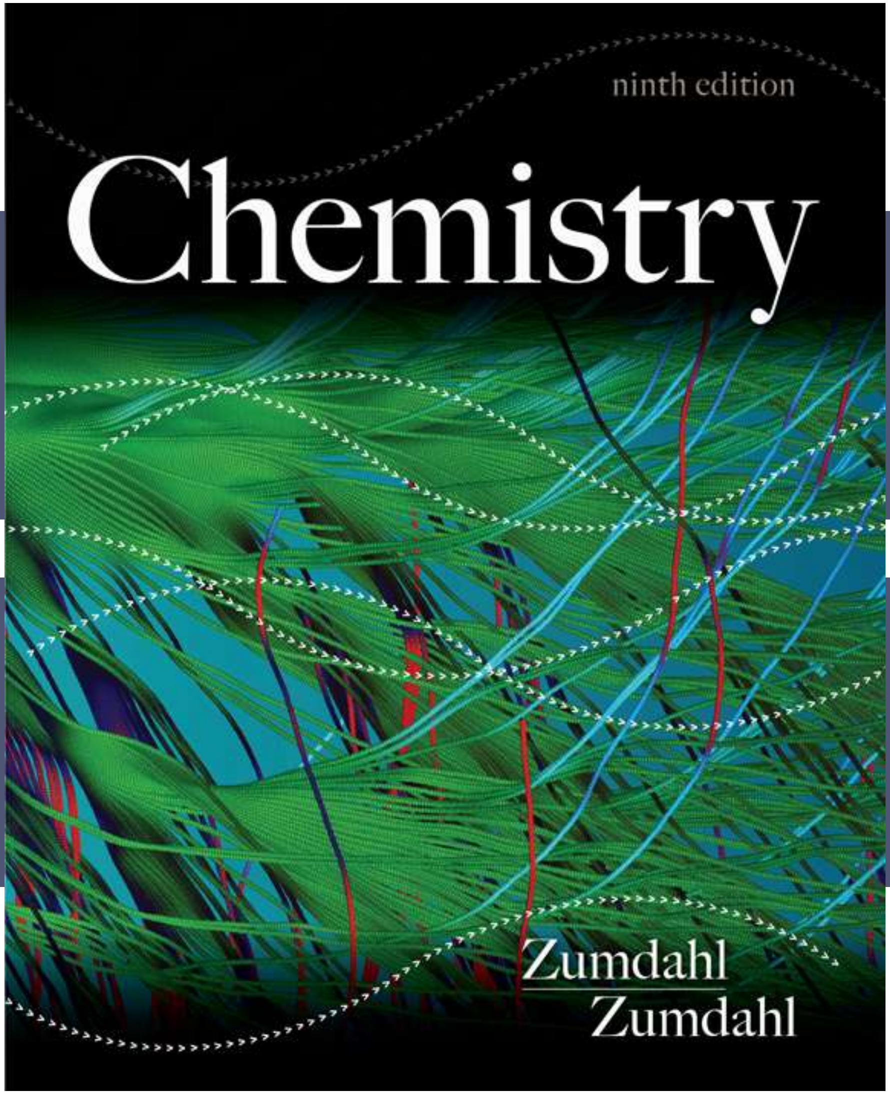


Chapter 14

Acids and Bases

Definitions of Acids and Bases

- Arrhenius: Acids produce H^+ ions in solution; bases produce OH^- ions.

