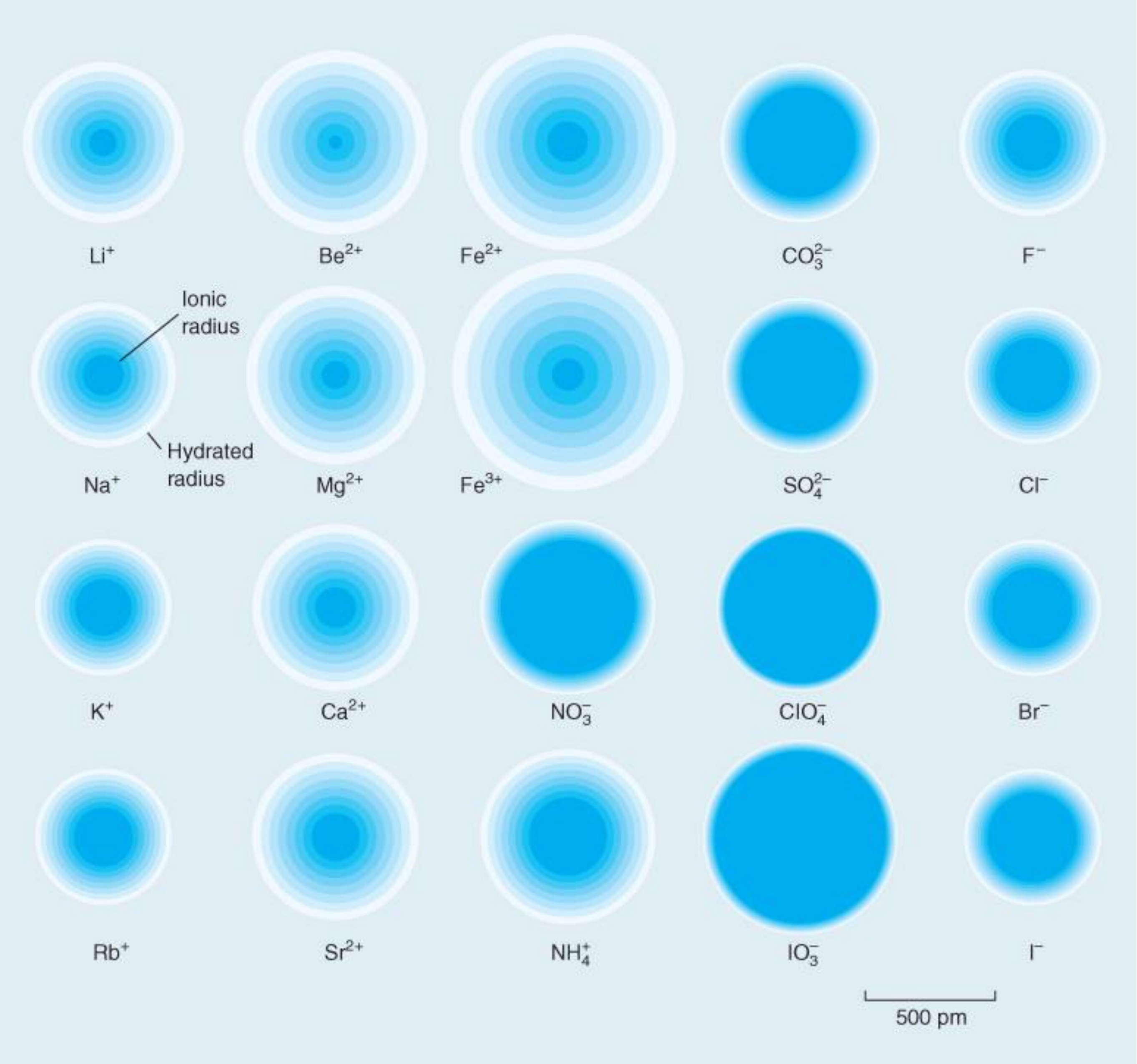
Chapter 8
Activity and the Systematic Treatment of Equilibrium

Overview

Introduction

Ionic and hydrated radii:

- Ions and molecules in solution are surrounded by an organized sheath of solvent molecules. Water binds to cations through the oxygen atom.
- Smaller, more highly charged ions bind more water molecules and behave as larger species in solution.
- The ***activity*** of aqueous ions is related to the size of the hydrated species.



Li^+
Be^{2+}
Fe^{2+}
CO_3^{2-}
F^-
Ionic radius
Na^+
Hydrated radius
Mg^{2+}
Fe^{3+}
SO_4^{2-}
Cl^-
K^+
Ca^{2+}
NO_3^-
ClO_4^-
Br^-
Rb^+
Sr^{2+}
NH_4^+
IO_3^-
I^-
500 pm

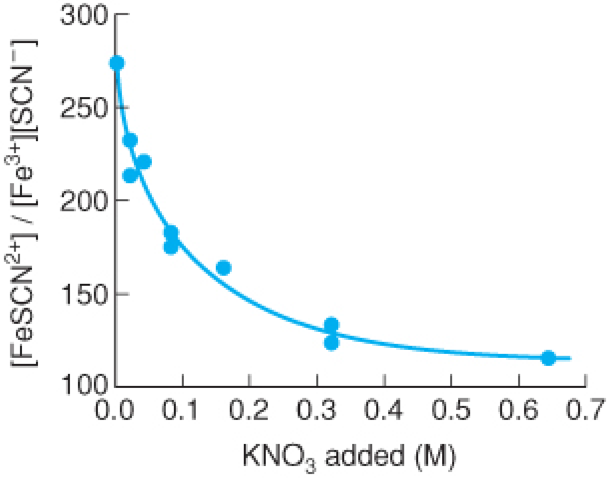
Introduction

- Consider the following equilibrium reaction:

$$\mathrm{Fe^{3+} + SCN^{-} \rightleftarrows Fe(SCN)^{2+}}$$

(Pale yellow) **(Red)**

$$K = \frac{[\mathrm{Fe(SCN)^{2+}}]}{[\mathrm{Fe^{3+}}][\mathrm{SCN^{-}}]}$$



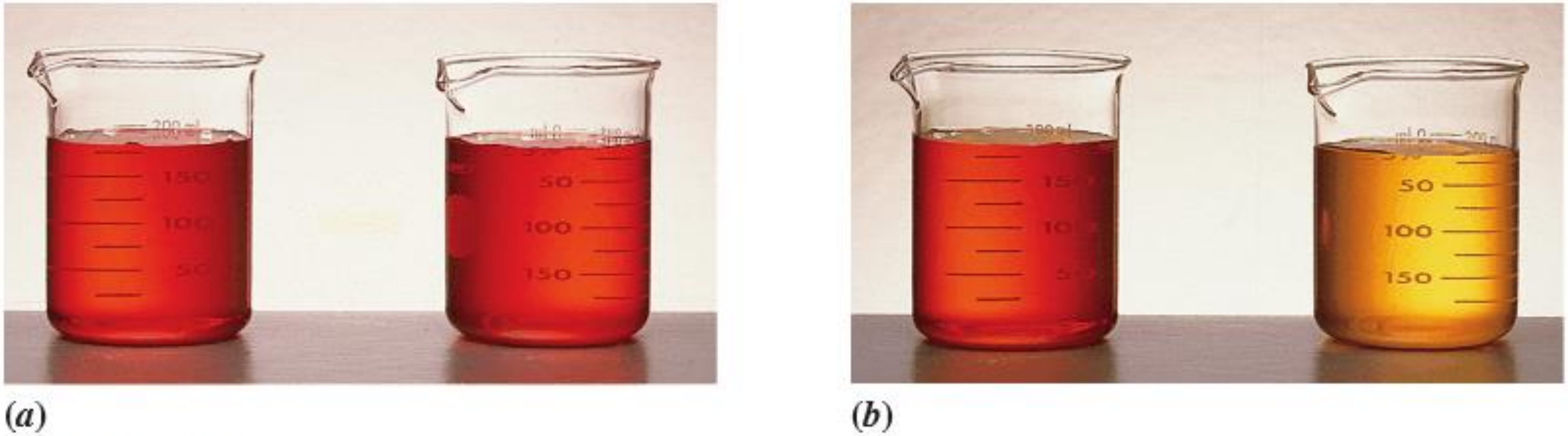
- The concentration quotient *K* decreases if you add the “inert” salt KNO_3 to the solution.
- That is, the equilibrium “constant” is not really constant. Why does this occur?

$$Fe^{3+} + SCN^- \rightleftarrows Fe(SCN)^{2+}$$

(red)

Solutions same

Add inert salt KNO_3



COLOR PLATE 3 Effect of Ionic Strength on Ionic Dissociation (Demonstration 8-1) (*a*) Two beakers containing identical solutions with $Fe(SCN)^{2+}$, Fe^{3+}, and SCN^-. (*b*) The red color of $Fe(SCN)^{2+}$ fades when KNO_3 is added to the right-hand beaker because the equilibrium $Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$ shifts to the left. [© Macmillan, Photo by Ken Karp.]

