3^{2-}$ | –0.756 | –1.293 |
| **Lead** | | |
| $PbO_{2(s)} + 4H^{+} + 2e^{-} \rightleftarrows Pb^{2+} + 2H_2O$ | 1.458 | –0.253 |
| $3PbO_{2(s)} + 2H_2O + 4e^{-} \rightleftarrows Pb_3O_{4(s)} + 4OH^{-}$ | 0.269 | –1.136 |
| $Pb_3O_{4(s)} + H_2O + 2e^{-} \rightleftarrows 3PbO_{(s, red)} + 2OH^{-}$ | 0.224 | –1.211 |
| $Pb_3O_{4(s)} + H_2O + 2e^{-} \rightleftarrows 3PbO_{(s, yellow)} + 2OH^{-}$ | 0.207 | –1.177 |
| $Pb^{2+} + 2e^{-} \rightleftarrows Pb_{(s)}$ | –0.126 | –0.395 |
| **Manganese** | | |
| $MnO_4^{-} + 4H^{+} + 3e^{-} \rightleftarrows \beta\text{-}MnO_{2(s)} + 2H_2O$ | 1.692 | –0.671 |
| $Mn^{3+} + e^{-} \rightleftarrows Mn^{2+}$ | 1.56 | 1.8 |
| $MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftarrows Mn^{2+} + 2H_2O$ | 1.507 | –0.646 |
| $Mn_2O_{3(s)} + 6H^{+} + 2e^{-} \rightleftarrows 2Mn^{2+} + 3H_2O$ | 1.485 | –0.926 |
| $\beta\text{-}MnO_{2(s)} + 4H^{+} + 2e^{-} \rightleftarrows Mn^{2+} + 2H_2O$ | 1.23 | –0.609 |
| $MnO_4^{-} + e^{-} \rightleftarrows MnO_4^{2-}$ | 0.56 | –2.05 |
| $\gamma\text{-}MnO_{2(s)} + H_2O + e^{-} \rightleftarrows \alpha\text{-}MnOOH_{(s)} + OH^{-}$ | 0.30 | |
| $3Mn_2O_{3(s)} + H_2O + 2e^{-} \rightleftarrows 2Mn_3O_{4(s)} + 2OH^{-}$ | 0.002 | –1.256 |
| $Mn_3O_{4(s)} + 4H_2O + 2e^{-} \rightleftarrows 3Mn(OH)_{2(s)} + 2OH^{-}$ | –0.352 | –1.61 |
| $Mn^{2+} + 2e^{-} \rightleftarrows Mn_{(s)}$ | –1.182 | –1.129 |
| $Mn(OH)_{2(s)} + 2e^{-} \rightleftarrows Mn_{(s)}$ | –1.565 | –1.10 |
| **Oxygen** | | |
| $O_{3(g)} + 2H^{+} + 2e^{-} \rightleftarrows O_{2(g)} + H_2O$ | 2.075 | –0.489 |
| $H_2O_{2(g)} + 2H^{+} + 2e^{-} \rightleftarrows 2H_2O$ | 1.763 | –0.698 |
| $½O_{2(g)} + 2H^{+} + 2e^{-} \rightleftarrows H_2O$ | 1.2291 | –0.8456 |
| $O_{2(g)} + 2H^{+} + 2e^{-} \rightleftarrows H_2O_2$ | 0.695 | –0.993 |
| **Ruthenium** | | |
| $RuO_{4(s)} + H_2O \rightleftarrows H_2RuO_5$ $\log[H_2RuO_5] = -0.88$ | | |
| $RuO_4^{2-} + 4H^{+} + 2e^{-} \rightleftarrows RuO_{2(s)} + 2H_2O$ | 2.005 | |
| $RuO_4^{-} + 4H^{+} + 3e^{-} \rightleftarrows RuO_{2(s)} + 2H_2O$ | 1.533 | |
| $H_2RuO_5 + 4H^{+} + 4e^{-} \rightleftarrows RuO_{2(s)} + 3H_2O$ | 1.40 | |
| $RuO_{4(s)} + 4H^{+} + 4e^{-} \rightleftarrows RuO_{2(s)} + 2H_2O$ | 1.387 | |
| $H_2RuO_5 + e^{-} \rightleftarrows RuO_4^{-} + H_2O$ | 1.001 | |
| $RuO_4^{-} + e^{-} \rightleftarrows RuO_4^{2-}$ | 0.589 | |
| **Zinc** | | |
| $ZnOH^{+} + H^{+} + 2e^{-} \rightleftarrows Zn_{(s)} + H_2O$ | –0.497 | 0.03 |
| $Zn^{2+} + 2e^{-} \rightleftarrows Zn_{(s)}$ | –0.762 | 0.119 |
| $Zn(OH)_3^{-} + 2e^{-} \rightleftarrows Zn_{(s)} + 3OH^{-}$ | –1.183 | |
| $Zn(OH)_4^{2-} + 2e^{-} \rightleftarrows Zn_{(s)} + 4OH^{-}$ | –1.199 | |
| $Zn(OH)_{2(s)} + 2e^{-} \rightleftarrows Zn_{(s)} + 2OH^{-}$ | –1.249 | |
| $ZnO_{(s)} + H_2O + 2e^{-} \rightleftarrows Zn_{(s)} + 2OH^{-}$ | –1.260 | |

[a] Most values from Harris, D.C. 2007. *Quantitative Chemical Analysis*. 7th ed., New York NY: W.H. Freeman. A good source for more values is Bratsch, S.G. 1989. *J. Chem. Ref. Data* 18:1, available at www.nist.gov/data/PDFfiles/jpcrd355.pdf (Oct 2011), and Bard, A.J., Parsons, R., Jordan, J. 1985. *Standard Potentials in Aqueous Solution*, New York: Marcel Dekker.

## E.8 BIOCHEMICAL DATA

Standard state for soluble species is an ideal solution at 1 M except for water, which is relative to the Lewis-Randall standard state. The data are for the untransformed Gibbs energies and enthalpies.

| Name[a] | $\Delta G^{o}_{f,298.15}$ (kJ/mol) | $\Delta H^{o}_{f,298.15}$ (kJ/mol) | $z_i$ | $N_H$ | $N_{Mg}$ |
|---|---|---|---|---|---|
| NADox | 0 | 0 | –1 | 26 | 0 |
| NADred | 22.65 | –31.94 | –2 | 27 | 0 |
| $ATP^{4-}$ | –2768.1 | –3619.21 | –4 | 12 | 0 |
| $ATP^{3-}$ | –2811.48 | –3612.91 | –3 | 13 | 0 |
| $ATP^{2-}$ | –2838.18 | –3627.91 | –2 | 14 | 0 |
| $MgATP^{2-}$ | –3258.68 | –4063.31 | –2 | 12 | 1 |
| $MgHATP^{1-}$ | –3287.5 | –4063.01 | –1 | 13 | 1 |
| $Mg_2ATP$ | –3729.33 | –4519.51 | 0 | 12 | 2 |

**b.** The voltage is found by taking the difference in reduction potentials found in Appendix E. The standard potential is found by the differences in *reduction* potentials, $E^\circ = 0.3 - (-1.26) = 1.56$ V. The potential under operating conditions is given by

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

Since all the species except for $H_2O$ are solids, they exist in the pure state as a first approximation. (In actual practice the MnOOH forms a solid solution with $MnO_2$, but we ignore the effect here.) The activity of water is near 1 in the paste and $[OH^-]$ does not appear, and thus it has no effect on the equilibrium voltage. Therefore, the battery should give a constant 1.56 V throughout its life.

Note that we are neglecting transport effects and the solid solution behavior. Thus, the actual voltage drops as the battery dies owing in part to these effects. The Gibbs energy of reaction is $\Delta G = -n_e FE = -2(96485)1.56 = -301$ kJ/mol, a spontaneous reaction when the circuit is closed.