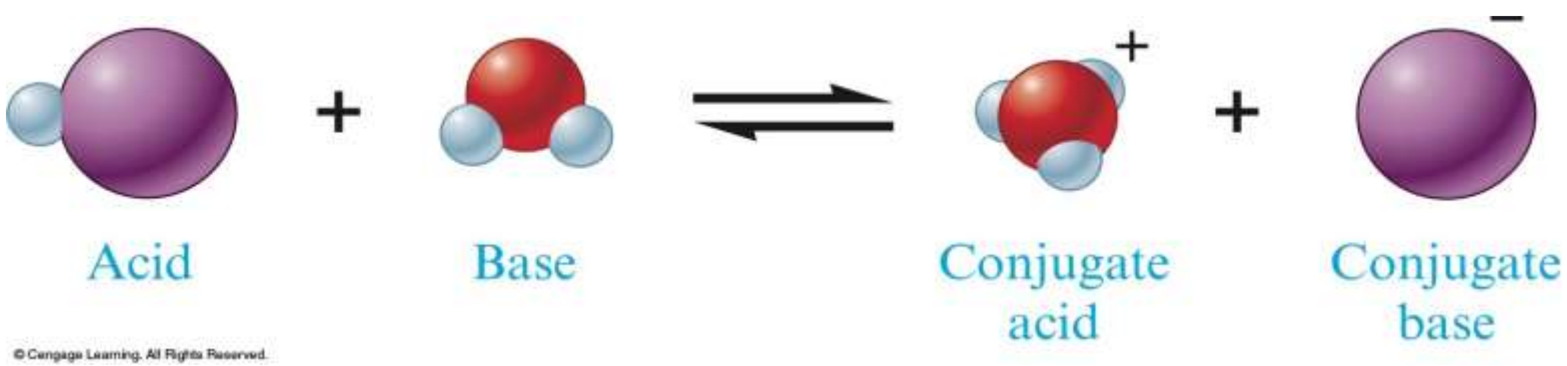
$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
$$NaOH_{(aq)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)}$$

- Brønsted–Lowry: Acids are proton (H^+) donors, bases are proton acceptors.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons Cl^- + H_3O^+$$

Acid-base conjugate pair

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$



- HA and A^- are acid/base conjugate pair.

  HA is the conjugate <u>acid</u> of A^-; A^- is the conjugate <u>base</u> of HA
- Conjugate acid/base pair are related by **<u>one</u>** proton transfer.

Acid Strength

- Strong acid:
  - Ionization equilibrium lies far to the right.
  - Yields a weak conjugate base.

$$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

- Strong base: $NaOH_{(aq)} \rightarrow OH^{-}_{(aq)} + Na^{+}_{(aq)}$
- Weak acid:
  - Ionization equilibrium lies far to the left.
  - The weaker the acid, The stronger its conjugate base.

$$CH_3COOH_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

- Weak base: $NH_{3(aq)} + H_2O \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$

Water as an acid and a base

- Water is amphoteric: (Auto ionization)
  - Behaves either as an acid or as a base.
  - $H_2O_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3^+O_{(aq)} + OH^-_{(aq)}$

- At 25° C:

  $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
- In aqueous solutions the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14} at 25° C.

Three possible situations in aqueous solutions

- $[H^+] = [OH^-]$; neutral solution
- $[H^+] > [OH^-]$; acidic solution
- $[OH^-] > [H^+]$; basic solution

$$HA_{(aq)} + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

acid | base | conjugate acid | conjugate base

What is the equilibrium constant expression for an acid acting in water?

$$K = \frac{[H_3O^+][A^-]}{[HA]}$$

If the equilibrium lies to the right, the value for K_a is large (or >1)