8-1:The Effect of Ionic Strength on Solubility of Salts

- Adding an “inert” salt (KNO_3) to a sparingly soluble salt ($CaSO_4$) increases the solubility of the sparingly soluble salts.

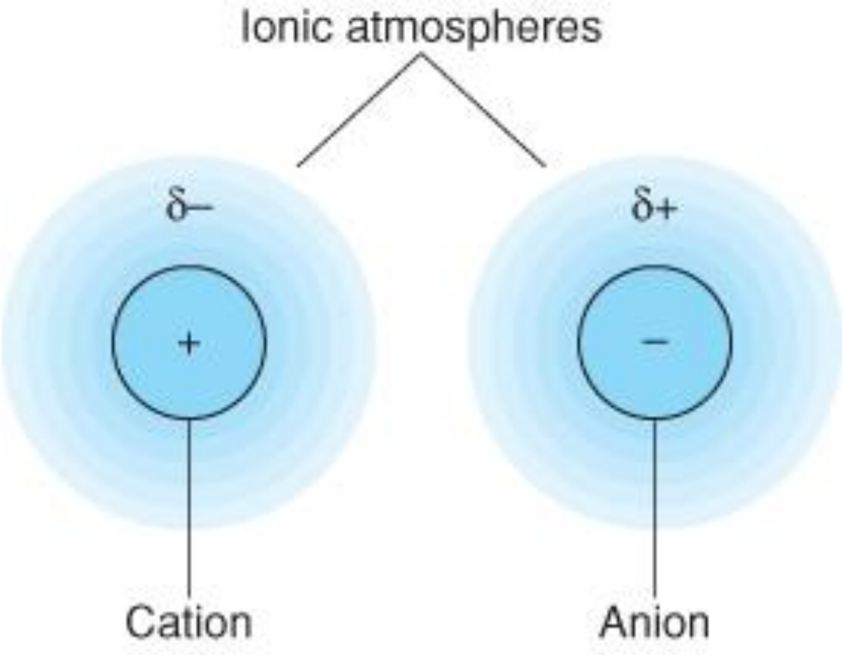
$$CaSO_4(s) \rightleftarrows Ca^{2+} + SO_4^{2-}$$

- Adding ions (in the form of KNO_3) increases the **ionic strength** of the solution. This in turn increases the charge on the ionic atmosphere.
- The **ionic atmosphere** attenuates (decreases) the attraction between the Ca^{2+} and SO_4^{2-}, thus increasing the solubility.

8-1:The Effect of Ionic Strength on Solubility of Salts

The ionic atmosphere:

- Region of net positive or negative charge around an anion or cation in a solution.
  - In a solution containing an inert salt, an **anion** is surrounded by excess cations and a **cation** is surrounded by excess anions.
  - The greater the **ionic strength** of a solution, the higher the charge in the ionic atmosphere.
  - The net attraction between the cation with its ionic atmosphere and the anion with its ionic atmosphere is smaller than it would be between pure cation and anion in the absence of ionic atmospheres.



- An **inert** salt such as KNO_3 affects the ionic atmosphere.
- In the solution, the **cation** is surrounded by the NO_3^- ions (δ^-), and the **anion** is surrounded by the K^+ ions (δ^+).
- The net result is a decrease of the attractive forces between the cation and anion pair.
- Increasing ionic strength promotes dissociation into ions.

8-1:The Effect of Ionic Strength on Solubility of Salts

Ionic strength: $\boldsymbol{\mu}$ is a measure of the total concentration of ions in solution.

$$\boldsymbol{\mu} = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 \ldots..)$$

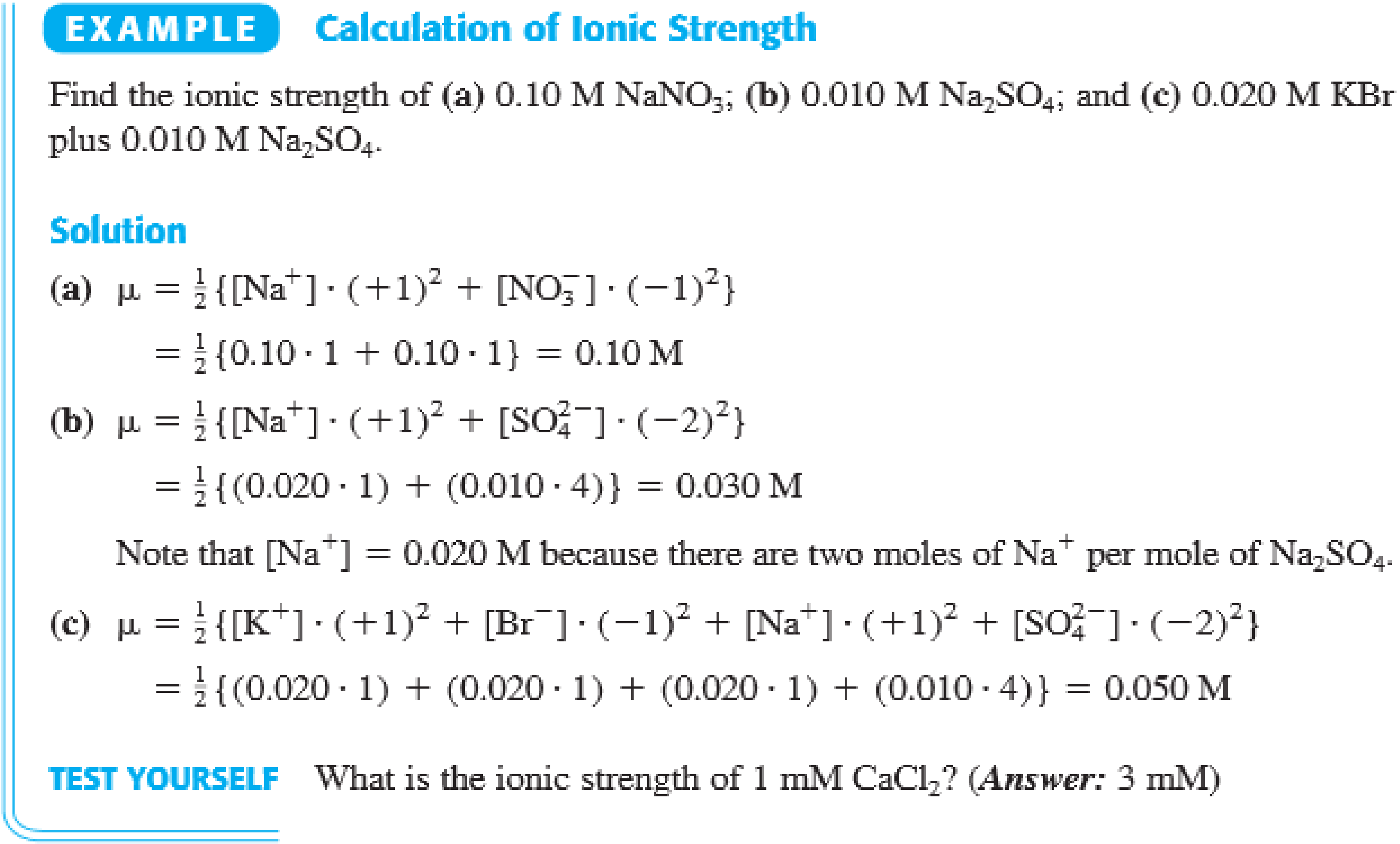
All ions in the solution

c = concentration of ion

z = charge on ion

The more highly charged an ion, the more it is counted.

8-1:The Effect of Ionic Strength on Solubility of Salts



EXAMPLE **Calculation of Ionic Strength**

Find the ionic strength of **(a)** 0.10 M $NaNO_3$; **(b)** 0.010 M Na_2SO_4; and **(c)** 0.020 M KBr plus 0.010 M Na_2SO_4.

Solution

(a) $\mu = \frac{1}{2}\{[Na^+]\cdot(+1)^2 + [NO_3^-]\cdot(-1)^2\}$

$= \frac{1}{2}\{0.10\cdot 1 + 0.10\cdot 1\} = 0.10\text{ M}$

(b) $\mu = \frac{1}{2}\{[Na^+]\cdot(+1)^2 + [SO_4^{2-}]\cdot(-2)^2\}$

$= \frac{1}{2}\{(0.020\cdot 1) + (0.010\cdot 4)\} = 0.030\text{ M}$

Note that $[Na^+] = 0.020$ M because there are two moles of Na^+ per mole of Na_2SO_4.

(c) $\mu = \frac{1}{2}\{[K^+]\cdot(+1)^2 + [Br^-]\cdot(-1)^2 + [Na^+]\cdot(+1)^2 + [SO_4^{2-}]\cdot(-2)^2\}$

$= \frac{1}{2}\{(0.020\cdot 1) + (0.020\cdot 1) + (0.020\cdot 1) + (0.010\cdot 4)\} = 0.050\text{ M}$

TEST YOURSELF What is the ionic strength of 1 mM $CaCl_2$? (*Answer:* 3 mM)

8-2: Activity Coefficients

- The activity of species C is its concentration multiplied by its **activity coefficient,** γ.

$$a_c = [C]\gamma_c$$

- The activity coefficient measures the deviation of behavior from ideality (i.e., $a_c = [C]$) or $\gamma_c = 1$).
- Activity is a dimensionless quantity.
  - If C is a solute means [C]/(1 M)
  - If C is a gas means (pressure of C in bars)/(1 bar)
  - Activity of a pure solid or liquid is, by definition, unity.

