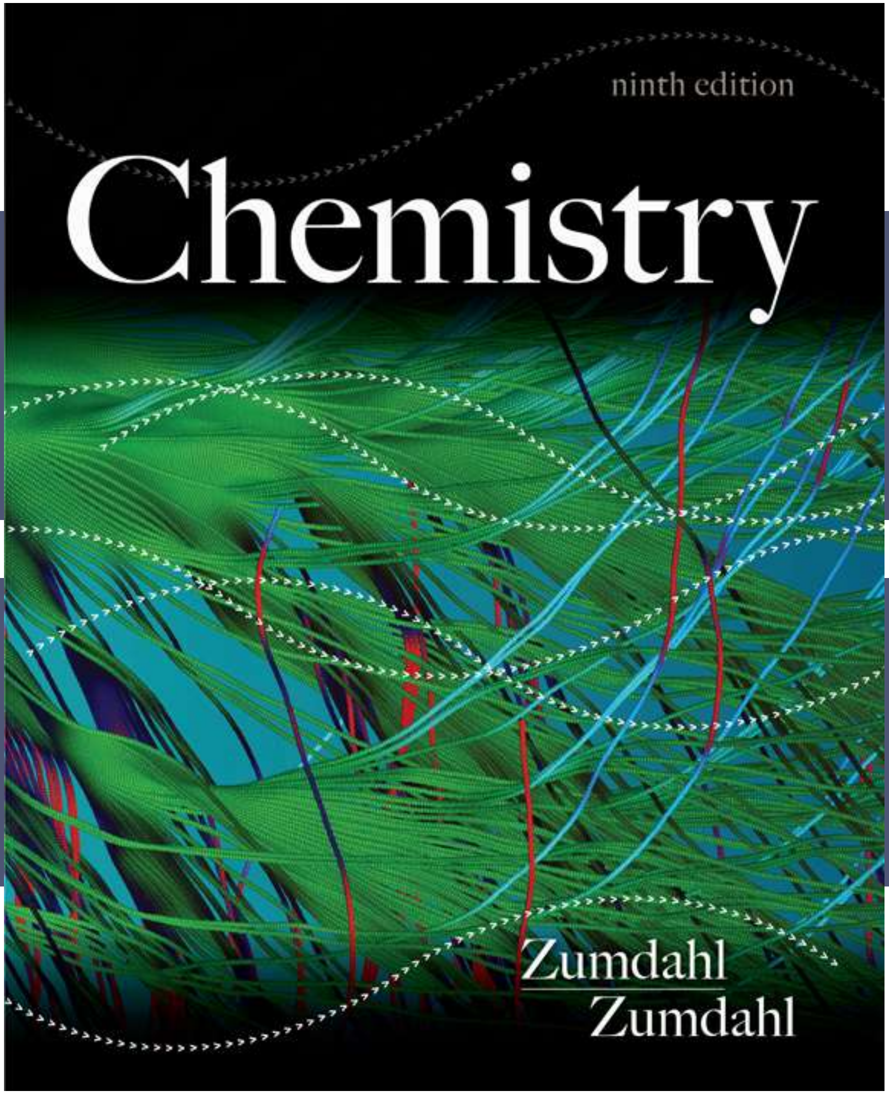


Chapter 14

Acids and Bases

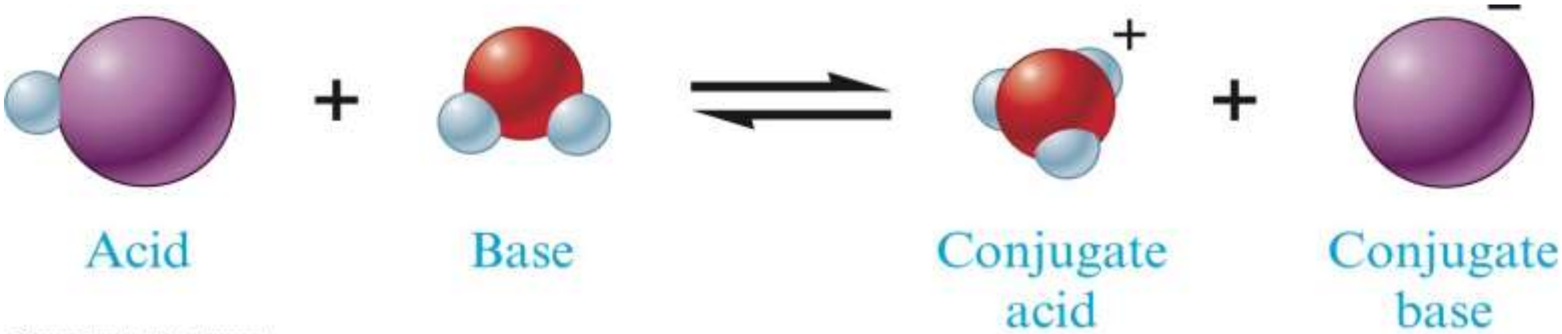
Models of Acids and Bases

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

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



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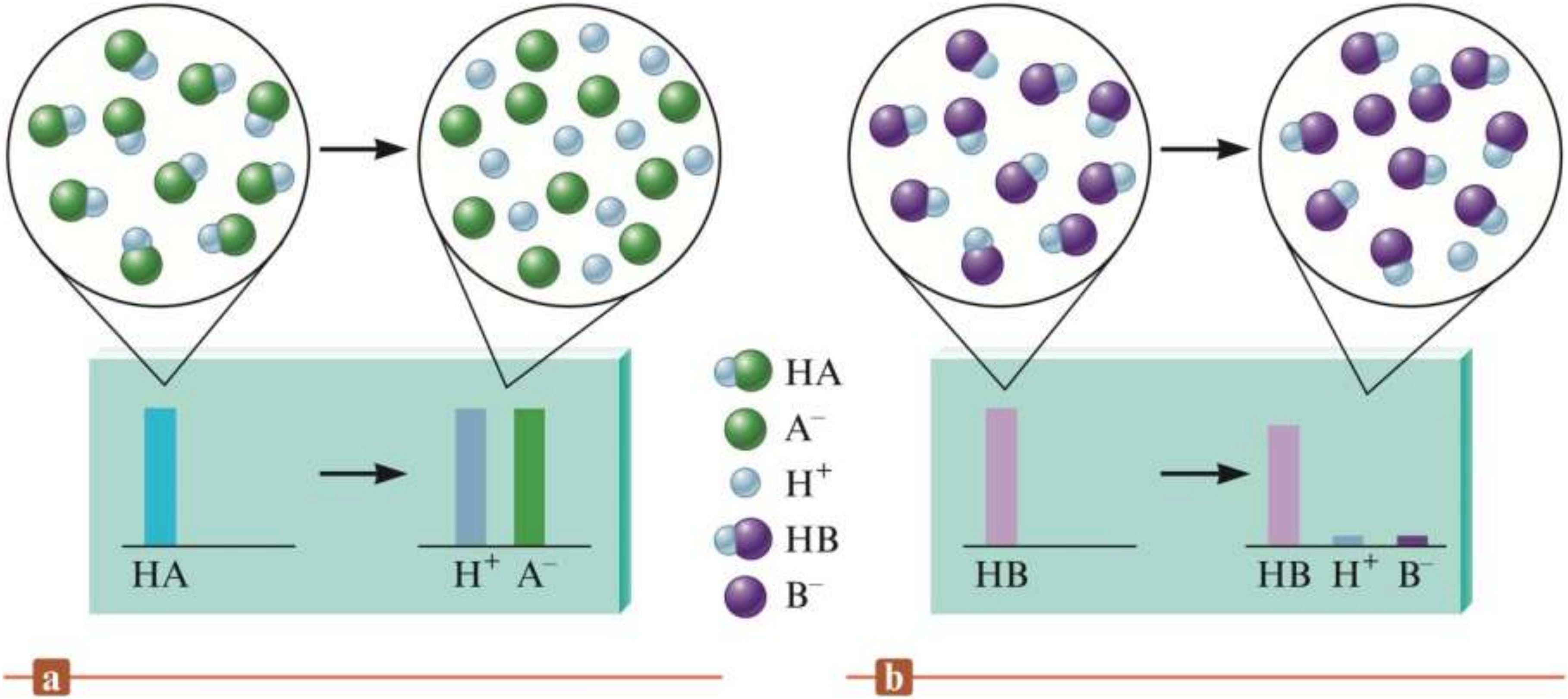
- Conjugate base is everything that remains of the acid molecule after a proton is lost.
- Conjugate acid is formed when the proton is transferred to the base.

Section 14.2
Acid Strength

- Strong acid:
  - Ionization equilibrium lies far to the right.
  - Yields a weak conjugate base.
- Weak acid:
  - Ionization equilibrium lies far to the left.
  - Weaker the acid, stronger its conjugate base.