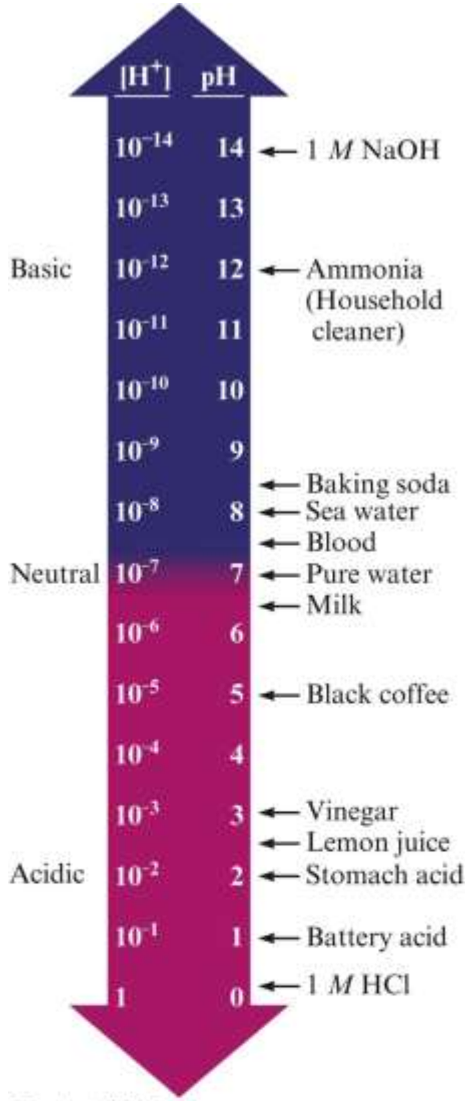
If the equilibrium lies to the left, the value for K_a is small (or <1)

K_b

- $pH = -\log[H^+]$,
- pH changes by 1 for every power of 10 change in $[H^+]$.
- A compact way to represent solution acidity.
- pH decreases as $[H^+]$ increases.
- Significant figures:
  - The number of decimal places in the log is equal to the number of significant figures in the original number.

- pH = 7; neutral   -log 1x10-7 = 7
- pH > 7; basic
  - The Higher the pH, The more basic the solution.
- pH < 7; acidic
  - Lower the pH, more acidic.

The pH Scale and pH Values of Some Common Substances



EXERCISE!

Calculate the pH for a solution of 1.0×10^{-4} M H^+?
(Use the calculator)

$$pH = -\log(1.0 \times 10^{-4}) = 4.00$$

EXERCISE!

The pH of a solution is 5.85. What is the $[H^+]$ for this solution?

$pH = - \log [H^+] = 5.85$

$\log [H^+] = - 5.85$

$[H^+] = \text{inv. } \log (- 5.85)$ *(use the calculator)*

$= 1.4 \times 10^{-6}\ M$

pH and pOH

- Recall:

$$K_w = [H^+][OH^-]$$

$$-\log K_w = -\log[H^+] - \log[OH^-]$$

$$pK_w = pH + pOH$$

$$14.00 = pH + pOH$$

Calculate the pOH for each of the following solutions.

a) 1.0×10^{-4} *M* H^{+}

pH = - log (1.0×10^{-4}) = 4.00

pOH = 14.0 – pH = 14.0 – 4.0 = 10.00

b) 0.040 *M* OH^{-}

pOH = - log $[OH^{-}]$ = - log (0.040)

= 1.40

The pH of a solution is 5.85. What is the $[OH^-]$ for this solution?

$[H^+]$= inv. log (-5.85) = …. = 1.4×10^{-6}

$[OH^-] = K_w/[H^+]$; *always* : $K_w = [H^+][OH^-]$

$= 1.00 \times 10^{-14}/1.4 \times 10^{-6}$

$= 7.1 \times 10^{-9}$ *M*

Consider an aqueous solution of 2.0×10^{-3} *M* HCl.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Since HCl is strong acid, the major species in solution are:

H^+, Cl^-, H_2O

What is the pH?

$$pH = -\log [H^+] = -\log (2.0 \times 10^{-3})$$

$$= 2.70$$

Calculate the pH of a 1.5×10^{-2} *M* solution of HNO_3?

$$[H^+]_{total} = [H^+]_{HNO_3} + [H^+]_{H_2O} \approx [H^+]_{HNO_3} = 1.5 \times 10^{-2}$$

The major source for H^+ is from the nitric acid, HNO_3. So:

$$pH = -\log(1.5 \times 10^{-2}) = 1.82$$

- ***Important Note:***

  In aqueous solutions, the reaction of water dissociation below is always taking place.

