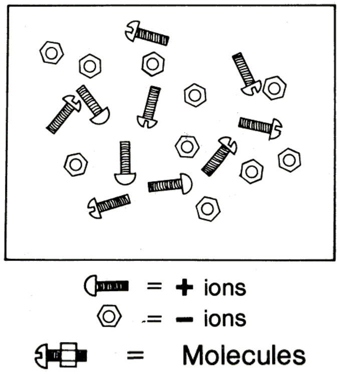
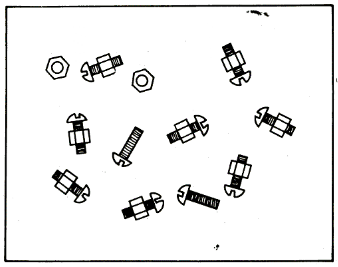
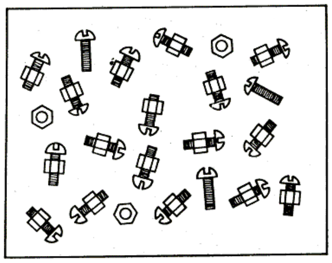
Strong vs. Weak Acids



strong acid / salt



weak acid



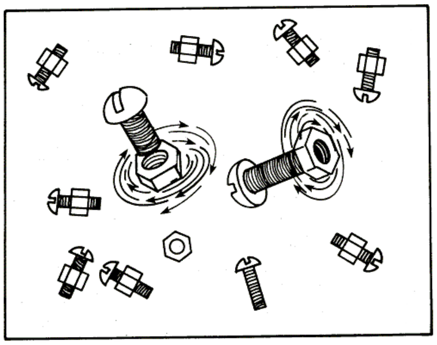
weaker acid
(higher conc.)

"Strong/weak" refers to the **degree** of dissociation.

Acid/base dissociation is a **dynamic equilibrium.**

Each molecule is constantly and rapidly dissociating/associating.

When we say, "40% of HA is dissociated", we actually mean "the molecules of HA are dissociated 40% of the time".



Strengths of Acids and Bases (Sec. 6-7)

Strong acids and bases are strong electrolytes:
they fully dissociate into ions in solution.

$HClO_4 \rightarrow H^+_{(aq)} + ClO_4^-{}_{(aq)}$
$HNO_3 \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$
$KOH \rightarrow K^+_{(aq)} + OH^-_{(aq)}$

with very large equilibrium constants for the dissociation.

Strong acids (or bases) are easily titrated with strong bases (or acids).

$H^+ + OH^- \rightarrow H_2O$ titration rxn

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = [H^+][OH^-] = 1.0\times10^{-14}$

$K_{eq} = 1/K_w = 1.0\times10^{14}$ titration equilibrium

Table 6-2 **Common strong acids and bases**

Formula	Name
ACIDS	
HCl	Hydrochloric acid (hydrogen chloride)
HBr	Hydrogen bromide
HI	Hydrogen iodide
H_2SO_4[a]	Sulfuric acid
HNO_3	Nitric acid
$HClO_4$	Perchloric acid
BASES	
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
R_4NOH[b]	Quaternary ammonium hydroxide

a. For H_2SO_4, only the first proton ionization is complete. Dissociation of the second proton has an equilibrium constant of 1.0×10^{-2}.

b. This is a general formula for any hydroxide salt of an ammonium cation containing four organic groups. An example is tetrabutylammonium hydroxide: $(CH_3CH_2CH_2CH_2)_4N^+OH^-$.

Weak acids and bases

Weak acids and bases are weak electrolytes: They do not fully dissociate to form ions in solution.

$HA \rightleftharpoons H^+ + A^-$ acid hydrolysis, K_a
$A^- + H_2O \rightleftharpoons HA + OH^-$ base hydrolysis, K_b

Equilibrium constants K_a and K_b are much less than one.

Typical weak acids:	**Typical weak bases:**
Carboxylic acids RCOOH	Carboxylic anions $RCOO^-$
Protonated amines R_3NH^+	Amines R_3N
Inorganic ions:	Inorganic ions:
HPO_4^{2-}, $H_2PO_4^-$	PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$
HSO_4^-	SO_4^{2-}
HCO_3^-	CO_3^{2-}, HCO_3^-

Weak acids (or weak bases) are titrated with strong bases (or acids).