- Activities must be used when incorporating ionic strength effects on equilibrium calculations.

8-2: Activity Coefficients

- Write the equilibrium constant expression using **activities**. This is known as the **thermodynamic equilibrium constant**.

$CaSO_4(s) \rightleftarrows Ca^{2+} + SO_4^{2-}$

$$K_{sp} = (\mathbf{a}_{Ca^{2+}})(\mathbf{a}_{SO_4^{2-}})$$

$$\mathbf{a}_{Ca^{2+}} = [Ca^{2+}]\,\gamma_{Ca^{2+}}$$

$$\mathbf{a}_{SO_4^{2-}} = [SO_4^{2-}]\,\gamma_{SO_4^{2-}}$$

$$K_{sp} = ([Ca^{2+}]\,\gamma_{Ca^{2+}})([SO_4^{2-}]\,\gamma_{SO_4^{2-}})$$

Write the thermodynamic equilibrium constant expression:

- $2H_2O \rightleftarrows H_3O^+ + OH^-$

$\gamma_{H_3O^+} = 0.83$

$\gamma_{OH^-} = 0.76$

$$K_W = (\gamma_{H_3O^+}[H_3O^+])(\gamma_{OH^-}[OH^-])$$

$$\left\{\frac{1.0x10^{-14}}{\gamma_{H_3O^+}\gamma_{OH^-}}\right\} = [H_3O^+][OH^-]$$

$K_w' = 1.6 \times 10^{-14} = [H_3O^+][OH^-]$

8-2: Activity Coefficients

- Effect of Ionic Strength, Ion Charge, and Ion Size on the Activity Coefficient over the range of ionic strengths from 0 to 0.1 M, the effect of each variable on activity coefficients is as follows:

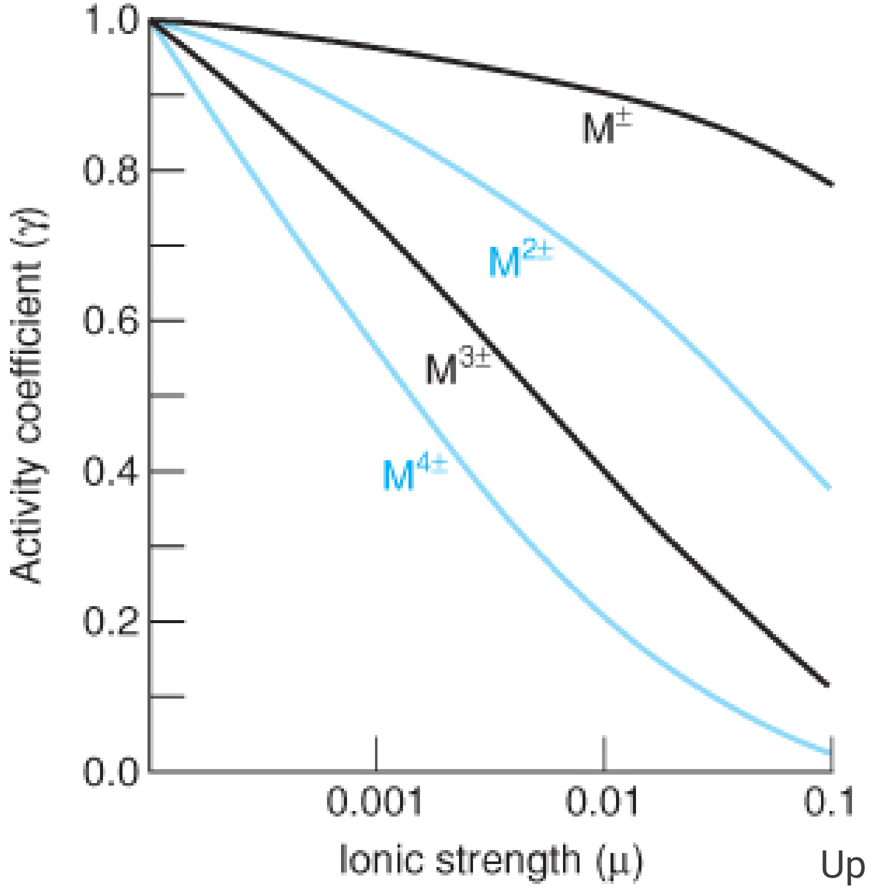


Figure 8-4

8-2: Activity Coefficients

Finding activity coefficients:

1) Calculate using the Debye-Hückel equation
2) Look up in table (see Table 8-1)
3) Interpolate from Table 8-1