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

 But it is not always the main contributor of H^+ or OH^-.

Consider a 0.80 *M* aqueous solution of the weak acid HCN (K_a = 6.2 × 10^{-10}).

$K_a >> K_w$, so, the second equilibrium below controls the pH.

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$ $K_a = 6.2 \times 10^{-10}$

0.80	0	0	*(initially)*
(0.80 – x)	x	x	*(at equilibrium)*

$K_a = x^2 / (0.80 - x)$; $x << 0.80$, so $0.80 - x \approx 0.80$

$6.2 \times 10^{-10} = x^2 / 0.80$

$x^2 = 4.69 \times 10^{-10}$

$x = 2.16 \times 10^{-5} = [H^+]$, pH = 4.67

Calculate the pH of a 0.50 *M* aqueous solution of the weak acid HF. ($K_a = 7.2 \times 10^{-4}$) **(YOU DO IT)**

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$ $K_a = 7.2 \times 10^{-4}$

0.50   0   0   *(initially)*

(0.50 – x)   x   x   *(at equilibrium)*

The second reaction controls the pH.

0.50 is much smaller that x.

$7.2 \times 10^{-4} = x^2 / 0.50$ $x = [H^+]$

$x^2 = 3.6 \times 10^{-4}$; x = 0.019 ; pH = - log(3.6×10^{-4}) = 1.72

Exercise:

A solution of 8.00 *M* formic acid ($HCHO_2$) has $K_a = 1.8 \times 10^{-4}$, calculate its pH? **(YOU DO IT)**

Answer: pH=1.42

- Arrhenius: bases produce OH^- ions.
- Brønsted–Lowry: bases are proton acceptors.
- In a basic solution at 25° C, pH > 7.
- Ionic compounds containing OH^- are generally considered strong bases.
  - $LiOH$, $NaOH$, KOH, $Ca(OH)_2$
- $pOH = -\log[OH^-]$
- $pH = 14.00 - pOH$

Calculate the pH of a 2.0×10^{-3} *M* solution of sodium hydroxide.

$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$ *(strong base)*

Since NaOH is strong, $[OH^-] = [NaOH] = 2.0 \times 10^{-3}$

$[H^+] = K_w/[OH^-] = 1.0 \times 10^{-14}/2.0 \times 10^{-3}$

$= 5.0 \times 10^{-12}$

$pH = -\log[H^+] = -\log(5.0 \times 10^{-12})$

$= 11.30$ *(basic)*

- Equilibrium expression for weak bases uses K_b.

$$CN^-_{(aq.)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq.)} + OH^-_{(aq.)}$$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

- pH calculations for solutions of weak bases are very similar to those for weak acids.
- $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
- $pOH = -\log[OH^-]$
- $pH = 14.00 - pOH$

Calculate the pH of a 2.0 *M* solution of ammonia (NH_3).

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$; $K_w = 1.0 \times 10^{-14}$

$NH_{3(aq)} + H_3O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$; $K_b = 1.8 \times 10^{-5}$

2.0	0	0	*(initially)*
2.0 – x	x	x	*(at equilibrium)*

Reaction 2 controls the pH, x is much smaller than 2.0.

$K_b = x^2 / 2.0 = 1.8 \times 10^{-5}$; $x^2 = 3.6 \times 10^{-5}$

$x = 6.0 \times 10^{-3} = [OH^-]$;

$pOH = -\log(6.0 \times 10^{-3}) = 2.22$; and $pH = 11.78$

Models of Acids and Bases

- Two factors for acidity in binary compounds:
  - Bond Polarity (high is good)
  - Bond Strength (low is good)