$HA + OH^- \rightarrow A^- + H_2O$ titration rxn
$K_{eq} = 1/K_b = K_a/K_w$ titration equilibrium

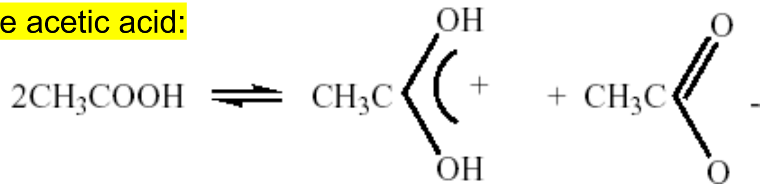
Autoprotolysis (Sec. 6-5)

Acid-base chemistry almost always involves the solvent as well as solutes

Autoprotolysis: reaction of a neutral protic solvent to form a protonated and deprotonated species

Water: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

Pure acetic acid:



$K_w = 3.5 \times 10^{-15}$

Amphoteric behaviour: when the same molecule can act as an acid or a base.

(Read p. 164 on the effect of autoprotolysis on adding a small concentration of base and acid to water. e.g., in a 1×10^{-8}M HCl solution, the $[H+] \neq 1\times10^{-8}$M)

Impact of Solvent (not in text)

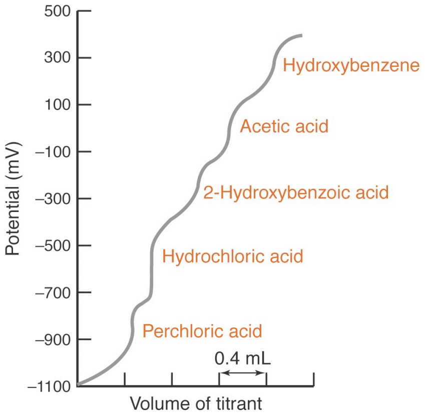
- the strongest acid or base in a solution is the protonated or deprotonated solvent

Water: strongest acid is H_3O^+ Leveling effect
strongest base is OH^-.

Acetic acid reveals the differences between strong acids, because they are all weaker than $CH_3COOH_2^+$ (differentiating solvent).

$$HClO_4 + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + ClO_4^- \qquad K = 1.3 \times 10^{-5}$$

$$HCl + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + Cl \qquad K = 5.8 \times 10^{-8}$$



Weak Acid Hydrolysis: Review

Weak Acids: HA or BH^+ hydrolyzes (dissociates) with a small equilibrium constant K_a

$$HA \rightleftharpoons H^+ + A^-$$

weak acid conjugate base

$$BH^+ \rightleftharpoons H^+ + B$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{or} \qquad K_a = \frac{[H^+][B]}{[BH^+]}$$

We represent K_a in log form using the pX function, i.e.,

$pK_a = -\log [K_a]$ as $[K_a]$ ↑; pK_a ↓

Weak Bases: A^- or B hydrolyzes with a small equilibrium constant K_b

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad \text{or} \qquad A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad \text{or} \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

K_a and K_b are related through K_w

$$K_a \cdot K_b = \frac{[H^+][A^-]}{[HA]} \bullet \frac{[HA][OH^-]}{[A^-]} = [H^+][OH^-] = K_w$$

So we also see that: $pK_w = pK_a + pK_b = 14$

Hydrolysis Calculations

1) What is present in the solution?
    weak acid? HA
    weak base? A^{-}
    mixture of both?

2) What equilibrium rxn takes place for that species?
    acid hydrolysis $HA \Leftrightarrow A^{-} + H^{+}$ or $BH^{+} \Leftrightarrow B + H^{+}$
    base hydrolysis $A^{-} + H_2O \Leftrightarrow HA + OH^{-}$ or $B + H_2O \Leftrightarrow BH^{+} + OH^{-}$
    mixture of the two may have complex hydrolysis

3) What equilibrium equation describes the reaction?
    K_a if acid hydrolysis
    K_b if base hydrolysis
    Buffer equation if a mixture

4) How can you use the stoichiometry given by the hydrolysis rxn?
    $[H^{+}] = [A^{-}]$ if acid hydrolysis
    $[HA] = [OH^{-}]$ if base hydrolysis
    how much HA and A^{-} formed by adding strong acid or base if it is a buffer?