**Bioprocess Engineering (Fermentation)**

## Degree of Reduction

$$\gamma_{red} = (4f + a - 2b - 3c + 6d + 5e)/f \qquad \text{carbon-containing} \qquad 18.88$$

$$C_fH_aO_b + rO_2 \rightleftarrows fCO_2 + \frac{a}{2}H_2O \qquad 18.87$$

Stoichiometry $r = f + a/4 - b/2$

Oxidation State
O2 is 0; in products is -2
Moles of electrons transferred to oxygen

$$4r = 4f + a - 2b$$

The degree of reduction multipliers are +4 for C; +1 for H; -2 for O;
-3 for N (ammonia); +6 for S ($H_2SO_4$); +5 for P (phosphoric acid)

Reaction of acetaldehyde $C_2H_4O$ Degree of reduction 2(4)+4(1)+1(-2)=10 *or* 5 per carbon.
To determine *r* for $O_2$, 2*r*(-2) = -10 so r = -2.5 to yield zero on the left of 18.88
On the right of 18.88, For $CO_2$, 1(4)+2(-2) = 0 and for $H_2O$, 2(1)+1(-2) = 0
Two sides balance

An average elemental formula for cell mass is $CH_{1.8}O_{0.5}N_{0.2}$, with a degree of reduction of 4.2 per *C*-mole, slightly higher than glucose. For compounds not containing carbon, the degree of reduction is expressed per mole of that compound. For the compound $H_aO_bN_cS_dP_e$,

$$\gamma_{red} = (a - 2b - 3c + 6d + 5e) \qquad \text{not carbon-containing} \qquad 18.89$$

A fermentation can be represented with a pseudo-reaction, balancing inputs and outputs. For example, on the basis of one *C*-mole of substrate $CH_aO_bN_cS_d$,

$$CH_aO_bN_cS_d + Y_o(O_2) + Y_n(NH_3) + Y_{aux}(CH_e O_fN_gS_h) \rightarrow Y_{biomass}(CH_iO_jN_kS_l) + Y_{product}(CH_m O_nN_pS_q) + Y_{CO_2}(CO_2) + Y_w(H_2O) + Y_S(H_2SO_4)$$

where the *Y* values on the left are for the nutrients and on the right are for the products and by-products. The number of moles for each species is the value of the corresponding coefficient *Y*.

# Biological Equilibrium Reactions

Reactions occur with a buffer so [H+] is ignored (indicated by prime)

$$\mathrm{ATP} + \mathrm{H_2O} \rightleftarrows \mathrm{ADP} + \mathrm{H_3PO_4} \qquad \text{or} \qquad \mathrm{ATP} + \mathrm{H_2O} \rightleftarrows \mathrm{ADP} + \mathrm{P}_i \qquad 18.94$$

$$\boxed{\Delta G' = \Delta G'^\circ + RT \ln \prod_i [i]^{\nu_i} \qquad \Delta G'^\circ = -RT \ln K_c'} \qquad 18.93$$

$$K_c' = \frac{[\mathrm{ADP}][\mathrm{P}_i]}{[\mathrm{ATP}]} = \exp\left(\frac{\Delta G'^\circ_{f,\mathrm{ADP}} + \Delta G'^\circ_{f,\mathrm{P}_i} - \Delta G'^\circ_{f,\mathrm{ATP}} - \Delta G'^\circ_{f,\mathrm{H_2O}}}{RT}\right) \qquad 18.95$$

Water is pure so activity is 1

## Example 18.10. ATP hydrolysis

**a.** Calculate the transformed standard state Gibbs energy of reaction and equilibrium constant $K_c'$ for hydrolysis of ATP at $pH_c = 7$, pMg = 3, 298.15 K, ionic strength, $I = 0.25$ m, where the following data apply.

**b.** Show whether the reaction is endergonic or exergonic at the above conditions when the apparent concentrations are[a] [ATP] = 0.00185 M, [ADP] = 0.0014 M, $[P_i]$ = 0.001 M. If the reaction is exergonic, at what concentration of ADP does it reach equilibrium if the concentration of phosphate and ATP are constant?

[a] In the human body, [ATP]/[ADP] ~ 10. Alberts, B.; Bray, D.; Hopkin, K.; Johnson, A.; Lewis, J.; Raff J.; Roberts, K.; Walter, P. *Essential Cell Biology*, 3rd ed., New York: NY, Garland Science, (2010), pg. 465.

Gibbs energies of formation at $pH_c = 7$, pMg = 3, 298.15K, $I = 0.25$ mol/kg

| | ATP | $H_2O$ | ADP | $P_i$ |
|---|---|---|---|---|
| $\Delta G'^{\circ}_{f,i}$ (kJ/mol) | –2298 | –156 | –1426 | –1060 |

First, note that the Gibbs energy of water is different from the value in Appendix E because of the transformation. The transformed standard state Gibbs energy of reaction is –1426 – 1060 + 2298 + 156 = – 32 kJ/mol. The equilibrium constant will be

$$\exp\left(\frac{-\Delta G'^{\circ}_{f,i}}{RT}\right) = K_c' = \exp\left(\frac{32000}{8.314(298.15)}\right) = 4.04\times10^5$$

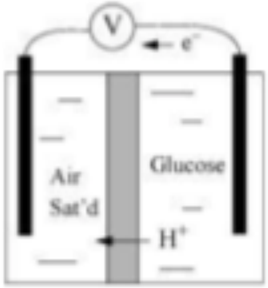
**b.** The propensity for reaction at the given concentrations is

$$\Delta G'_{f,i} = \Delta G'^{\circ}_{f,i} + RT\ln\frac{[ADP][P_i]}{[ATP]} = -32000 + 8.314(298.15)\ln\frac{[0.0014][0.001]}{0.00185} = -49.8\text{kJ/mol}$$

The reaction is even more strongly exergonic than the standard state. Equilibrium occurs when $[ADP] = k_c[ATP]/[P_i] = 5.3\times10^8(0.00185)/0.001 = 9.8\times10^8$M. Of course, such a high concentration never happens, so the reaction is always favorable at reasonable concentrations. Instead of hydrolyzing ATP and "losing the energy," the phosphate is transferred to glucose in a coupled reaction, the subject of a homework problem.

**Example 18.11. Biological fuel cell**

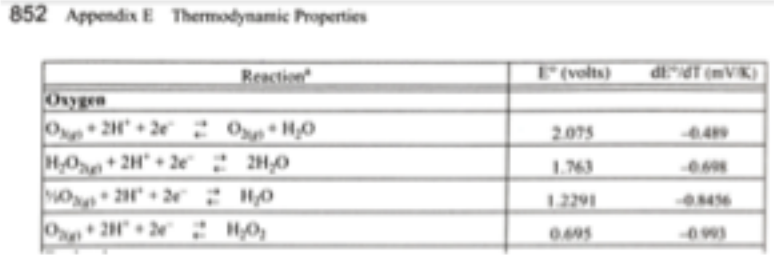
A biological fuel cell is a portable electrical source that can be refueled. Electrical current is generated by a biological redox couple. In an ideal fuel cell, the enzymes would be immobilized on the electrodes and maintain the same activity as if free. In the conceptualized fuel cell on the right, glucose is to be oxidized to gluconolactone in the right cell, catalyzed by immobilized glucose oxidase. Oxygen is excluded from the right cell to avoid loss of electrons by bulk oxidation. The left cell is saturated with air, and a reduction of $O_2$ to $H_2O_2$ catalyzed by immobilized laccase is envisioned. Electrons are to flow through the external circuit and $H^+$ is to flow through the membrane. Each side of the cell is buffered to $pH_c = 7$, $I = 0.25$ M at $T = 298.15$ K. Suppose the concentrations on the right side are [glucose] = 0.1 M, [gluconolactone] = 0.05 M, and on the left side $[H_2O_2] = 0.05$ M. Determine the transformed standard state half-cell potentials and the voltage expected from the cell under stated concentrations. The standard state Gibbs energies of relevant species are shown below at the stated conditions.



| | $H_2O_{2(aq)}$ | Glucose | Gluconolactone |
|---|---|---|---|
| $\Delta G'^{\circ}_{f,i}$ (kJ/mol) | –52 | –427 | –496 |