Bond Strengths and Acid Strengths for Hydrogen Halides

Table 14.7 | Bond Strengths and Acid Strengths for Hydrogen Halides

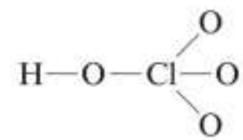
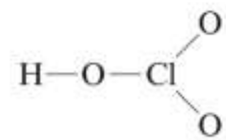
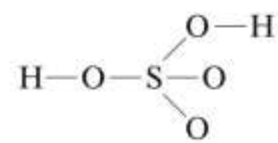
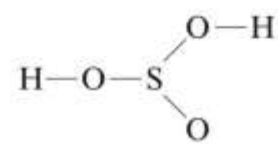
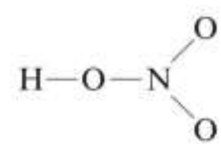
H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Oxyacids

- Contains the group H–O–X.
- For a given series the acid strength increases with an increase in the number of oxygen atoms attached to the central atom.
- The greater the ability of X to draw electrons toward itself, the greater the acidity of the molecule.

Several Series of Oxyacids and Their K_a Values

Table 14.8 | Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$		Large ($\sim 10^7$)
$HClO_3$		~ 1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
$HClO$	H—O—Cl	3.5×10^{-8}
H_2SO_4		Large
H_2SO_3		1.5×10^{-2}
HNO_3		Large
HNO_2	H—O—N—O	4.0×10^{-4}

Comparison of Electronegativity of X and K_a Value

Table 14.9 | Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	$\sim 10^{-15}$

Oxides

- Acidic Oxides (Acid Anhydrides):
  - O—X bond is strong and covalent.

SO_2, NO_2, CO_2

- When H—O—X grouping is dissolved in water, the O—X bond will remain intact. It will be the polar and relatively weak H—O bond that will tend to break, releasing a proton.

Oxides

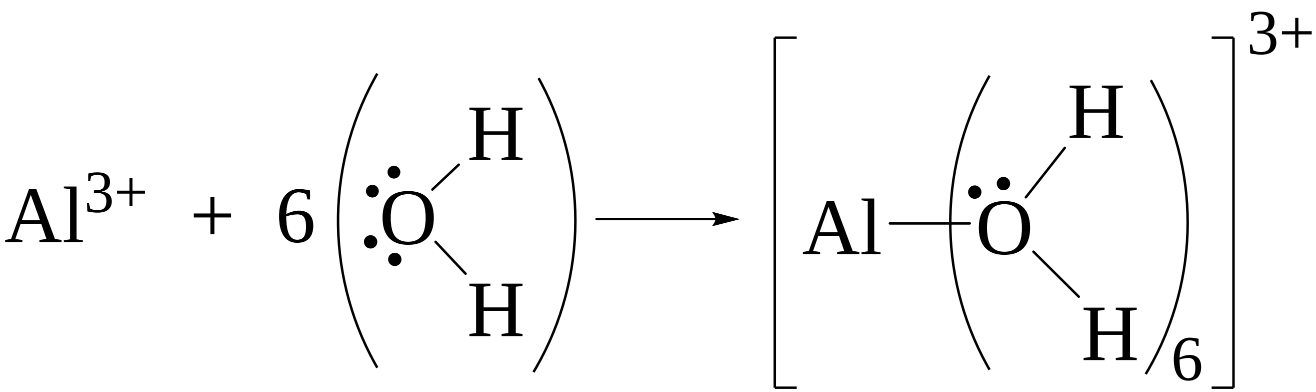
- Basic Oxides (Basic Anhydrides):
  - O—X bond is ionic.

K_2O, CaO

- If X has a very low electronegativity, the O—X bond will be ionic and subject to being broken in polar water, producing a basic solution.

Lewis Acids and Bases

- Lewis acid: electron pair *acceptor*
- Lewis base: electron pair *donor*



Lewis acid   Lewis base

Three Models for Acids and Bases

Table 14.10 | Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

<u>ATTENTION</u>

THI IS THE LAST SLID IN THE COURSE

For Chemistry 108

Salts

- Ionic compounds.
- When dissolved in water, break up into its ions (which can behave as acids or bases).