8-2: Activity Coefficients

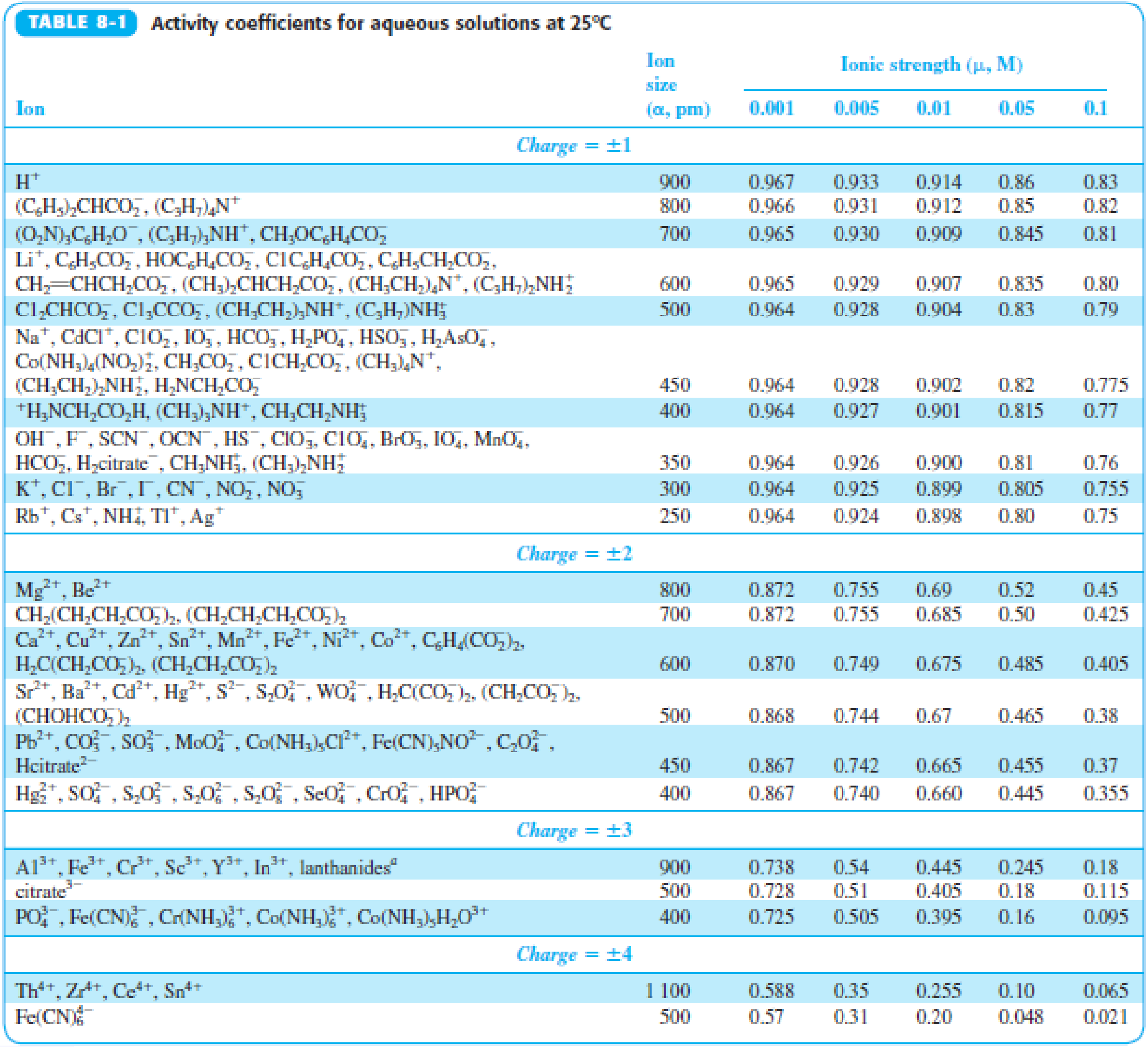


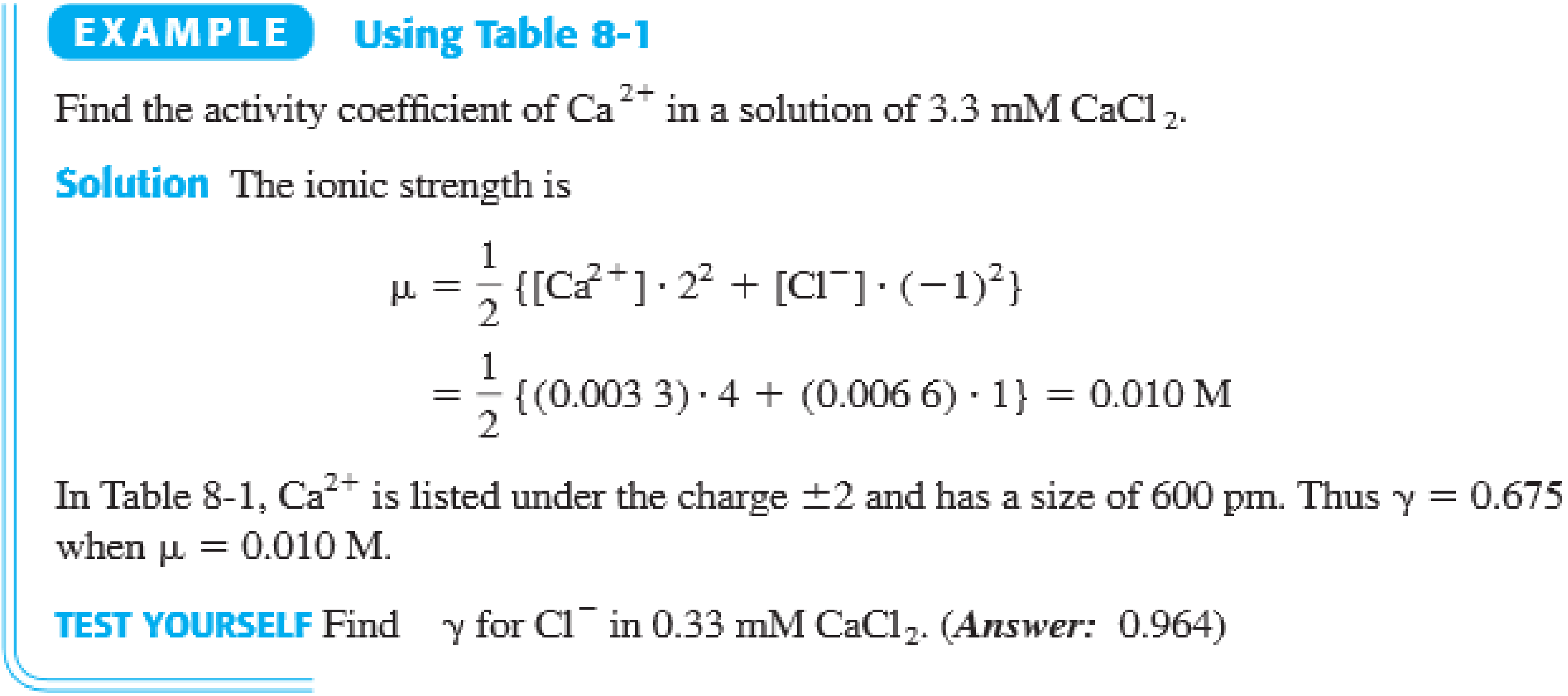
TABLE 8-1 **Activity coefficients for aqueous solutions at 25°C**

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2						
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3						
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
$citrate^{3-}$	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4						
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

[illegible] Kielland, J. Am. Chem. Soc. 1937, 59, 1675.

8-2: Activity Coefficients



EXAMPLE **Using Table 8-1**

Find the activity coefficient of Ca^{2+} in a solution of 3.3 mM $CaCl_2$.

Solution The ionic strength is

$$\mu = \frac{1}{2}\{[Ca^{2+}]\cdot 2^2 + [Cl^-]\cdot(-1)^2\}$$
$$= \frac{1}{2}\{(0.003\,3)\cdot 4 + (0.006\,6)\cdot 1\} = 0.010\ M$$

In Table 8-1, Ca^{2+} is listed under the charge ±2 and has a size of 600 pm. Thus $\gamma = 0.675$ when $\mu = 0.010$ M.

TEST YOURSELF Find γ for Cl^- in 0.33 mM $CaCl_2$. (*Answer:* 0.964)

8-2: Activity Coefficients

- The ionic atmosphere model leads to the **extended Debye-Hückel equation,** relating activity coefficients to ionic strength:

$$\log \gamma_x = \frac{-0.51\, z^2 \sqrt{\mu}}{1 + \left(\alpha \frac{\sqrt{\mu}}{305} \right)}$$

α is hydration radius in pm
μ is ionic strength in M
z is the charge on the ion

(α is found in Table 8-1.)

- Works fairly well for $\mu < 0.1$ M
- Approaches unity at low ionic strengths
- High ionic strength makes γ smaller

8-2: Activity Coefficients

Calculate the activity coefficient for the hydronium ion, H^+, in a solution that is 0.1 M in NaCl.

The ionic strength (calculated) is 0.1 M; $\alpha = 90\underline{0}$ pm (Table 8-4).

$$\log \gamma_x = \frac{-0.51\ z^2 \sqrt{\mu}}{1 + \left(\alpha \frac{\sqrt{\mu}}{305} \right)} \rightarrow \log \gamma_x = \frac{-0.51(1^+)^2 \sqrt{0.1}}{1 + \left(900 \frac{\sqrt{0.1}}{305} \right)}$$

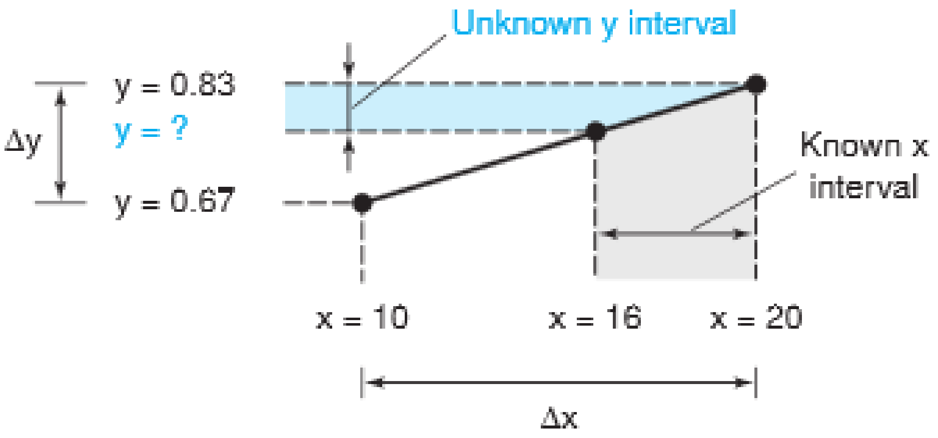
$$\log \gamma_{H+} = \frac{-0.16_{128}}{1.933} = -0.083_4$$

$$\gamma_{H+} = 0.83$$

8-2: Activity Coefficients

Interpolation from Table 8-1

x value	y value
10	0.67
16	?
20	0.83



To interpolate a value of *y*, we can set up a proportion:

Interpolation:

$$\frac{\text{Unknown y interval}}{\Delta y} = \frac{\text{known } x \text{ interval}}{\Delta x} \qquad \textbf{(8-7)}$$

$$\frac{0.83 - y}{0.83 - 0.67} = \frac{20 - 16}{20 - 10} \Rightarrow y = 0.76_6$$

For $x = 16$, our estimate of y is 0.76_6.