5) Solve the equations you set up.
    Require some conditions be met to ignore water autoprotolysis
    If $pK_a \geq 4$ or $K_a < 10^{-4}$, for acid hydrolysis we can simplify eq,
    or if $pK_b \geq 4$ or $K_b < 10^{-4}$, for base hydrolysis we can simplify

Example #1: Calc the $[H^{+}]$ of an aqueous, 0.150 M acetic acid solution. $K_a = 1.76 \times 10^{-5}$.

Example #2: Calc the $[H^{+}]$ of an aqueous, 0.150 M chloroacetic acid solution. K_a is 1.36×10^{-3}.

Example #3: Calc the $[H^{+}]$ of a 0.0750 M ammonia in water. The K_b for ammonia is 1.75×10^{-5}.

Example #4: Calc the pH of a solution of 0.10 M sodium acetate. The K_a for acetic acid is 1.76×10^{-5}.

Example #1: Calc the $[H^+]$ of an aqueous, 0.150 M acetic acid solution. $K_a = 1.76\times10^{-5}$.

HAc – a weak acid:

	HAc	$\rightleftharpoons$	H^+	+	Ac^-
Initial:	0.150M		0		0
Change:	-x		+x		+x
Equil.:	0.150M-x		x		x

$K_a = x \bullet x/(0.150M - x) = 1.76\times10^{-5}$
Since $K_a < 10^{-4}$, x is small compared to 0.150 M
Thus, $x^2/0.150M = 1.76 \times 10^{-5}$

So, $x = \sqrt{}(1.76 \times 10^{-5} \times 0.150M) = 1.624808 \times 10^{-3}$ M
$[H^+] = 1.62 \times 10^{-3}$ M

Example #2: Calc the $[H^+]$ of an aqueous, 0.150 M chloroacetic acid solution.
K_a is 1.36×10^{-3}.

Chloroacetic acid – a weak acid:

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.150		0		0
Change	-x		+x		+x
Equil:	0.150 – x		x		x

$K_a = x \bullet x/(0.150 - x) = 1.36\times10^{-3}$

Because $K_a > 10^{-4}$ so we cannot simplify the equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x^2 = 1.36\times10^{-3}\,(0.150 - x)$
$x^2 = 1.36\times10^{-3} \times 0.150 - 1.36\times10^{-3}x$
$x^2 + 1.36\times10^{-3}x - 2.04\times10^{-4} = 0$
$x = [-1.36\times10^{-3} \pm \sqrt{(1.36\times10^{-3})^2 - 4\times1\times(-2.04\times10^{-4})}\,]\,/(2\times1)$

So $[H^+] = x = 0.0136$ M

Example #3: Calc the $[H^+]$ of a 0.0750 M ammonia in water. The K_b for ammonia is 1.75×10^{-5}.

Ammonia in water – a weak base:

	NH_3 + H_2O	$\rightleftharpoons$	NH_4^+	+ OH^-
Initial:	0.0750		0	0
Change	-x		+x	+x
Equil:	0.0750 – x		x	x

$K_b = x \bullet x/(0.0750M - x) = 1.75\times10^{-5}$

Because $K_b < 10^{-4}$, we can simplify the equation by: $0.0750M - x = 0.0750M$

Thus, $x^2/0.0750 = 1.75 \times 10^{-5}$

So, $x = \sqrt{1.75 \times 10^{-5} \times 0.0750} = 1.15 \times 10^{-3}$ M

$[OH^-] = 1.15 \times 10^{-3}$ M

Finally, $[H^+] = 1.0\text{x}10^{-14}/[OH^-] = 1.0\text{x}10^{-14}/1.15\times10^{-3} = 8.7\times10^{-12}M$

Example #4: Calc the pH of a solution of 0.10 M sodium acetate. The K_a for acetic acid is 1.76×10^{-5}.