Salts

- The salt of a strong acid and a strong base gives a neutral solution.
  - KCl, $NaNO_3$

Salts

- A basic solution is formed if the anion of the salt is the conjugate base of a weak acid.
  - NaF, $CH_3COO^{-+}K$
  - $K_w = K_a \times K_b$
    - Use K_b when starting with base.

Salts

- An acidic solution is formed if the cation of the salt is the conjugate acid of a weak base.
  - NH_4Cl
  - $K_w = K_a \times K_b$
    - Use K_a when starting with acid.

Cation	Anion	Acidic or Basic	Example
neutral	neutral	neutral	$NaCl$
neutral	conjugate base of weak acid	basic	NaF
conjugate acid of weak base	neutral	acidic	NH_4Cl
conjugate acid of weak base	conjugate base of weak acid	depends on K_a & K_b values	$Al_2(SO_4)_3$

Qualitative Prediction of pH of Salt Solutions (from Weak Parents)

Table 14.5 | Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

EXERCISE!

$HC_2H_3O_2$ $K_a = 1.8 \times 10^{-5}$

HCN $K_a = 6.2 \times 10^{-10}$

Calculate the K_b values for: $C_2H_3O_2^-$ and CN^-

$K_b\ (C_2H_3O_2^-) = 5.6 \times 10^{-10}$

$K_b\ (CN^-) = 1.6 \times 10^{-5}$

CONCEPT CHECK!

Arrange the following 1.0 *M* solutions from lowest to highest pH.

HBr	NaOH	NH_4Cl
NaCN	NH_3	HCN
NaCl	HF	

Justify your answer.

HBr, HF, HCN, NH_4Cl, NaCl, NaCN, NH_3, NaOH

CONCEPT CHECK!

Consider a 0.30 *M* solution of NaF.

The K_a for HF is 7.2 × 10^{-4}.

What are the major species?

Na^+, F^-, H_2O

Let's Think About It…

- Why isn't NaF considered a major species?
- What are the possibilities for the dominant reactions?

Let's Think About It…

The possibilities for the dominant reactions are:

1. $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$
2. $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
3. $Na^+(aq) + H_2O(l) \rightleftharpoons NaOH + H^+(aq)$
4. $Na^+(aq) + F^-(aq) \rightleftharpoons NaF$

Let's Think About It…

- How do we decide which reaction controls the pH?

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$
$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- Determine the equilibrium constant for each reaction.

EXERCISE!

Calculate the pH of a 0.75 *M* aqueous solution of NaCN.

K_a for HCN is 6.2×10^{-10}.

Let's Think About It…

- What are the major species in solution?

Na^+, CN^-, H_2O

- Why isn't NaCN considered a major species?

Let's Think About It…

- What are all possibilities for the dominant reaction?
- The possibilities for the dominant reaction are:
  1. $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$
  2. $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
  3. $Na^+(aq) + H_2O(l) \rightleftharpoons NaOH + H^+(aq)$
  4. $Na^+(aq) + CN^-(aq) \rightleftharpoons NaCN$

- Which of these reactions really occur?

Let's Think About It…

- How do we decide which reaction controls the pH?

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Steps Toward Solving for pH

	$CN^{-}(aq)$ +	H_2O ⇌	$HCN(aq)$ +	$OH^{-}(aq)$
Initial	0.75 *M*		0	~ 0
Change	–x		+x	+x
Equilibrium	0.75–x		x	x

$K_b = 1.6 \times 10^{-5}$

pH = 11.54

When analyzing an acid-base equilibrium problem:

- Ask this question: What are the major species in the solution and what is their chemical behavior?
  - *What major species are present?*
  - *Does a reaction occur that can be assumed to go to completion?*
  - *What equilibrium dominates the solution?*
  - *Let the problem guide you. Be patient.*