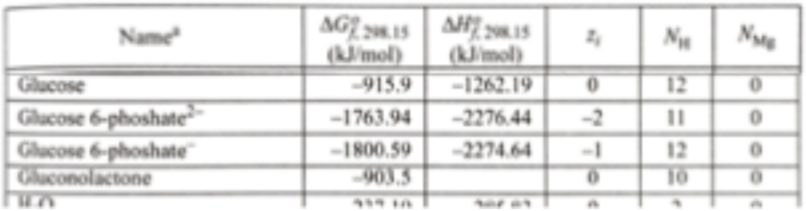
$$\text{glucose} \rightleftarrows \text{gluconolactone} + 2H^+ + 2e^-,$$

$$O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_{2(aq)}$$

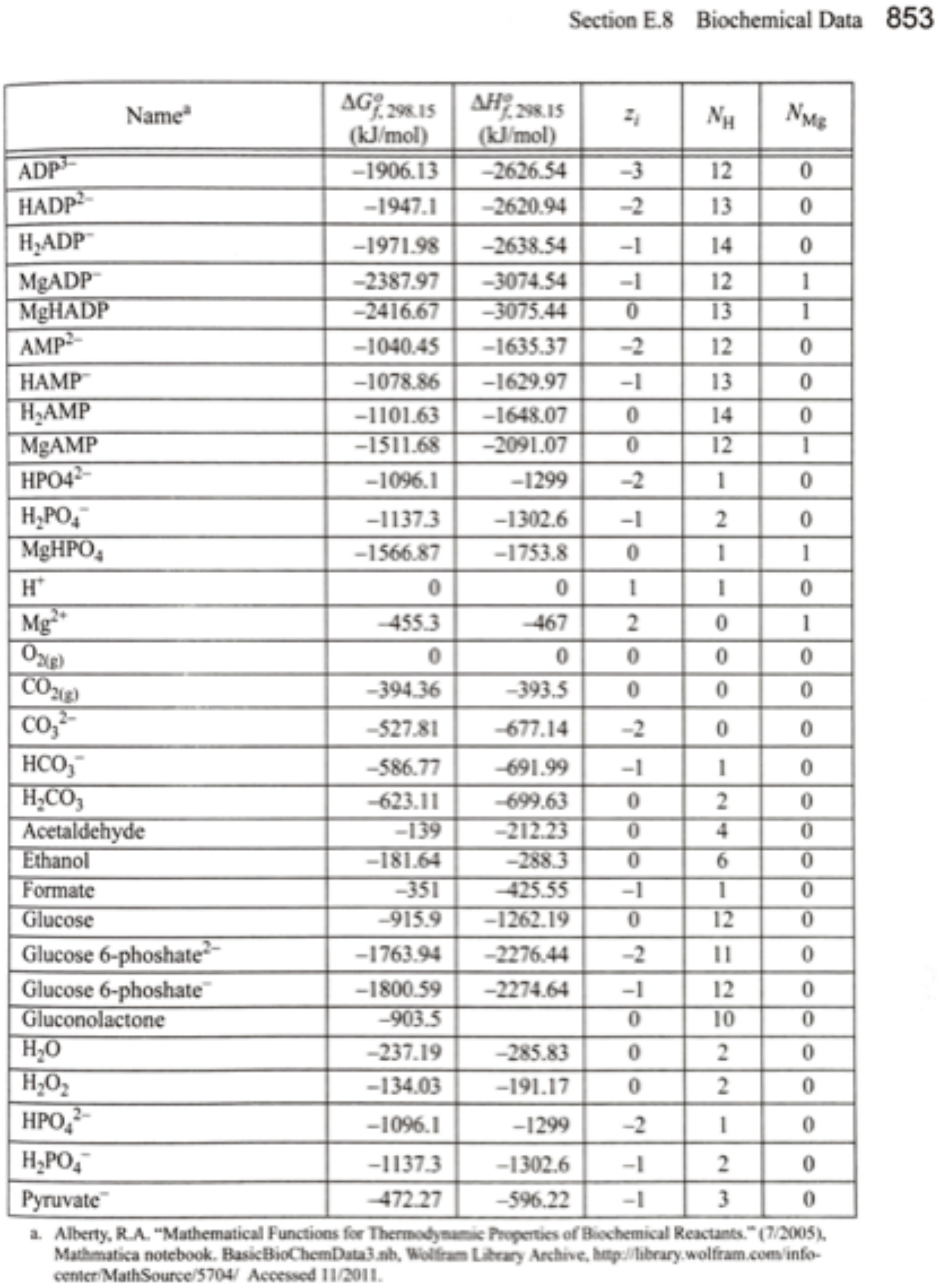


852 Appendix E Thermodynamic Properties

| Reaction[a] | E° (volts) | dE°/dT (mV/K) |
|---|---|---|
| **Oxygen** | | |
| $O_{3(g)} + 2H^+ + 2e^- \rightleftarrows O_{2(g)} + H_2O$ | 2.075 | –0.489 |
| $H_2O_{2(g)} + 2H^+ + 2e^- \rightleftarrows 2H_2O$ | 1.763 | –0.698 |
| $\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O$ | 1.2291 | –0.8456 |
| $O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_2$ | 0.695 | –0.993 |

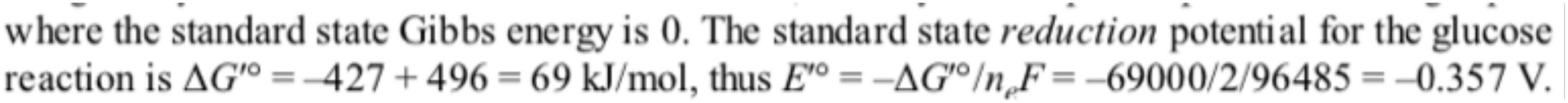


| Name[a] | $\Delta G^{o}_{f,298.15}$ (kJ/mol) | $\Delta H^{o}_{f,298.15}$ (kJ/mol) | $z_i$ | $N_H$ | $N_{Mg}$ |
|---|---|---|---|---|---|
| Glucose | –915.9 | –1262.19 | 0 | 12 | 0 |
| Glucose 6-phoshate$^{2-}$ | –1763.94 | –2276.44 | –2 | 11 | 0 |
| Glucose 6-phoshate$^{-}$ | –1800.59 | –2274.64 | –1 | 12 | 0 |
| Gluconolactone | –903.5 | | 0 | 10 | 0 |