	Ac^- + H_2O	=	HAc	+ OH^-
Initial:	0.10M		0	0
Change	-x		+x	+x
Equil:	0.10–x		x	x

$K_b = x \bullet x/(0.10M - x)$

$K_b = K_w/K_a = 1.0\text{x}10^{-14}/1.76\times10^{-5} = 5.6_8\times10^{-10}$

Because $K_b < 10^{-4}$, we can simplify the equation by: $0.10 - x = 0.10$

Thus, $x^2/0.10 = 5.68 \times 10^{-10}$

So, $x = \sqrt{5.68 \times 10^{-5} \times 0.10M} = 7.54 \times 10^{-6}$

or $[OH^-] = 7.54 \times 10^{-6}$ M

So, $[H^+] = 1.0\text{x}10^{-14}/[OH^-] = 1.0\text{x}10^{-14}/7.54\times10^{-6} = 1.3_3\times10^{-9}$

pH = - log $[H^+] = 8.87_6 = 8.88$

Fractional Composition (α) – fraction of specific form of a molecule relative to all forms of a molecule (Sec. 9-5)

α_{A-} = fraction of dissociation = fraction of an acid that is in the A^- form

$$\alpha_{A-} = \frac{[A^-]}{F_{acid}} = \frac{[A^-]}{[HA]+[A^-]} \qquad F_{acid} = \text{formal concentration (total of all forms)}$$

Exercise - Calculate the fraction of dissociation for Examples 1 and 2 (above):

Example 1: $[H^+] = 1.62 \times 10^{-3}$ M
$[A^-] = 1.62 \times 10^{-3}$ M $K_a = 1.76\times10^{-5}$
$\alpha_{A-} = 1.62 \times 10^{-3}$ M / 0.150 M
= 0.0108 or ~1%

Example 2: $[H^+] = 0.0136$ M
$[A^-] = 0.0136$ M $K_a = 1.36\times10^{-3}$
$\alpha_{A-} = 0.0136$ M / 0.150 M
= 0.0907 or ~ 10%

At $pK_a - 1$, $\alpha_{A-} \cong 0.99$, $\alpha_{HA} \cong 0.01$

At $pK_a + 1$, $\alpha_{A-} \cong 0.9$, $\alpha_{HA} \cong 0.1$

At pK_a, $\alpha_{A-} = \alpha_{HA} = 0.5$

At $pK_a - 1$, $\alpha_{A-} \cong 0.1$, $\alpha_{HA} \cong 0.9$

At $pK_a - 2$, $\alpha_{A-} \cong 0.01$, $\alpha_{HA} \cong 0.99$

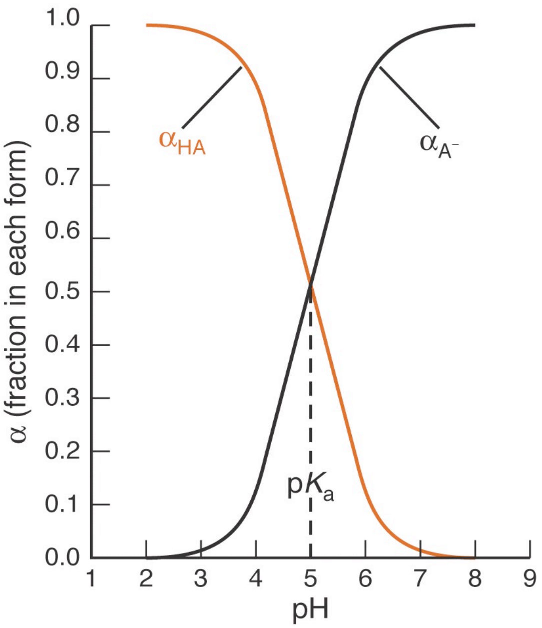


Figure 9-3 Harris

$$\alpha_{A-} = \frac{[A^-]}{F_{acid}} = \frac{[A^-]}{[HA]+[A^-]} = \frac{K_a}{[H^+]+K_a}$$

$$\alpha_{HA} = \frac{[H^+]}{[H^+]+K_a}$$

Buffers (Sec. 8-5)

Buffer: solution which resists changes in pH when acid or base is added or dilution occurs.

Buffers in pH 3-11 range are mixtures of an acid and its conjugate base.