8-2: Activity Coefficients

Activity coefficients

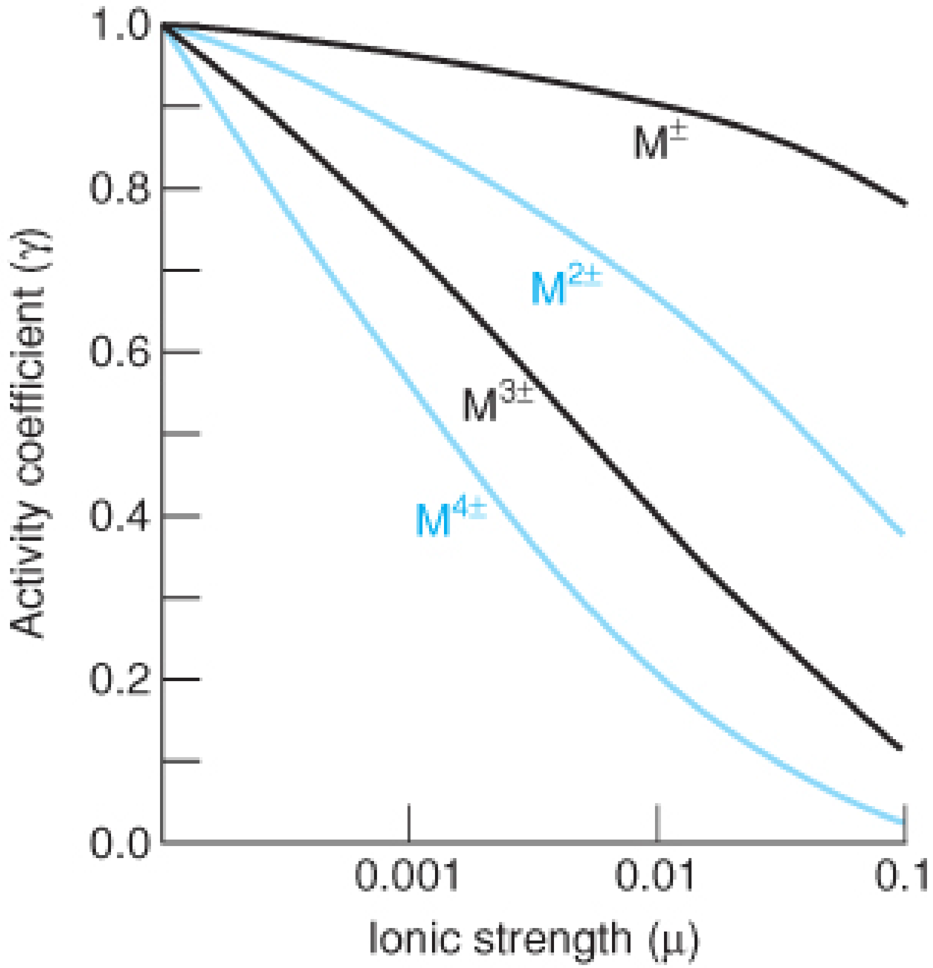


Figure 8-4

8-2: Activity Coefficients

Activity coefficients

1) As μ ↑, γ ↓ (Figure 8-4). The activity coefficient (γ) approaches unity as the ionic strength (μ) approaches 0.

2) As the magnitude of the charge of the ion increases, the departure of its activity coefficient from unity increases.

   Activity corrections are more important for ions with a charge of ±3 than for ions with a charge of ± 1 (Figure 8-4).

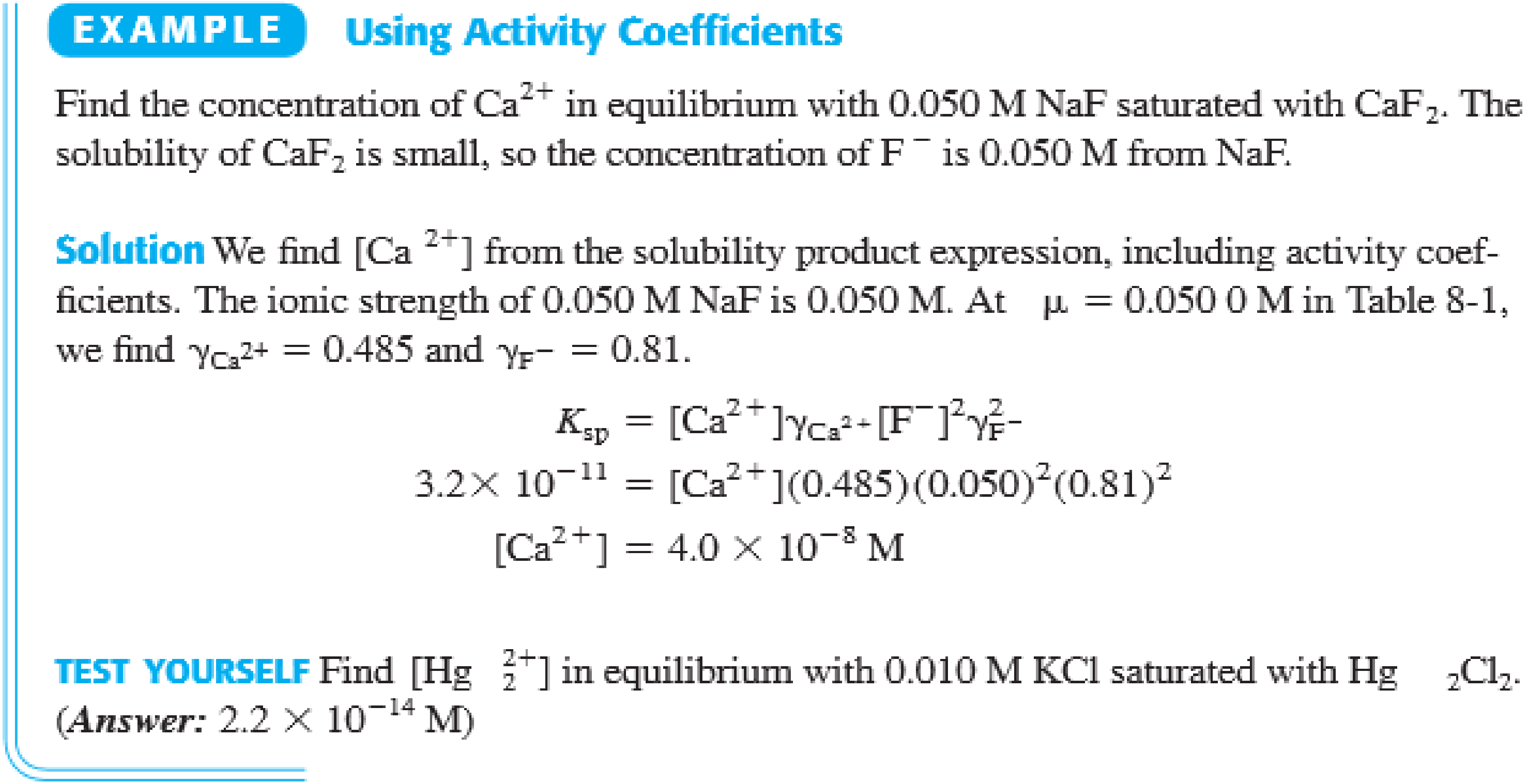
3) The smaller the ion size (α), the more important activity effects become.

8-2: Activity Coefficients

Activity coefficients of nonionic compounds:

- Neutral molecules: such as benzene and acetic acid, have no ionic atmosphere because they have no charge.
- To a good approximation, their activity coefficients are unity when the ionic strength is less than 0.1 M.
- *The activity of a neutral molecule will be assumed to be equal to its concentration*.

8-2: Activity Coefficients



EXAMPLE **Using Activity Coefficients**

Find the concentration of Ca^{2+} in equilibrium with 0.050 M NaF saturated with CaF_2. The solubility of CaF_2 is small, so the concentration of F^- is 0.050 M from NaF.

Solution We find $[Ca^{2+}]$ from the solubility product expression, including activity coefficients. The ionic strength of 0.050 M NaF is 0.050 M. At $\mu = 0.050\,0$ M in Table 8-1, we find $\gamma_{Ca^{2+}} = 0.485$ and $\gamma_{F^-} = 0.81$.

$$K_{sp} = [Ca^{2+}]\gamma_{Ca^{2+}}[F^-]^2\gamma^2_{F^-}$$

$$3.2 \times 10^{-11} = [Ca^{2+}](0.485)(0.050)^2(0.81)^2$$

$$[Ca^{2+}] = 4.0 \times 10^{-8}\ M$$

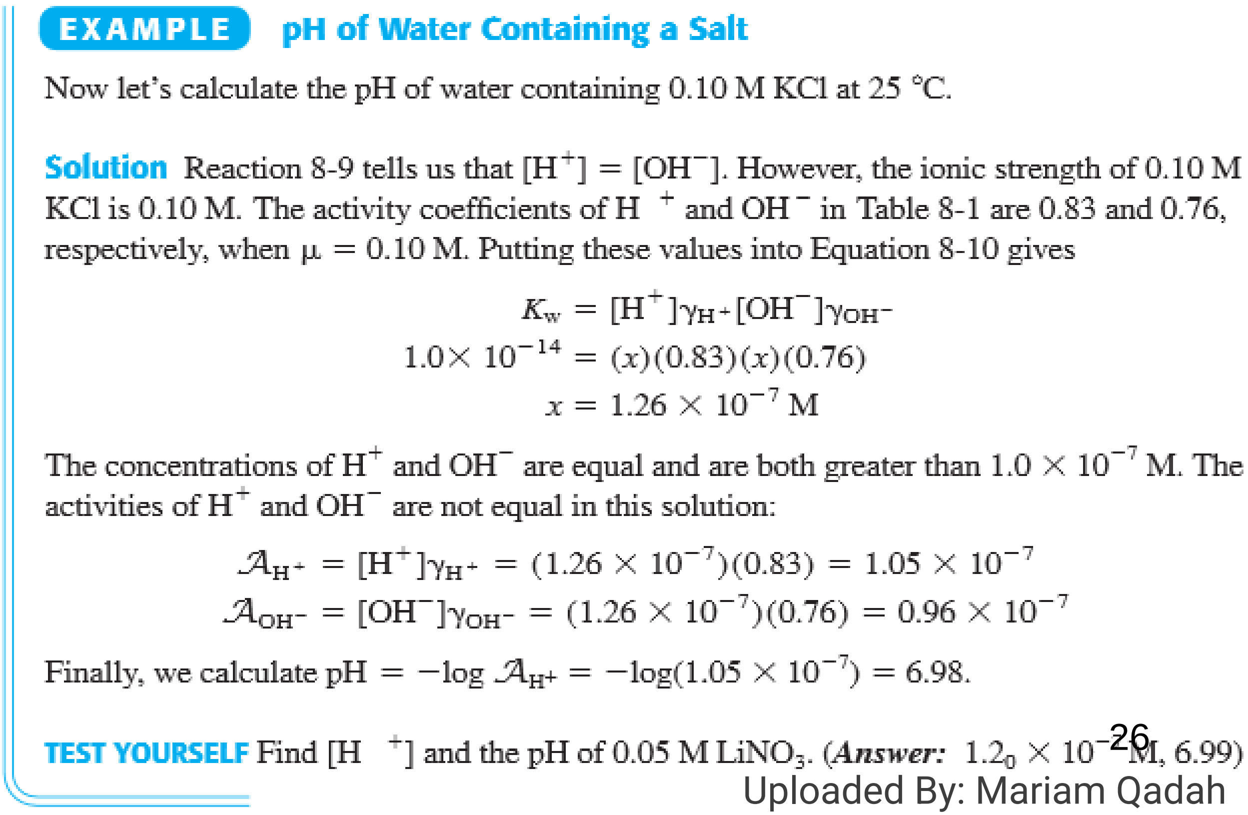
TEST YOURSELF Find $[Hg_2^{2+}]$ in equilibrium with 0.010 M KCl saturated with Hg_2Cl_2. (*Answer:* 2.2×10^{-14} M)