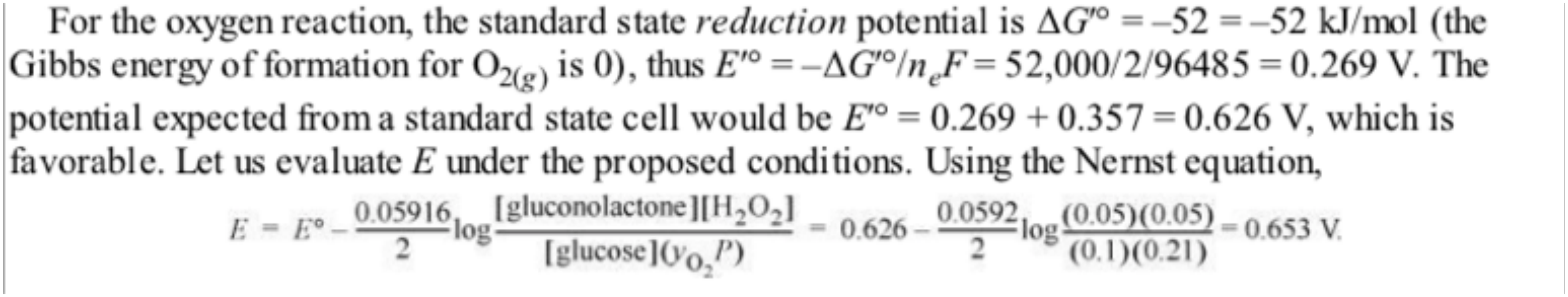


| Name[a] | $\Delta G^o_{f,298.15}$ (kJ/mol) | $\Delta H^o_{f,298.15}$ (kJ/mol) | $z_i$ | $N_H$ | $N_{Mg}$ |
|---|---|---|---|---|---|
| $ADP^{3-}$ | –1906.13 | –2626.54 | –3 | 12 | 0 |
| $HADP^{2-}$ | –1947.1 | –2620.94 | –2 | 13 | 0 |
| $H_2ADP^-$ | –1971.98 | –2638.54 | –1 | 14 | 0 |
| $MgADP^-$ | –2387.97 | –3074.54 | –1 | 12 | 1 |
| MgHADP | –2416.67 | –3075.44 | 0 | 13 | 1 |
| $AMP^{2-}$ | –1040.45 | –1635.37 | –2 | 12 | 0 |
| $HAMP^-$ | –1078.86 | –1629.97 | –1 | 13 | 0 |
| $H_2AMP$ | –1101.63 | –1648.07 | 0 | 14 | 0 |
| MgAMP | –1511.68 | –2091.07 | 0 | 12 | 1 |
| $HPO4^{2-}$ | –1096.1 | –1299 | –2 | 1 | 0 |
| $H_2PO_4^-$ | –1137.3 | –1302.6 | –1 | 2 | 0 |
| $MgHPO_4$ | –1566.87 | –1753.8 | 0 | 1 | 1 |
| $H^+$ | 0 | 0 | 1 | 1 | 0 |
| $Mg^{2+}$ | –455.3 | –467 | 2 | 0 | 1 |
| $O_{2(g)}$ | 0 | 0 | 0 | 0 | 0 |
| $CO_{2(g)}$ | –394.36 | –393.5 | 0 | 0 | 0 |
| $CO_3^{2-}$ | –527.81 | –677.14 | –2 | 0 | 0 |
| $HCO_3^-$ | –586.77 | –691.99 | –1 | 1 | 0 |
| $H_2CO_3$ | –623.11 | –699.63 | 0 | 2 | 0 |
| Acetaldehyde | –139 | –212.23 | 0 | 4 | 0 |
| Ethanol | –181.64 | –288.3 | 0 | 6 | 0 |
| Formate | –351 | –425.55 | –1 | 1 | 0 |
| Glucose | –915.9 | –1262.19 | 0 | 12 | 0 |
| Glucose 6-phoshate$^{2-}$ | –1763.94 | –2276.44 | –2 | 11 | 0 |
| Glucose 6-phoshate$^-$ | –1800.59 | –2274.64 | –1 | 12 | 0 |
| Gluconolactone | –903.5 |  | 0 | 10 | 0 |
| $H_2O$ | –237.19 | –285.83 | 0 | 2 | 0 |
| $H_2O_2$ | –134.03 | –191.17 | 0 | 2 | 0 |
| $HPO_4^{2-}$ | –1096.1 | –1299 | –2 | 1 | 0 |
| $H_2PO_4^-$ | –1137.3 | –1302.6 | –1 | 2 | 0 |
| Pyruvate$^-$ | –472.27 | –596.22 | –1 | 3 | 0 |

[a] Alberty, R.A. "Mathematical Functions for Thermodynamic Properties of Biochemical Reactants." (7/2005), Mathmatica notebook. BasicBioChemData3.nb, Wolfram Library Archive, http://library.wolfram.com/infocenter/MathSource/5704/ Accessed 11/2011.



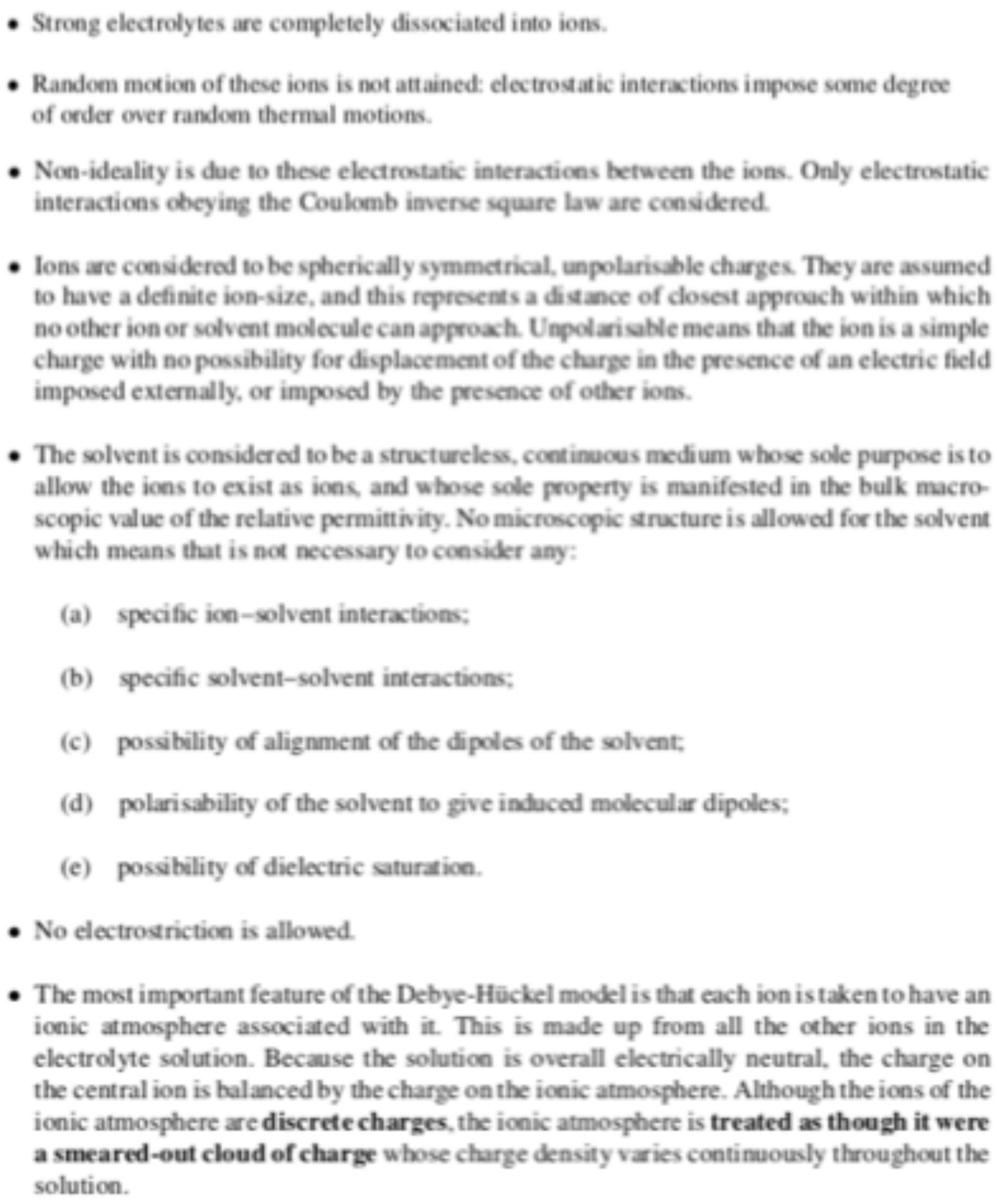
where the standard state Gibbs energy is 0. The standard state *reduction* potential for the glucose reaction is $\Delta G'^\circ = -427 + 496 = 69$ kJ/mol, thus $E'^\circ = -\Delta G'^\circ/n_eF = -69000/2/96485 = -0.357$ V.



For the oxygen reaction, the standard state *reduction* potential is $\Delta G'^\circ = -52 = -52$ kJ/mol (the Gibbs energy of formation for $O_{2(g)}$ is 0), thus $E'^\circ = -\Delta G'^\circ/n_eF = 52{,}000/2/96485 = 0.269$ V. The potential expected from a standard state cell would be $E'^\circ = 0.269 + 0.357 = 0.626$ V, which is favorable. Let us evaluate $E$ under the proposed conditions. Using the Nernst equation,

$$E = E^\circ - \frac{0.05916}{2}\log\frac{[\text{gluconolactone}][\text{H}_2\text{O}_2]}{[\text{glucose}](y_{\text{O}_2}P)} = 0.626 - \frac{0.0592}{2}\log\frac{(0.05)(0.05)}{(0.1)(0.21)} = 0.653 \text{ V.}$$

# Debye-Hückel Model



- Strong electrolytes are completely dissociated into ions.
- Random motion of these ions is not attained: electrostatic interactions impose some degree of order over random thermal motions.
- Non-ideality is due to these electrostatic interactions between the ions. Only electrostatic interactions obeying the Coulomb inverse square law are considered.
- Ions are considered to be spherically symmetrical, unpolarisable charges. They are assumed to have a definite ion-size, and this represents a distance of closest approach within which no other ion or solvent molecule can approach. Unpolarisable means that the ion is a simple charge with no possibility for displacement of the charge in the presence of an electric field imposed externally, or imposed by the presence of other ions.
- The solvent is considered to be a structureless, continuous medium whose sole purpose is to allow the ions to exist as ions, and whose sole property is manifested in the bulk macroscopic value of the relative permittivity. No microscopic structure is allowed for the solvent which means that is not necessary to consider any:

  (a) specific ion–solvent interactions;

  (b) specific solvent–solvent interactions;