Typical question when working with buffers - Example 5 (below)
Henderson-Hasselbalch Equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

	$HA \rightleftharpoons$	$A^- +$	H^+
Initial:	C_{HA}	C_{A-}	0
Change	-x	+x	+x
Equil:	$C_{HA} - x$	$C_{A-} + x$	x

$$pH = pK_a + \log\frac{C_{A^-}}{C_{HA}}$$

Example #5: What is the pH of a solution prepared by mixing 3.00 g of sodium acetate (MW 82.03 g/mol) with 5.00 mL of 12.0 M acetic acid and diluting to 2.00 L? $K_a = 1.76\times10^{-5}$.

C_{HAc} = 12.0 M x 5.00 mL/2000 mL = 0.0300 M
C_{NaAc} = (3.00 g/82.03 g/mol)/2.00 L = 0.0182_9 M

C_{HA} and $C_{A-} > 10^{-3}$ M; $K_a < 10^{-3}$ (approximation is valid)

$$pH = pK_a + \log\frac{C_{A^-}}{C_{HA}} = -\log(1.76\times10^{-5}) + \log(0.0182_9\text{M}/0.0300\text{M}) = 4.540$$

Example #6: Calc the pH of a solution that is 0.120 M in NH_3 and 0.0750 M in NH_4Cl. $K_b = 1.75\times10^{-5}$.

C_{NH4+} = 0.0750 M
C_{NH3} = 0.120 M
$K_a = K_w/K_b = 1.01\text{x}10^{-14}/1.75\times10^{-5} = 5.71\times10^{-10}$

C_{HA} or $C_{A-} > 10^{-3}$ M; $K_a < 10^{-3}$ (approximation is valid)

$pH = pK_a + \log C_{NH3}/C_{NH4+} = -\log(5.71\times10^{-10}) + \log(0.120\text{M}/0.0750\text{M}) = 9.448$

Effect of Dilution on Buffers

Case 1. A 100-mL buffer solution containing 0.1 M HA and 0.05 M NaA is diluted 10 times, calc the pH change ($K_a = 1\times10^{-5}$).

pH of original solution:
$pH = pK_a + \log C_{NaA} / C_{HA} = 5.0 + \log(0.05M/0.1M) = 4.7$

pH of diluted solution:
$C_{HA} = 0.1M \times 1/10 = 0.01$ M
$C_{NaA} = 0.05M \times 1/10 = 0.005$ M
C_{HA} or $C_{A-} > 10^{-3}$M; $K_a < 10^{-3}$ (approximation is valid)
$pH = pK_a + \log C_{NaA} / C_{HA} = 5.0 + \log(0.005/0.01) = 4.7$

Case 2. A 100-mL buffer solution containing 0.1 M HA and 0.05 M NaA is diluted 1000 times, calc the pH change ($K_a = 1\times10^{-5}$).

pH of original solution:
$pH = pK_a + \log C_{NaA} / C_{HA} = 5.0 + \log(0.05M/0.1M) = 4.7$

pH of diluted solution:
$C_{HA} = 0.1M \times 1/1000 = 0.000\ 1$ M
$C_{NaA} = 0.05M \times 1/1000 = 0.000\ 05$ M
~~C_{HA} or $C_{A-} > 10^{-3}$M~~; $K_a < 10^{-3}$ (approximation is no longer valid)

	HA	⇌	H^+	+	A^-
Initial	1×10^{-4}M		0		5×10^{-5}M
Change	-x		+x		+x
Equil	1×10^{-4}M-x		x		5×10^{-5}M+x

Solving quadratic ⇒ $x = 1.{}_{4509}\times10^{-5}$ M = $[H^+]$; pH = 4.83

Effect of Adding Acid or Base

0.1 mole of NaOH is added to a 1.0-L buffer solution containing 0.2 M HA & 0.1 M NaA, calc the pH change (assume the volume does not change when NaOH is added) ($K_a = 1\times10^{-6}$).

pH of original solution:

$pH = pK_a + \log C_{NaA} / C_{HA} = 6.0 + \log(0.1/0.2) = 5.7$

pH of the mixture:

	HA	+	NaOH	→	NaA + H_2O
Initial:	0.2M		0		0.1M
Addition			+0.1mol/1L		
Change	-0.1 M		0		+0.1 M
Final:	0.1 M				0.2 M

$pH = pK_a + \log C_{NaA} / C_{HA} = 6.0 + \log(0.2M/0.1M) = 6.3$

Buffer Capacity (β) (pg. 177)

a) Buffer capacity is a measure of how well a buffer solution resists changes in pH when strong acid or base is added.