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.2 \times 10^{-18}$,

$\gamma = 0.660$, 0.899 for Hg_2^{2+} and Cl^-, respectively (Table 8-1).

8-3: pH Revisited

- When we measure pH with a pH meter, we are attempting to measure the negative logarithm of the hydrogen ion **activity,** not its concentration.
- $pH = -Log\ (a_{H+})$
- $pH = -Log\ [H^+]\ \gamma_{H+}$



EXAMPLE **pH of Water Containing a Salt**

Now let's calculate the pH of water containing 0.10 M KCl at 25 °C.

Solution Reaction 8-9 tells us that $[H^+] = [OH^-]$. However, the ionic strength of 0.10 M KCl is 0.10 M. The activity coefficients of H^+ and OH^- in Table 8-1 are 0.83 and 0.76, respectively, when $\mu = 0.10$ M. Putting these values into Equation 8-10 gives

$$K_w = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-}$$
$$1.0 \times 10^{-14} = (x)(0.83)(x)(0.76)$$
$$x = 1.26 \times 10^{-7}\ M$$

The concentrations of H^+ and OH^- are equal and are both greater than 1.0×10^{-7} M. The activities of H^+ and OH^- are not equal in this solution:

$$\mathcal{A}_{H^+} = [H^+]\gamma_{H^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7}$$
$$\mathcal{A}_{OH^-} = [OH^-]\gamma_{OH^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7}$$

Finally, we calculate $pH = -\log \mathcal{A}_{H^+} = -\log(1.05 \times 10^{-7}) = 6.98$.

TEST YOURSELF Find $[H^+]$ and the pH of 0.05 M $LiNO_3$. (***Answer:*** $1.2_0 \times 10^{-7}$ M, 6.99)

8-4: Systematic Treatment of Equilibrium

- The systematic treatment of equilibrium is a way to deal with all types of chemical equilibria, regardless of their complexity.
- After setting up general equations, we often introduce specific conditions or judicious approximations that allow simplification.
- Write as many independent algebraic equations as there are unknowns (species) in the problem.
- Equations are generated by writing all the chemical equilibrium conditions plus two more: the balances of charge and of mass.
- There is only one charge balance in a given system, but there could be several mass balances.

7-4: Systematic Treatment of Equilibrium

Step1: write the pertinent reactions

Step 2: write the charge balance equation (only one!)

Step 3: write mass balance equations. There maybe more than one

Step 4: write the equilibrium constant expression for each chemical reaction. This step is the only one in which activity coefficients appear

Step 5: count the equations and the unknowns. There should be as many equations as unknowns (chemical species). If not, you must either find more equations or fix some concentrations at known values

Step 6: solve for all unknowns

8-4: Systematic Treatment of Equilibrium

- **Charge Balance:** An algebraic statement of electroneutrality: *The sum of the positive charges in solution equals the sum of the negative charges in solution.*

$\sum(+)$ charges = $\sum(–)$charges

Multiply concentrations by charge

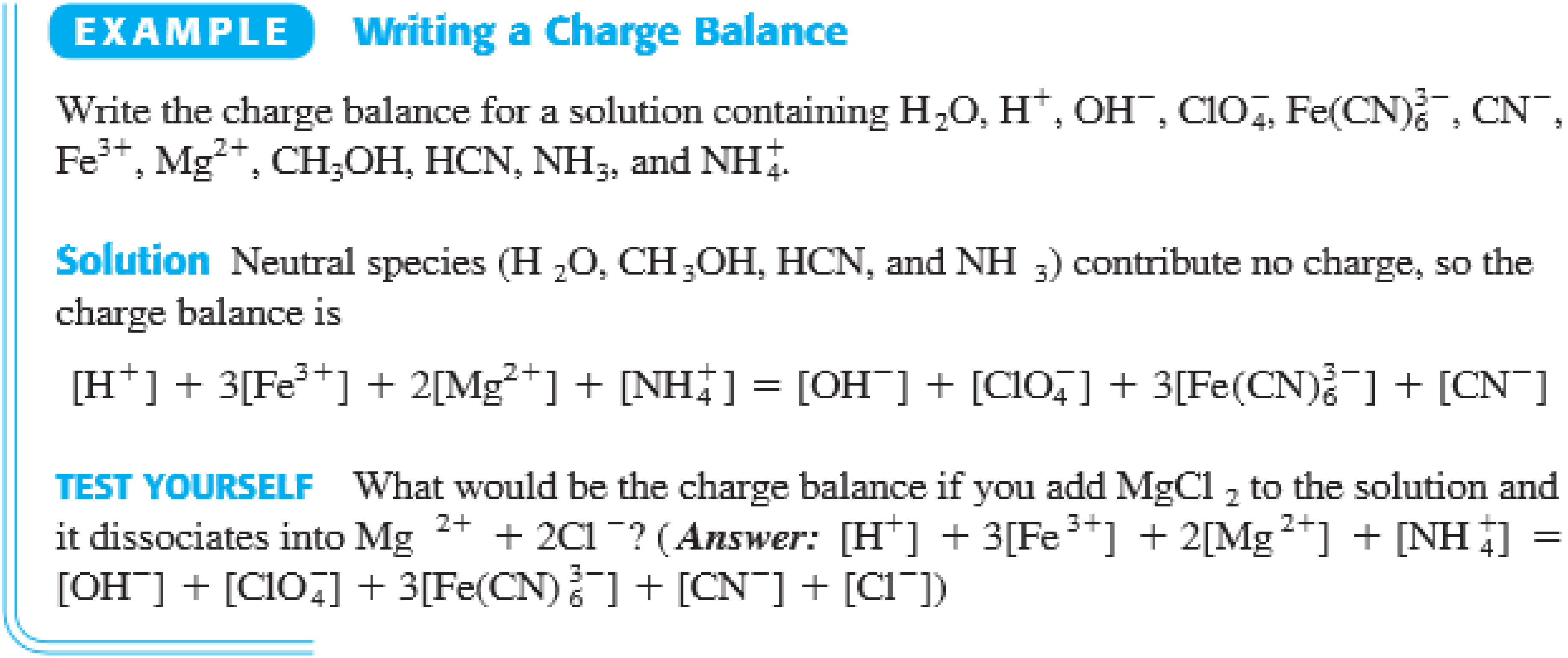
$[H^+]$ and $[OH^-]$ always present

$2 \times [Ca^{2+}]$ = total positive charge

Write the charge balance for an aqueous $CaCl_2$ solution

$$2\,[Ca^{2+}] + [H^+] = [OH^-] + [Cl^-]$$

8-4: Systematic Treatment of Equilibrium



EXAMPLE **Writing a Charge Balance**

Write the charge balance for a solution containing H_2O, H^+, OH^-, ClO_4^-, $Fe(CN)_6^{3-}$, CN^-, Fe^{3+}, Mg^{2+}, CH_3OH, HCN, NH_3, and NH_4^+.

Solution Neutral species (H_2O, CH_3OH, HCN, and NH_3) contribute no charge, so the charge balance is

$$[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = [OH^-] + [ClO_4^-] + 3[Fe(CN)_6^{3-}] + [CN^-]$$

TEST YOURSELF What would be the charge balance if you add $MgCl_2$ to the solution and it dissociates into $Mg^{2+} + 2Cl^-$? (***Answer:*** $[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = [OH^-] + [ClO_4^-] + 3[Fe(CN)_6^{3-}] + [CN^-] + [Cl^-]$)

8-4: Systematic Treatment of Equilibrium

- **Mass Balance:** also called the *material balance*, is a statement of the conservation of matter.

- **The mass balance states** that *the quantity of **all species** in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution*.

8-4: Systematic Treatment of Equilibrium

Mass balance relate the total mass of a species in terms of others and the formal concentration.