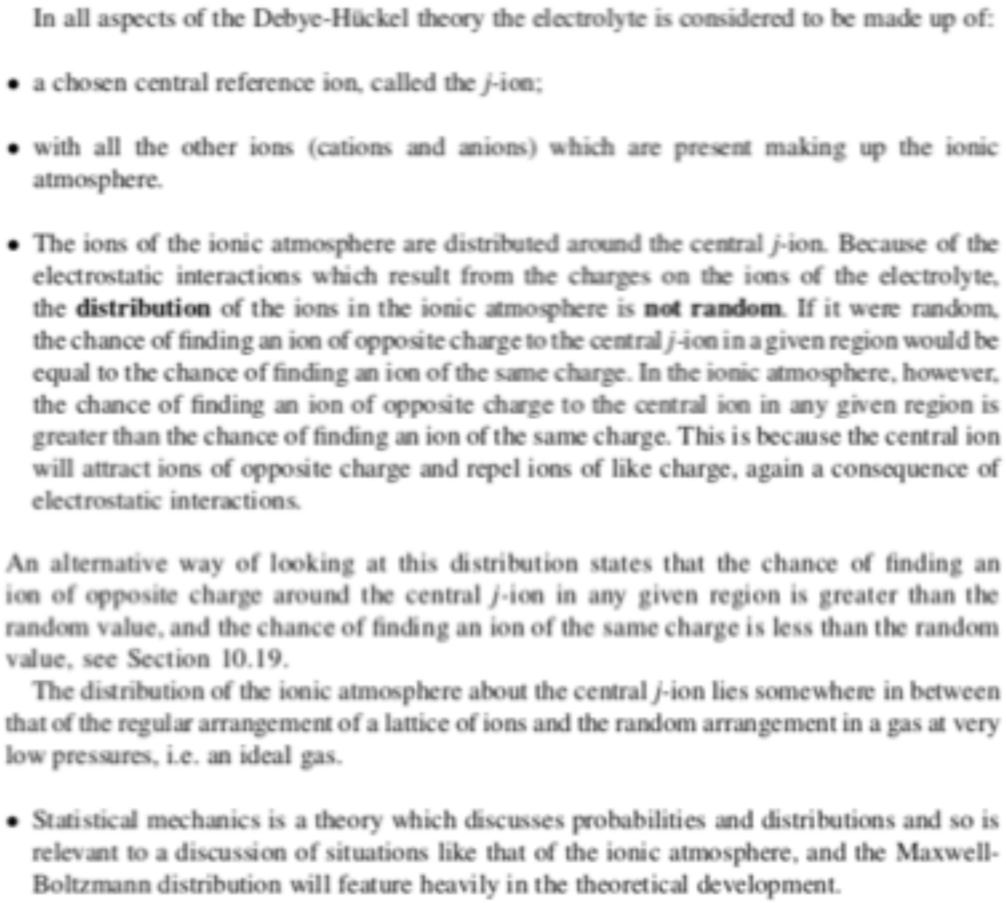
  (c) possibility of alignment of the dipoles of the solvent;

  (d) polarisability of the solvent to give induced molecular dipoles;

  (e) possibility of dielectric saturation.
- No electrostriction is allowed.
- The most important feature of the Debye-Hückel model is that each ion is taken to have an ionic atmosphere associated with it. This is made up from all the other ions in the electrolyte solution. Because the solution is overall electrically neutral, the charge on the central ion is balanced by the charge on the ionic atmosphere. Although the ions of the ionic atmosphere are **discrete charges**, the ionic atmosphere is **treated as though it were a smeared-out cloud of charge** whose charge density varies continuously throughout the solution.

Mean field

# Debye-Hückel Model



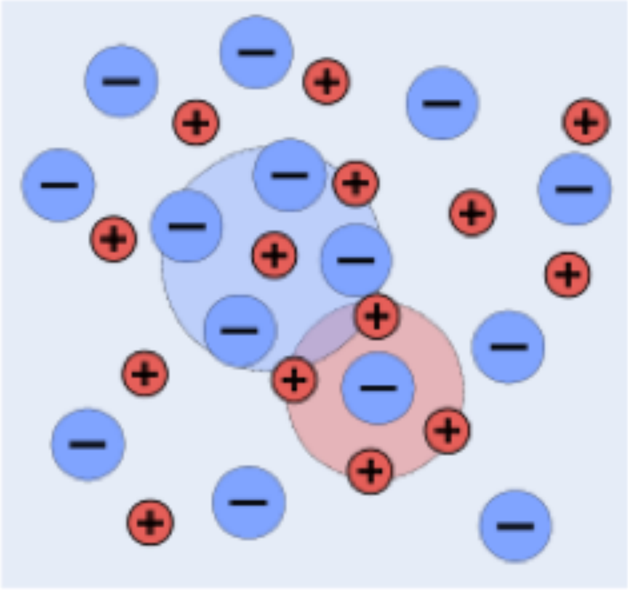
In all aspects of the Debye-Hückel theory the electrolyte is considered to be made up of:

- a chosen central reference ion, called the *j*-ion;
- with all the other ions (cations and anions) which are present making up the ionic atmosphere.
- The ions of the ionic atmosphere are distributed around the central *j*-ion. Because of the electrostatic interactions which result from the charges on the ions of the electrolyte, the **distribution** of the ions in the ionic atmosphere is **not random**. If it were random, the chance of finding an ion of opposite charge to the central *j*-ion in a given region would be equal to the chance of finding an ion of the same charge. In the ionic atmosphere, however, the chance of finding an ion of opposite charge to the central ion in any given region is greater than the chance of finding an ion of the same charge. This is because the central ion will attract ions of opposite charge and repel ions of like charge, again a consequence of electrostatic interactions.

An alternative way of looking at this distribution states that the chance of finding an ion of opposite charge around the central *j*-ion in any given region is greater than the random value, and the chance of finding an ion of the same charge is less than the random value, see Section 10.19.

The distribution of the ionic atmosphere about the central *j*-ion lies somewhere in between that of the regular arrangement of a lattice of ions and the random arrangement in a gas at very low pressures, i.e. an ideal gas.

- Statistical mechanics is a theory which discusses probabilities and distributions and so is relevant to a discussion of situations like that of the ionic atmosphere, and the Maxwell-Boltzmann distribution will feature heavily in the theoretical development.



Coulomb's Law

$$\text{force} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2} \qquad (10.2)$$

$$w = \int_a^b f\,\mathrm{d}r$$

Work to place an ion in a solution of other ions

$$\text{potential energy} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r}\frac{1}{r}$$

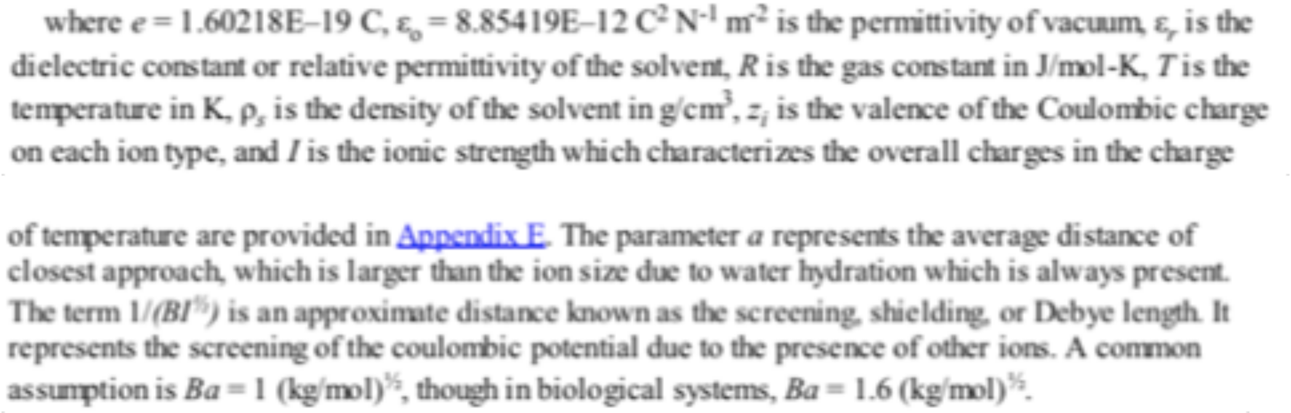
# Debye-Hückel Model

$$\frac{G^E}{RT} = \frac{-4x_s M_{w,s} A_\gamma}{1000(Ba)^3}\left[\ln(1 + Ba\sqrt{I}) - Ba\sqrt{I} + \frac{(Ba)^2 I}{2}\right] \qquad 18.102$$

$$\text{where } A_\gamma = \frac{N_A^2}{8\pi}\left(\frac{e^2}{\varepsilon_o \varepsilon_r RT}\right)^{3/2} \frac{(2000\rho_s)^{1/2}}{2.303} = \frac{1.8249\text{E}6(\rho_s)^{1/2}}{(\varepsilon_r T)^{3/2}} \qquad 18.103$$

$$\text{and } A_\gamma = 0.510(\text{kg/mol})^{1/2} \text{ for water at 25°C} \qquad 18.104$$

$$\text{ionic strength } I = 0.5\sum_{\text{ions}} m_i z_i^2 \qquad 18.105$$



where $e$ = 1.60218E–19 C, $\varepsilon_o$ = 8.85419E–12 $C^2 N^{-1} m^{-2}$ is the permittivity of vacuum, $\varepsilon_r$ is the dielectric constant or relative permittivity of the solvent, $R$ is the gas constant in J/mol-K, $T$ is the temperature in K, $\rho_s$ is the density of the solvent in g/cm$^3$, $z_i$ is the valence of the Coulombic charge on each ion type, and $I$ is the ionic strength which characterizes the overall charges in the charge

of temperature are provided in Appendix E. The parameter $a$ represents the average distance of closest approach, which is larger than the ion size due to water hydration which is always present. The term $1/(BI^{½})$ is an approximate distance known as the screening, shielding, or Debye length. It represents the screening of the coulombic potential due to the presence of other ions. A common assumption is $Ba$ = 1 (kg/mol)$^{½}$, though in biological systems, $Ba$ = 1.6 (kg/mol)$^{½}$.