(b) Buffer capacity is defined as the quantity of strong acid or strong base needed to cause 1.0-L of the buffer to undergo a pH change of 1.0 unit

(c) Since a buffer will resist changes in pH, as long as there is weak acid or weak base left to react, the greater the conc. of buffer components, the greater the buffer capacity.

(d) Good buffer capacity when pH ≈ pK_a
Buffer range = $pK_a \pm 1$ pH unit

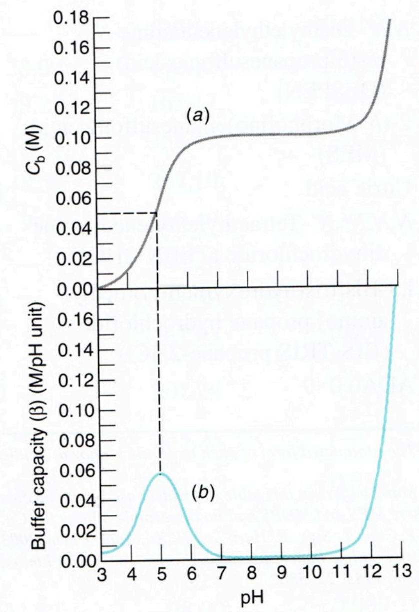


FIGURE 8-4 (a) C_b versus pH for a solution containing 0.100 F HA with $pK_a = 5.00$. (b) Buffer capacity versus pH for the same system reaches a maximum when $pH = pK_a$. The lower curve is the derivative of the upper curve.

Selecting a Buffer

We need to consider:
1)The desired pH
2)The chemical compatibility of the buffer components with the sample.

Common buffers: see Table 9-2 and Appendix G

Buffer	pKa	pH range
Phosphate (pKa1)	2.1	1.1-3.1
Phosphate (pKa2)	7.2	6.2-8.2
Phosphate (pKa3)	12.3	11.3-13.3
Acetate	4.8	3.8-5.8
Tris	8.06	7.1-9.1
Borate	9.2	8.2-10.2
MES	6.15	5.5-6.7
HEPES	7.55	6.5-8.5
Tricine	8.15	7.2-9.2

Making a Buffer

Two methods:
1) Mix an acid with its conjugate base.
2) Mix a weak acid (or base) with a strong base (or acid).

Making a Buffer in Real Life (p. 177)

(with a pH meter, to fine-tune pH)

1. Weigh out 1 form (e.g. acid) and dissolve in water (~4/5 of final volume).
2. Monitor the pH with a pH electrode.
3. Add strong electrolyte (e.g. base) until pH is exact.
4. Quantitatively transfer solution into a volumetric flask.
5. Dilute to mark and mix.

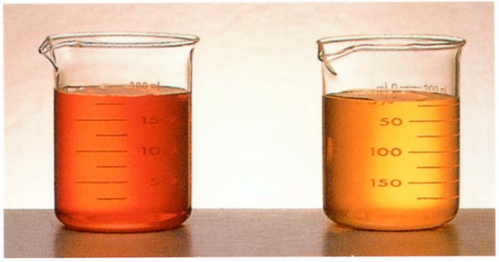
Activity vs. Concentration (Chap. 7)

Example from text:

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

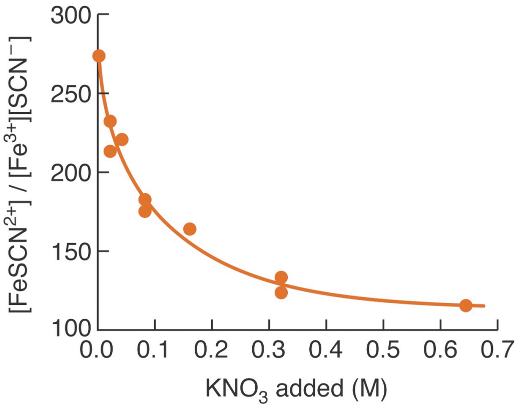
$$K = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^{-}]}$$

(pale yellow, colorless) (red)