Write the mass balance for a 0.1 M Na_2S solution.

$Na_2S \rightarrow 2Na^+ + S^{2-}$

We will also have:

$S^{2-} + H_2O \rightarrow HS^- + OH^-$

$HS^- + H_2O \rightarrow H_2S + OH^-$

$[Na^+] = 2[S^{2-}]_{total}$

$0.1\ M = [S^{2-}]_{total} = [S^{2-}] + [HS^-] + [H_2S]$

8-5: Applying the Systematic Treatment of Equilibrium

- In the systematic treatment of equilibrium, write pertinent equilibrium expressions, as well as the charge and mass balances.
- Be sure that you have as many equations as unknowns and then solve for the concentrations by using algebra with approximations or spreadsheets with the Solver routine.
- For Solver, we *estimate* (number of unknowns) – (number of equilibria) initial pC values and then let Solver find the pC values (and ionic strength) that minimize the sum of squares of the charge and mass balances. The ionic strength value is a byproduct of the optimization.

8-5: Applying the Systematic Treatment of Equilibrium

Find the concentrations of species in an aqueous solution containing 0.0100 mol NH_3 in 1.000 L. Ignore activities.

$$NH_3 + H_2O \xrightleftharpoons{K_b} NH_4^+ + OH^- \qquad K_b = 1.76 \times 10^{-5} \text{ at } 25°C \tag{8-13}$$

A second equilibrium in every aqueous solution is

$$H_2O \xrightleftharpoons{K_w} H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14} \text{ at } 25°C \tag{8-14}$$

Our goal is to find $[NH_3]$, $[NH_4^+]$, $[H^+]$, and $[OH^-]$.

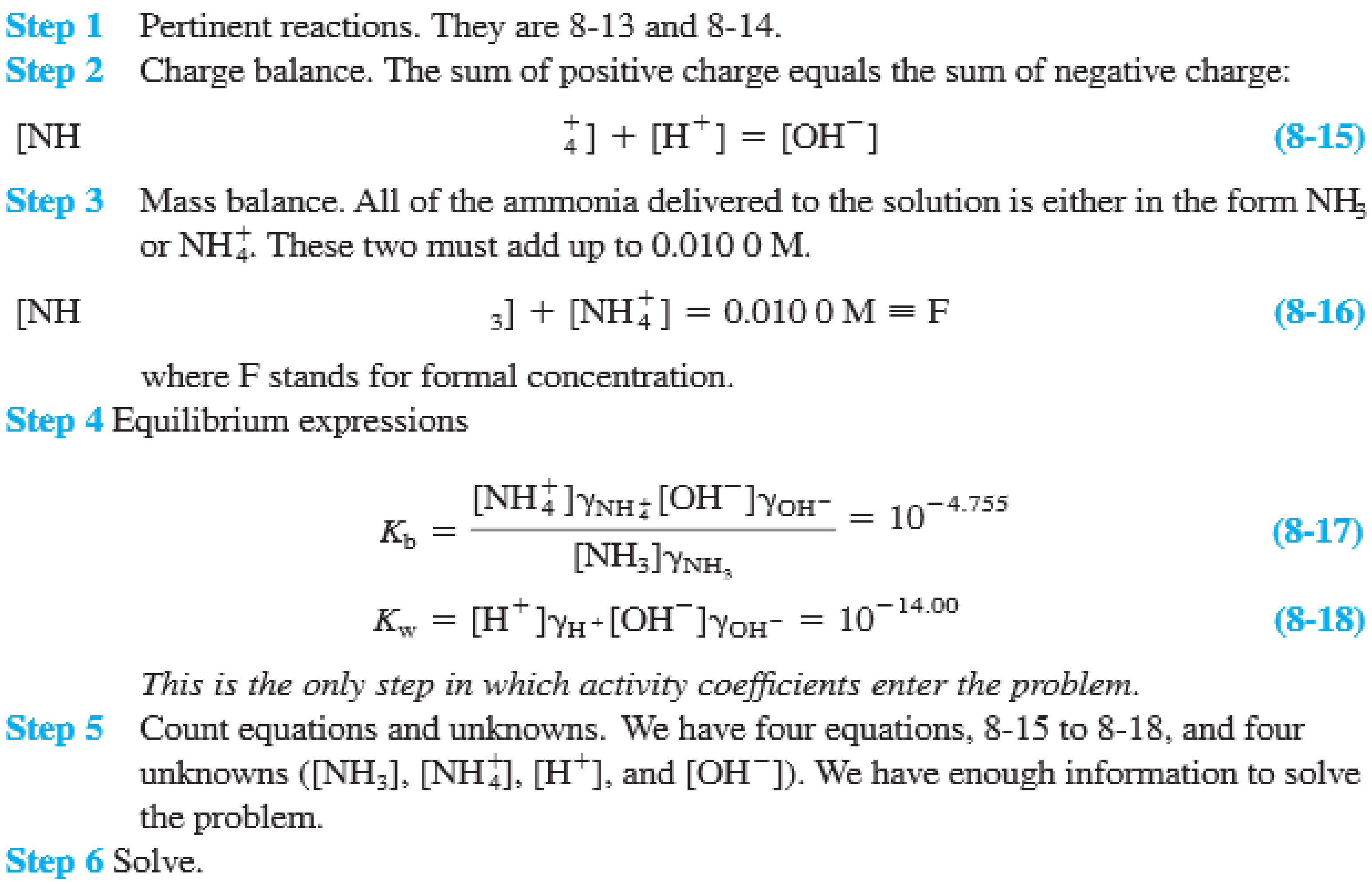
$P^{K}{}_{b}$ = -log K_b = 4.755

P^{Kw} = -log K_w = 14.00

$K_b = 10^{-PK}{}_{b} = 10^{-4.755}$

$K_w = 10^{-PKw} = 10^{-14.00}$

8-5: Applying the Systematic Treatment of Equilibrium



Step 1 Pertinent reactions. They are 8-13 and 8-14.

Step 2 Charge balance. The sum of positive charge equals the sum of negative charge:

$$[NH_4^+] + [H^+] = [OH^-] \qquad \text{(8-15)}$$

Step 3 Mass balance. All of the ammonia delivered to the solution is either in the form NH_3 or NH_4^+. These two must add up to 0.010 0 M.

$$[NH_3] + [NH_4^+] = 0.010\,0\text{ M} \equiv \text{F} \qquad \text{(8-16)}$$

where F stands for formal concentration.

Step 4 Equilibrium expressions

$$K_b = \frac{[NH_4^+]\gamma_{NH_4^+}[OH^-]\gamma_{OH^-}}{[NH_3]\gamma_{NH_3}} = 10^{-4.755} \qquad \text{(8-17)}$$

$$K_w = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} = 10^{-14.00} \qquad \text{(8-18)}$$

This is the only step in which activity coefficients enter the problem.

Step 5 Count equations and unknowns. We have four equations, 8-15 to 8-18, and four unknowns ($[NH_3]$, $[NH_4^+]$, $[H^+]$, and $[OH^-]$). We have enough information to solve the problem.

Step 6 Solve.

8-5: Applying the Systematic Treatment of Equilibrium

Starting with the charge balance:

$$[\mathrm{NH_4^+}] + [\mathrm{H^+}] = [\mathrm{OH^-}]$$

Substitute for OH^- using K_w / $[H^+]$:

$$[\mathrm{NH_4^+}] + [\mathrm{H^+}] = \frac{K_\mathrm{w}}{[\mathrm{H^+}]}$$

Solve for $[NH_4^+]$:

$$[\mathrm{NH_4^+}] = \frac{K_\mathrm{w}}{[\mathrm{H^+}]} - [\mathrm{H^+}]$$

But the mass balance is:

$$[\mathrm{NH_3}] = \mathrm{F} - [\mathrm{NH_4^+}]$$

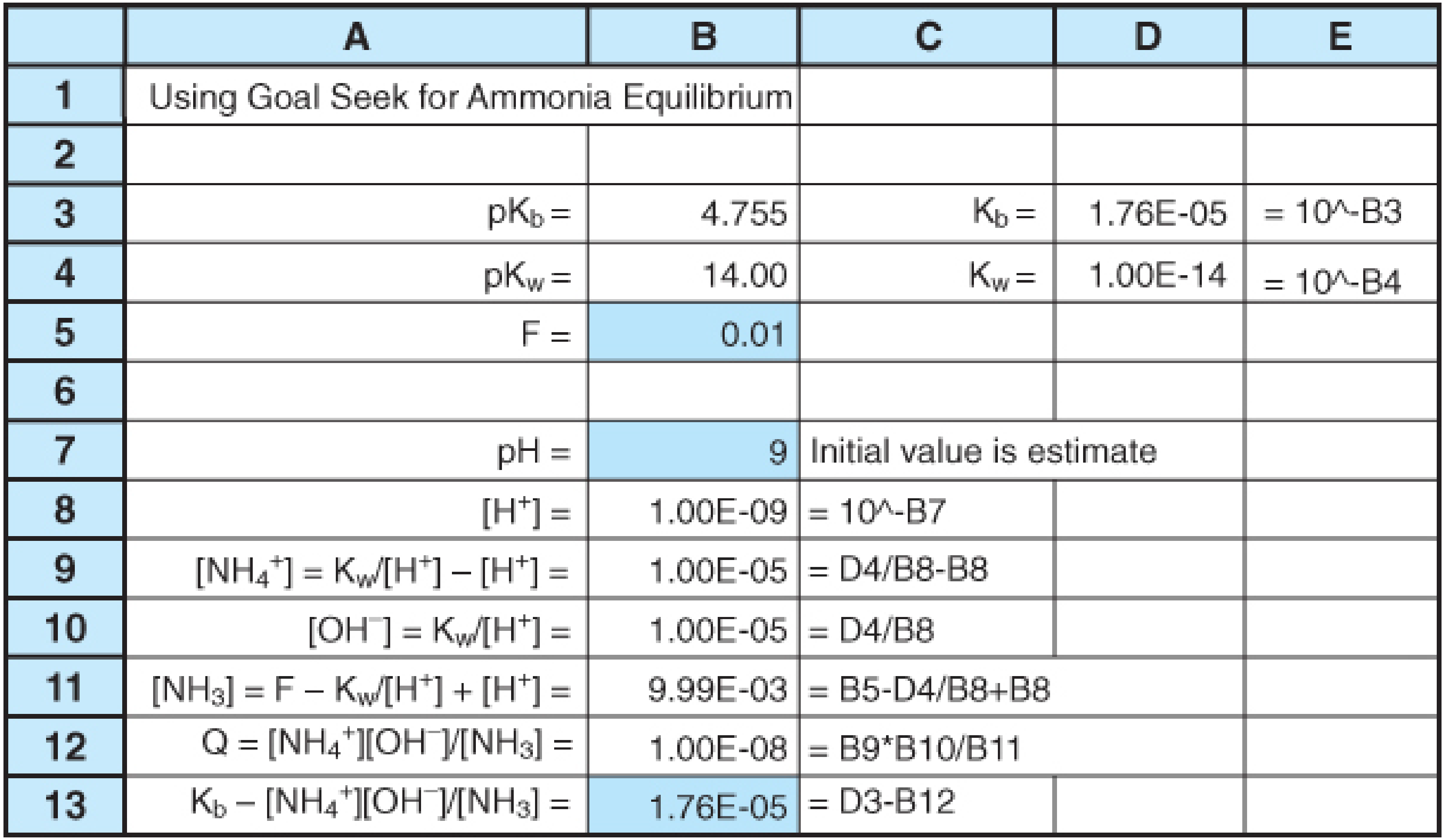
Replace $[NH_4^+]$ with $K_w/[H^+] – [H^+]$:

$$[\mathrm{NH_3}] = \mathrm{F} - [\mathrm{NH_4^+}] = \mathrm{F} - \left(\frac{K_\mathrm{w}}{[\mathrm{H^+}]} - [\mathrm{H^+}]\right)$$

Use Goal Seek to solve for $[H^+]$:

$$K_\mathrm{b} = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} = \frac{\left(\frac{K_\mathrm{w}}{[\mathrm{H^+}]} - [\mathrm{H^+}]\right)\left(\frac{K_\mathrm{w}}{[\mathrm{H^+}]}\right)}{\left(\mathrm{F} - \frac{K_\mathrm{w}}{[\mathrm{H^+}]} + [\mathrm{H^+}]\right)}$$

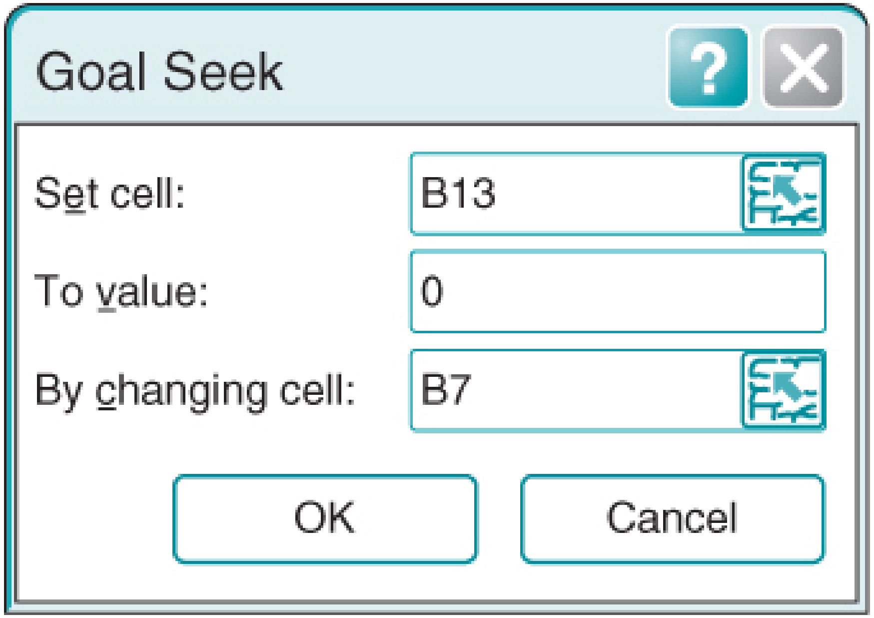
8-5: Applying the Systematic Treatment of Equilibrium



	A	B	C	D	E
1	Using Goal Seek for Ammonia Equilibrium				
2					
3	pK_b =	4.755	K_b =	1.76E-05	= 10^-B3
4	pK_w =	14.00	K_w =	1.00E-14	= 10^-B4
5	F =	0.01			
6					
7	pH =	9	Initial value is estimate		
8	$[H^+]$ =	1.00E-09	= 10^-B7		
9	$[NH_4^+] = K_w/[H^+] - [H^+]$ =	1.00E-05	= D4/B8-B8		
10	$[OH^-] = K_w/[H^+]$ =	1.00E-05	= D4/B8		
11	$[NH_3] = F - K_w/[H^+] + [H^+]$ =	9.99E-03	= B5-D4/B8+B8		
12	$Q = [NH_4^+][OH^-]/[NH_3]$ =	1.00E-08	= B9*B10/B11		
13	$K_b - [NH_4^+][OH^-]/[NH_3]$ =	1.76E-05	= D3-B12		

Using reaction 8-13, K_b, and K_w values, and assuming $[NH_3] >> [OH^-]$ at equilibrium, we can calculate $[H^+]$ to be 7.54×10^{-12} M, and pH = 10.62. use 10.60 in cell B7 instead of 9.

8-5: Applying the Systematic Treatment of Equilibrium

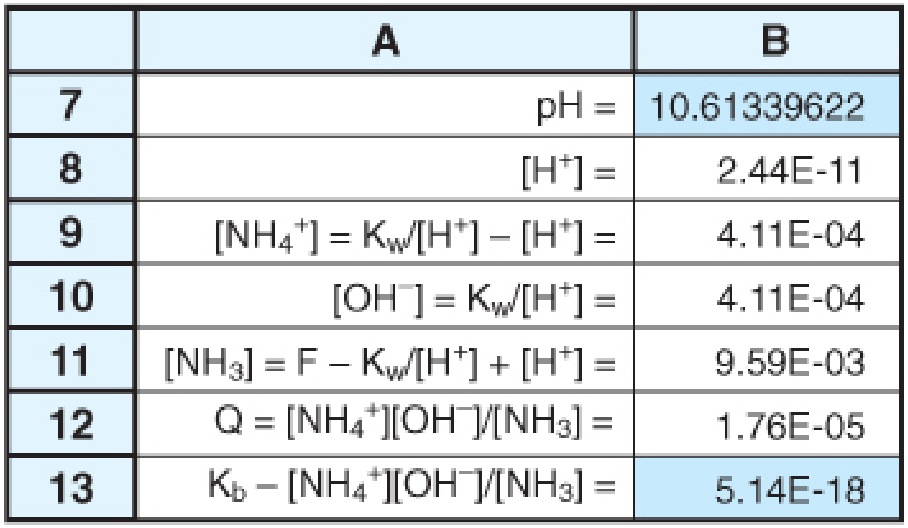


Set cell: B13

To value: 0

By changing cell: B7

(a)



	A	B
7	pH =	10.61339622
8	$[H^+]$ =	2.44E-11
9	$[NH_4^+] = K_w/[H^+] - [H^+]$ =	4.11E-04
10	$[OH^-] = K_w/[H^+]$ =	4.11E-04
11	$[NH_3] = F - K_w/[H^+] + [H^+]$ =	9.59E-03
12	$Q = [NH_4^+][OH^-]/[NH_3]$ =	1.76E-05
13	$K_b - [NH_4^+][OH^-]/[NH_3]$ =	5.14E-18

(b)

7-5: Applying the Systematic Treatment of Equilibrium

Now what ?

- Approximate: In basic solutions, the concentration of OH- is much larger than the H+ concentration so you can neglect $[H^+]$

$K_b = [OH^-]^2/0.01 – [OH^-]$ quadratic equation

- Solve for [OH-]
- Evaluate the other unknowns