$$\log_{10}\gamma_i^{\square} = \frac{-z_i^2 A_\gamma \sqrt{I}}{1 + Ba\sqrt{I}} \text{ up to } I = 0.1 \text{ m} \qquad 18.106$$

# Activity Coefficient of Water

$$\log_{10}\gamma_s = \frac{2A_\gamma M_{w,s}}{1000(Ba)^3}\left\{1 + Ba\sqrt{I} - \frac{1}{1 + Ba\sqrt{I}} - 2\ln(1 + Ba\sqrt{I})\right\} \qquad 18.107$$

Can be determined by measuring the osmotic pressure

$$\Pi = \frac{RT}{V_s}\,\frac{M_{w,s}\sum_{electrolytes} m_i}{1000}\Phi \qquad 18.109$$

$$\Phi = \frac{-1000}{M_{w,s}\sum_{electrolytes} m_i}\ln a_s \qquad 18.108$$

# Chlorination of Water

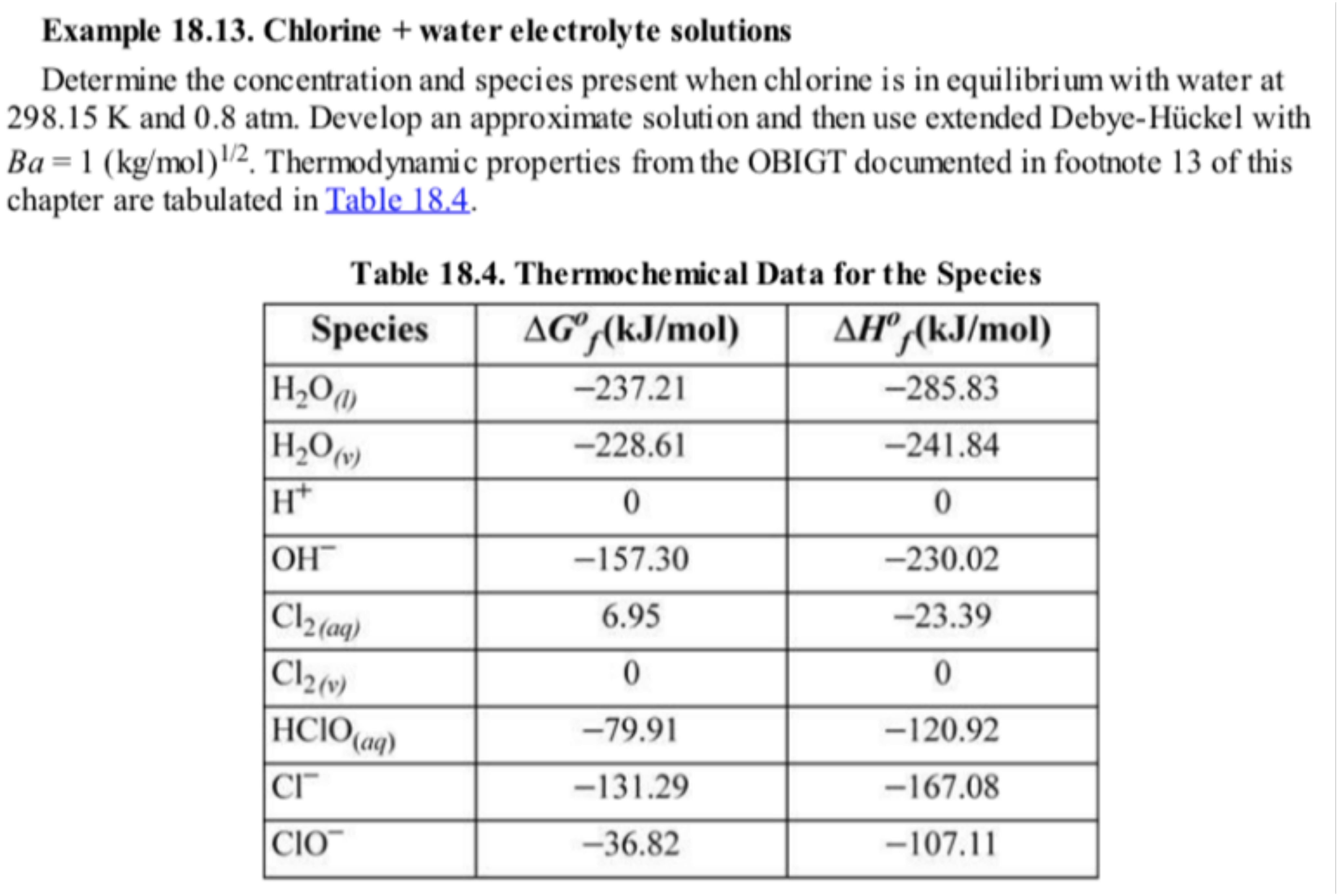
$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-{}_{(aq)} \qquad K_{a2} = \frac{a_{H^+}a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} \qquad 18.129$$

$$H_2O_{(v)} \rightleftarrows H_2O_{(l)} \qquad K = \frac{a_{H_2O}}{y_{H_2O}P} = \frac{1}{P^{sat}_{H_2O}} \qquad 18.130$$

$$Cl_{2(v)} \rightleftarrows Cl_{2(aq)} \qquad K_{H(Cl_2)} = \frac{a_{Cl_2}}{y_{Cl_2}P} \qquad 18.131$$



**Example 18.13. Chlorine + water electrolyte solutions**

Determine the concentration and species present when chlorine is in equilibrium with water at 298.15 K and 0.8 atm. Develop an approximate solution and then use extended Debye-Hückel with $Ba = 1\ (\text{kg/mol})^{1/2}$. Thermodynamic properties from the OBIGT documented in footnote 13 of this chapter are tabulated in Table 18.4.

**Table 18.4. Thermochemical Data for the Species**

| Species | $\Delta G^o_f$(kJ/mol) | $\Delta H^o_f$(kJ/mol) |
|---|---|---|
| $H_2O_{(l)}$ | −237.21 | −285.83 |
| $H_2O_{(v)}$ | −228.61 | −241.84 |
| $H^+$ | 0 | 0 |
| $OH^-$ | −157.30 | −230.02 |
| $Cl_{2(aq)}$ | 6.95 | −23.39 |
| $Cl_{2(v)}$ | 0 | 0 |
| $HClO_{(aq)}$ | −79.91 | −120.92 |
| $Cl^-$ | −131.29 | −167.08 |
| $ClO^-$ | −36.82 | −107.11 |

We first work the problem assuming ideal solutions. This provides an approximate answer. Then we may use the activity coefficients to refine the answer. Using the Gibbs energies of formation, the equilibrium constants are: $pK_{a1} = 3.339$, $pK_{a2} = 7.549$, and $K_{H(Cl_2)} = 0.0606$, where $K_H$ is Henry's constant for $Cl_2$.

Since chlorine forms the strong acid HCl and the weak hypochlorous acid when dissolving in pure water, we expect pH < 7. Note that the weak hypochlorous acid should be almost totally protonated below pH = pK – 1 = 6.5. Since a strong acid HCl is being formed, this seems very likely. Let us proceed with that assumption. This enables us to disregard the dissociation of Eqn. 18.128 as a first approximation.