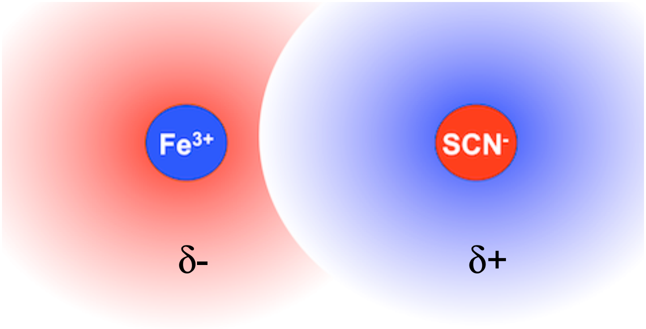
The red color fades when KNO_3 is added to the right-hand beaker because equil shifts to the left.

Ions are shielded from each other by other 'spectator' ions in solution (K^+ and NO_3^-)



Activity - value that replaces concentration in a thermodynamically correct equilibrium expression:

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



Ionic atmosphere:
An anion is surrounded by excess cations.
An cation is surrounded by excess anions.

Ionic Strength (p. 144)

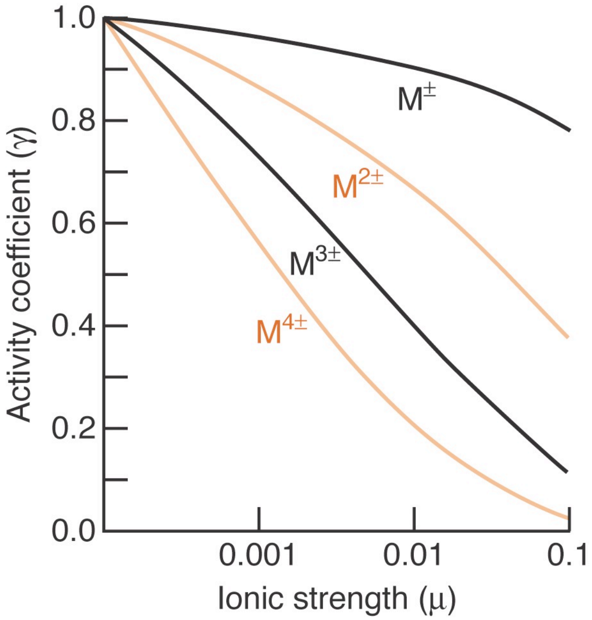
$$\mu = \frac{1}{2}\sum_i c_i z_i^2 ;$$

c is concentration and z is the charge on ion

Example: Mixture of 0.02 M KBr and 0.03 M Na_2SO_4

$$\mu = \frac{1}{2}\{\underbrace{0.02M(1)^2}_{K^+} + \underbrace{0.02M(-1)^2}_{Br^-} + \underbrace{0.06M(1)^2}_{Na^+} + \underbrace{0.03M(-2)^2}_{SO_4^{2-}}\}$$

μ = 0.11 M



$A = \gamma C$

A = activity
C = concentration
γ = activity coefficient

Activity Coefficient (p. 146)

$$\log \gamma_i = \frac{-0.51 z^2 \sqrt{\mu}}{1 + \frac{\alpha \sqrt{\mu}}{305}} \quad \text{(Eqn. 7-6)}$$

z is charge on the ion "i"
μ is the ionic strength in Molarity
α is the hydrated radius of the ion in picometers

Table of activity coefficients (γ) in Harris (Table 7-1).

<u>Unless explicitly instructed to use activity, use conc. for all equilibrium calculations.</u>

For equilibrium calculations, use K (in conc units) determined at a relevant ionic strength.

Maintain constant ionic strength in samples and standards.

Exercise: Calculate pH of phosphate buffer made with 16.67 mM Na_2HPO_4 and 8.33 mM Na_3PO_4; a) neglecting activity; and b) including activity

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad pK_{a3} = 12.15$$

a) Neglecting activity effects: pH = 12.15 + log (8.33mM/16.67mM) = 11.85

b) $\mu = \frac{1}{2}\left\{2(17mM)(1)^2 + (17mM)(-2)^2 + 3(8mM)(1)^2 + (8mM)(-3)^2\right\}$ = 0.1 M

γ_{2-} = 0.37 and γ_{3-} = 0.12

pH = 12.15 + log (0.12*8.33/0.37*16.67) = 11.36