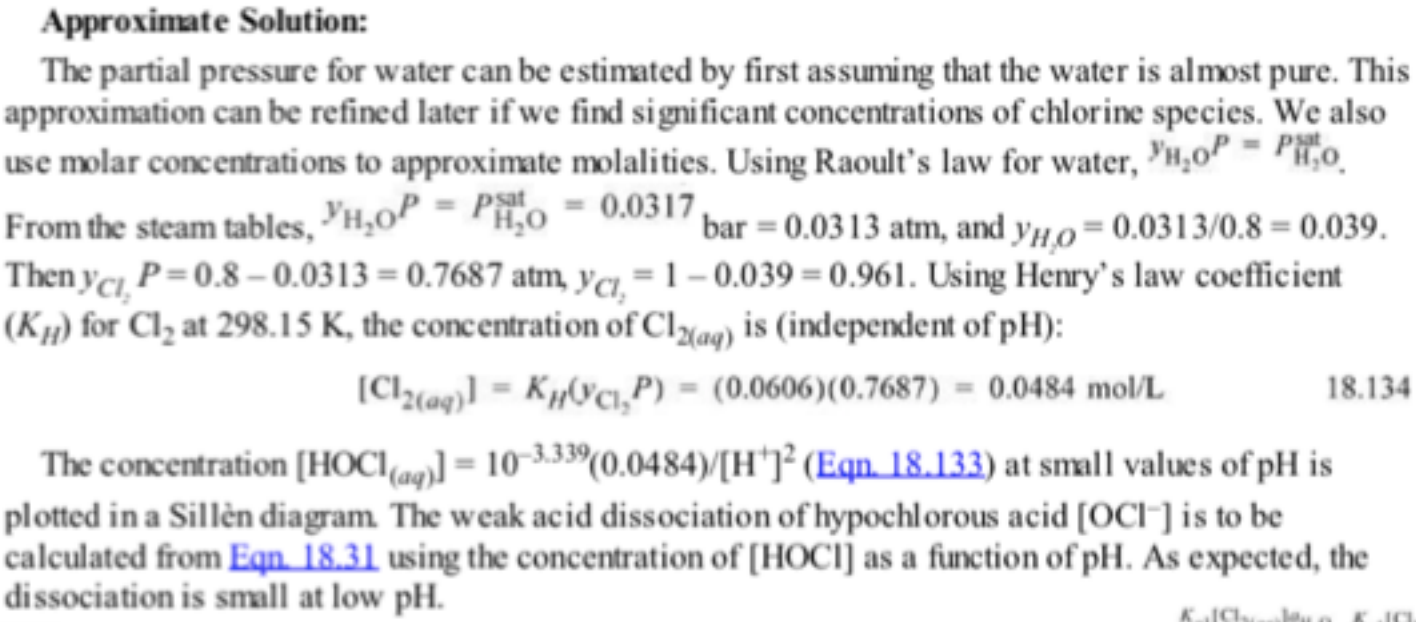
The three reaction equilibria are summarized in Eqns. 18.127–18.129. The charge balance is

$$[H^+] = [Cl^-] + [ClO^-] + [OH^-] = [Cl^-] + \ldots \qquad 18.132$$

where $[ClO^-]$ is ignored because the dissociation of hypochlorous is small when the pH is small and $[OH^-]$ is ignored when pH is small. Thus, the equilibria of Eqn. 18.127 can be approximated as

$$[HClO_{(aq)}] \approx \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+] - \ldots)} \approx \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$



**Approximate Solution:**

The partial pressure for water can be estimated by first assuming that the water is almost pure. This approximation can be refined later if we find significant concentrations of chlorine species. We also use molar concentrations to approximate molalities. Using Raoult's law for water, $y_{H_2O}P = P^{sat}_{H_2O}$.

From the steam tables, $y_{H_2O}P = P^{sat}_{H_2O} = 0.0317$ bar = 0.0313 atm, and $y_{H_2O} = 0.0313/0.8 = 0.039$. Then $y_{Cl_2}P = 0.8 - 0.0313 = 0.7687$ atm, $y_{Cl_2} = 1 - 0.039 = 0.961$. Using Henry's law coefficient ($K_H$) for $Cl_2$ at 298.15 K, the concentration of $Cl_{2(aq)}$ is (independent of pH):

$$[Cl_{2(aq)}] = K_H(y_{Cl_2}P) = (0.0606)(0.7687) = 0.0484 \text{ mol/L} \qquad 18.134$$

The concentration $[HOCl_{(aq)}] = 10^{-3.339}(0.0484)/[H^+]^2$ (Eqn. 18.133) at small values of pH is plotted in a Sillèn diagram. The weak acid dissociation of hypochlorous acid $[OCl^-]$ is to be calculated from Eqn. 18.31 using the concentration of [HOCl] as a function of pH. As expected, the dissociation is small at low pH.

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

$$[HClO_{(aq)}] = \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+] - \ldots)} \approx \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$

Double $[H^+]$ makes it about 0.3 higher

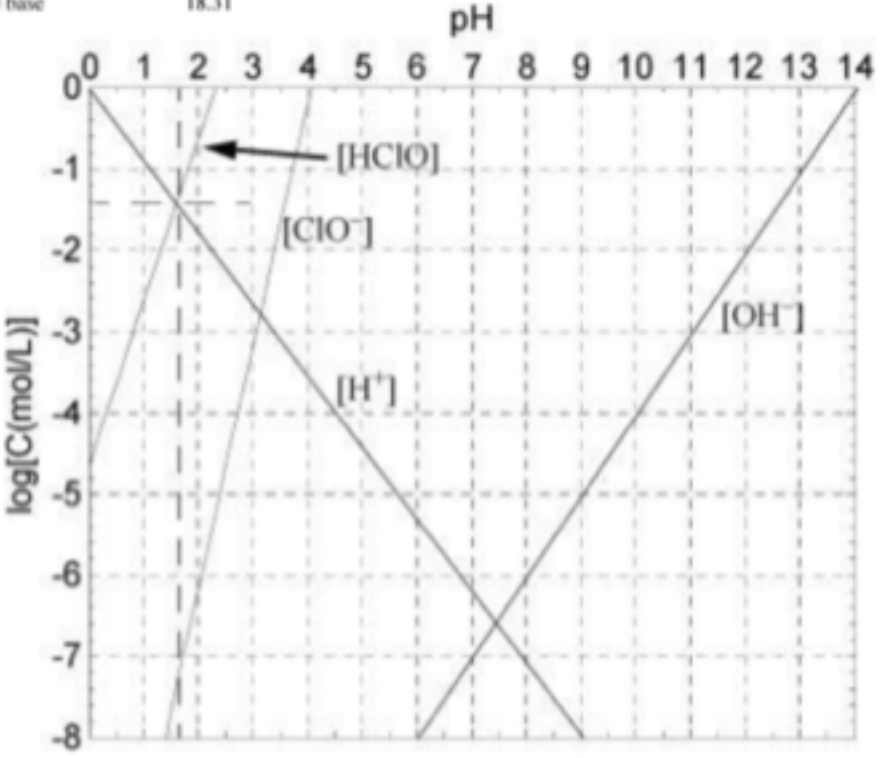


**Figure 18.14. Determination of equilibria for the chlorine system.**

The weak acid curve in Fig. 18.14 is much different from curves in previous examples because, in this case, the overall concentration of weak acid is changing rapidly with pH. Now consider the material balance associated with Eqns. 18.127 and 18.128. Since Eqn. 18.128 does not occur to a significant extent, to a good approximation by the stoichiometry of Eqn. 18.127 $[H^+] = [Cl^-] = [HOCl]$. This occurs at the intersection shown by the dotted lines. The approximate solution is pH = 1.55, $[H^+] = [Cl^-] = [HOCl] = 10^{-1.55} = 0.0282$ mol/L. Note on the diagram that $[OCl–] = 10^{-7.5} = 3.2E\text{-}8$. Now, we can use these as initial guesses in a more rigorous answer.

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+}a_{Cl^-}a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}}a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-_{(aq)} \qquad K_{a2} = \frac{a_{H^+}a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

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

$$[HClO_{(aq)}] = \frac{K_{a1}[Cl_{2(aq)}]a_{H_2O}}{[H^+]([H^+] - ...)} = \frac{K_{a1}[Cl_{2(aq)}]}{[H^+]^2} \qquad 18.133$$

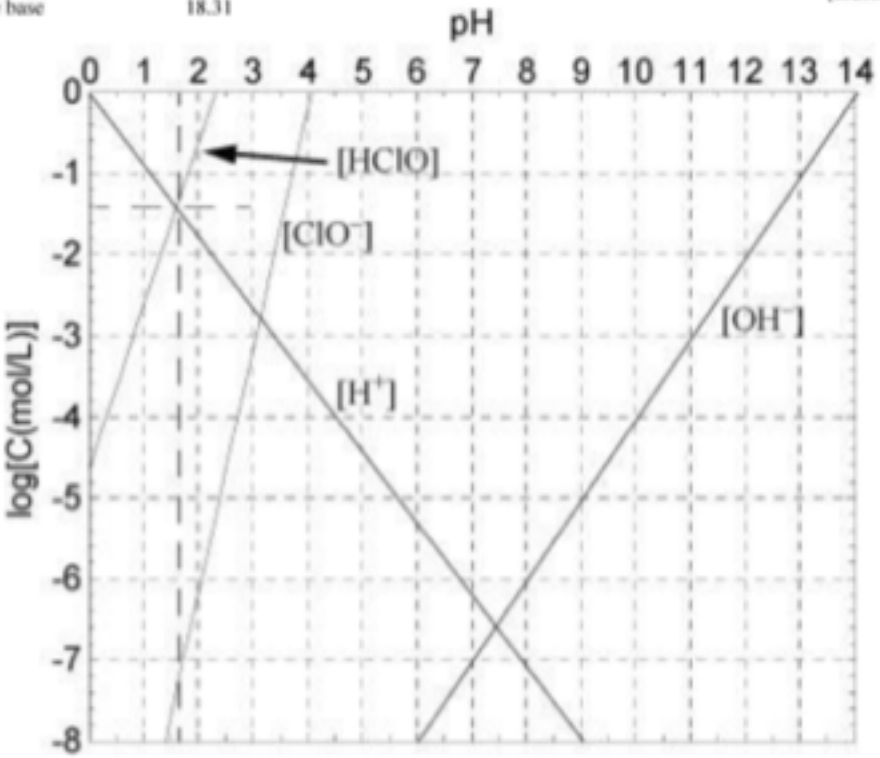


**Figure 18.14. Determination of equilibria for the chlorine system.**

Double $[H^+]$ makes it about 0.3 higher

**Calculation with Activity Coefficients:**

Thermodynamic properties for the components are tabulated below and in the spreadsheet: CL2H2O.xlsx. Note that the data tabulated below include values for $Cl_2$ and $H_2O$ in both the vapor and aqueous phases. The Gibbs energies are used to calculate the VLE distribution coefficients as a "reaction."

To solve the nine equations (five equilibria, three atom balances, and one charge balance) simultaneously, we must identify nine unknowns. The nine unknowns selected here are the species listed in Table 18.4: the liquid moles of $H_2O$, $Cl_2$, HClO, $H^+$, $Cl^-$, $ClO^-$, and $OH^-$, and the vapor moles of $H_2O_{(v)}$ and $Cl_{2(v)}$. The basis is 1 liter of liquid water ($n^i_{H_2O} = 55.51$ moles) and $n^i_{Cl_2} = 0.9$ moles initially.

The detailed calculation are handled as a reactive flash. Three atom balances must be satisfied–H, O, Cl, along with the charge balance. The atom balances and charge balance are shown in Table 18.5 for the basis of 1 liter of liquid water and 0.9 moles of $Cl_2$. The compositions for iteration are summarized in Table 18.6.

**Table 18.4. Thermochemical Data for the Species**

| Species | $\Delta G^o_f$(kJ/mol) | $\Delta H^o_f$(kJ/mol) |
|---|---|---|
| $H_2O_{(l)}$ | −237.21 | −285.83 |
| $H_2O_{(v)}$ | −228.61 | −241.84 |
| $H^+$ | 0 | 0 |
| $OH^-$ | −157.30 | −230.02 |
| $Cl_{2(aq)}$ | 6.95 | −23.39 |
| $Cl_{2(v)}$ | 0 | 0 |
| $HClO_{(aq)}$ | −79.91 | −120.92 |
| $Cl^-$ | −131.29 | −167.08 |
| $ClO^-$ | −36.82 | −107.11 |

$$Cl_{2(aq)} + H_2O \rightleftarrows H^+ + Cl^- + HClO_{(aq)} \qquad K_{a1} = \frac{a_{H^+} a_{Cl^-} a_{HClO_{(aq)}}}{a_{Cl_{2(aq)}} a_{H_2O}} \qquad 18.127$$

$$HClO_{(aq)} \rightleftarrows H^+ + ClO^-_{(aq)} \qquad K_{a2} = \frac{a_{H^+} a_{ClO^-}}{a_{HClO_{(aq)}}} \qquad 18.128$$

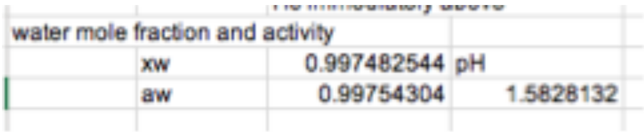
$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} \qquad 18.129$$

$$H_2O_{(v)} \rightleftarrows H_2O_{(l)} \quad K = \frac{a_{H_2O}}{y_{H_2O}P} = \frac{1}{P^{sat}_{H_2O}} \qquad 18.130$$

$$Cl_{2(v)} \rightleftarrows Cl_{2(aq)} \quad K_{H(Cl_2)} = \frac{a_{Cl_2}}{y_{Cl_2}P} \qquad 18.131$$

**Table 18.6. Electrolyte Component Mole Numbers and Activities at the Converged Composition**

| Liquid | | | | Vapor | | |
|---|---|---|---|---|---|---|
| **Species** | **Moles** | **Molality** | $\gamma$□ | **Species** | **Moles** | $y$ |
| $H_2O$ | 55.44564 | ---- | 1.000060649 | $H_2O$ | 0.03322 | 3.88E-02 |
| $Cl_{2(aq)}$ | 4.65E-02 | 0.046591564 | 1 | $Cl_2$ | 0.82233 | 9.61E-01 |
| HClO | 3.11E-02 | 0.031168318 | 1 | *sum* | 0.85555 | 1.00 |
| $H^+$ | 3.11E-02 | 0.031168399 | 0.838440619 | | | |
| $OH^-$ | 4.55E-13 | 4.55732E-13 | 0.838440619 | $y_{Cl2}P = 0.77$ | | |
| $ClO^-$ | 4.01E-08 | 4.01834E-08 | 0.838440619 | | | |
| $Cl^-$ | 3.11E-02 | 0.031168359 | 0.838440619 | | | |
| tot moles | 55.5856 | | | | | |
| Intermediate Calculations | | $I = 0.03117$ | | | | |
| | $x_{H2O} = 0.99748$ | pH = $-\log_{10}((0.0312)(0.838))$ | | | | |
| | $a_{H2O} = 0.9975$ | = 1.58 | | | | |



| | | | |
|---|---|---|---|
| water mole fraction and activity | | | |
| | xw | 0.997482544 | pH |
| | aw | 0.99754304 | 1.5828132 |

# Mean (Geometric Mean) Ionic Activity Coefficients

Mean Molality: $\boxed{m_{\pm} \equiv (m_{+}^{\nu_+} m_{-}^{\nu_-})^{1/\nu}}$ 18.138

Mean Ionic Activity Coefficient: $\boxed{\gamma_{\pm} \equiv (\gamma_{+}^{\nu_+} \gamma_{-}^{\nu_-})^{1/\nu}}$ 18.139

Stoichiometric Number $\nu \equiv (\nu_{+} + \nu_{-})$.

$$\log_{10}\gamma_{\pm} = \frac{-A_{\gamma}|z_{+}z_{-}|\sqrt{I}}{1 + Ba\sqrt{I}} \qquad 18.141$$

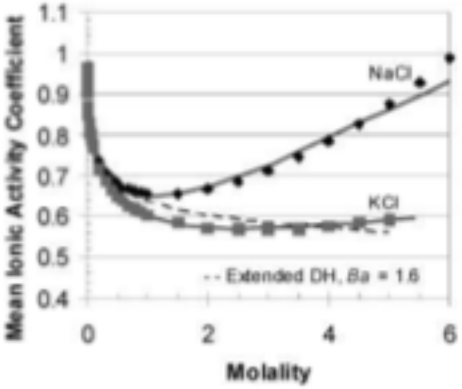


Figure 18.15. Mean ionic activity coefficient for NaCl, KCl and those predicted by the extended Debye-Hückel (DH) model at 298K. Dashed line is the extended Debye-Hückel, Solid lines are the unsymmetric eNRTL using default parameters in ASPEN Plus ver. 7.1. Experimental activity coefficients are from Hamer, W.J.; Wu, Y.-C., 1972. J. Phys. Chem. Ref. Data, 1:1047.