Section 14.2
Acid Strength



Strong acid

Weak acid

Various Ways to Describe Acid Strength

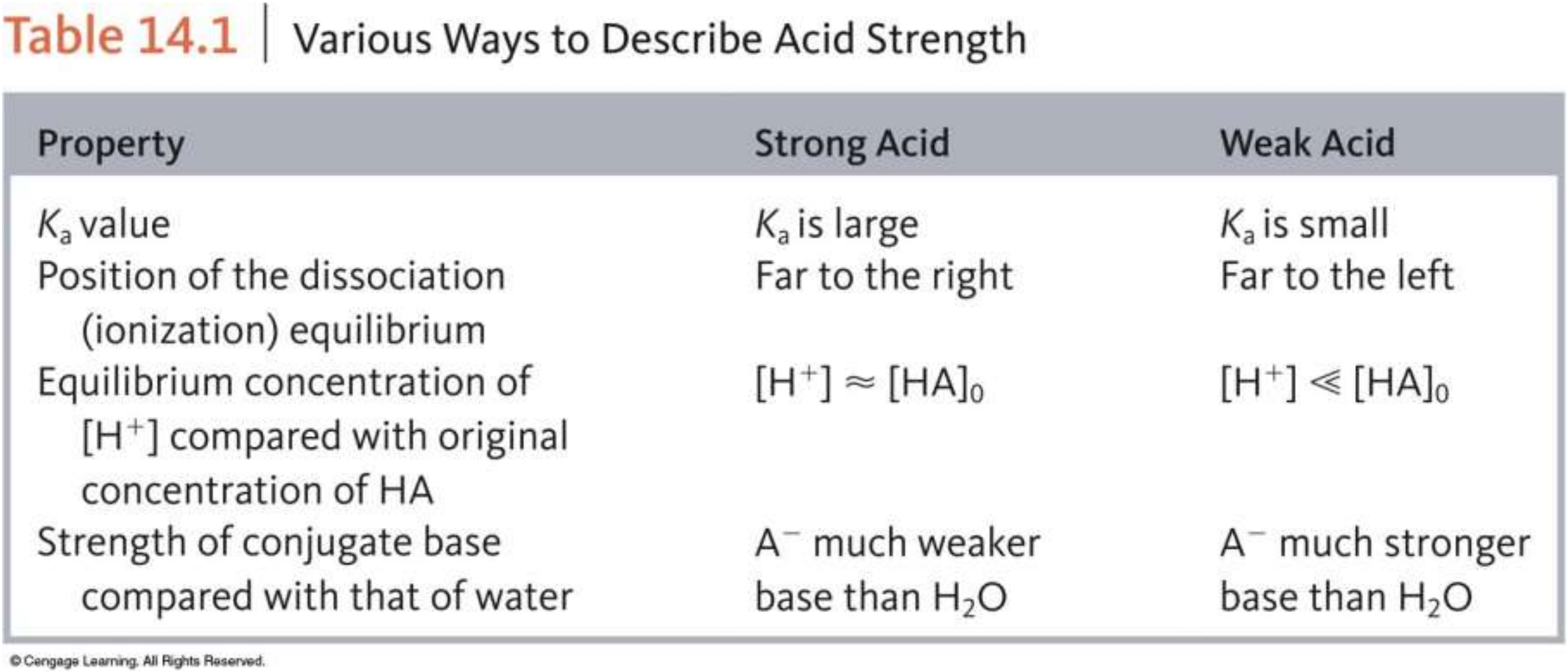


Table 14.1 | Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of $[H^+]$ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Water as an Acid and a Base

- Water is amphoteric:
  - Behaves either as an acid or as a base.
- At 25° C:

  $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
- *No matter what the solution contains*, the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14} at 25° C.

Three Possible Situations

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

CONCEPT CHECK!

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

acid base conjugate acid conjugate base

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

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

CONCEPT CHECK!

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)

CONCEPT CHECK!

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

If water is a better base than A^-, do products or reactants dominate at equilibrium?

Does this mean HA is a strong or weak acid?

Is the value for K_a greater or less than 1?

CONCEPT CHECK!

Consider a 1.0 *M* solution of HCl.

Order the following from strongest to weakest base and explain:

$H_2O(l)$

$A^-(aq)$ (from weak acid HA)

$Cl^-(aq)$

Let's Think About It...

- How good is $\text{Cl}^-(aq)$ as a base?
- Is $\text{A}^-(aq)$ a good base?

The bases from strongest to weakest are:

A^-, H_2O, Cl^-

CONCEPT CHECK!

Consider a solution of NaA where A^- is the anion from weak acid HA:

$A^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HA(aq)$	+	$OH^-(aq)$
base		acid		conjugate acid		conjugate base

a) Which way will equilibrium lie?

left

CONCEPT CHECK!

Consider a solution of NaA where A^- is the anion from weak acid HA:

$A^-(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HA(aq)$	$+$ $OH^-(aq)$
base		acid		conjugate acid	conjugate base

b) Is the value for K_b greater than or less than 1?

less than 1

CONCEPT CHECK!

Consider a solution of NaA where A^- is the anion from weak acid HA:

$$\underset{\text{base}}{A^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{HA(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

c) Does this mean A^- is a strong or weak base?

weak base

CONCEPT CHECK!

Acetic acid ($HC_2H_3O_2$) and HCN are both weak acids. Acetic acid is a stronger acid than HCN.

Arrange these bases from weakest to strongest and explain your answer:

H_2O Cl^- CN^- $C_2H_3O_2^-$

Let's Think About It…

- $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
  acid base conjugate acid conjugate base
- At 25° C, $K_w = 1.0 \times 10^{-14}$

The bases from weakest to strongest are:

Cl^-, H_2O, $C_2H_3O_2^-$, CN^-

CONCEPT CHECK!

Discuss whether the value of K for the reaction:

$$HCN(aq) + F^{-}(aq) \rightleftharpoons CN^{-}(aq) + HF(aq)$$

is >1 [✓ <1] $=1$

(K_a for HCN is 6.2×10^{-10}; K_a for HF is 7.2×10^{-4}.)

Explain your answer.

CONCEPT CHECK!

Calculate the value for K for the reaction:

$$\mathrm{HCN}(aq) + \mathrm{F}^{-}(aq) \rightleftharpoons \mathrm{CN}^{-}(aq) + \mathrm{HF}(aq)$$

(K_a for HCN is 6.2×10^{-10}; K_a for HF is 7.2×10^{-4}.)

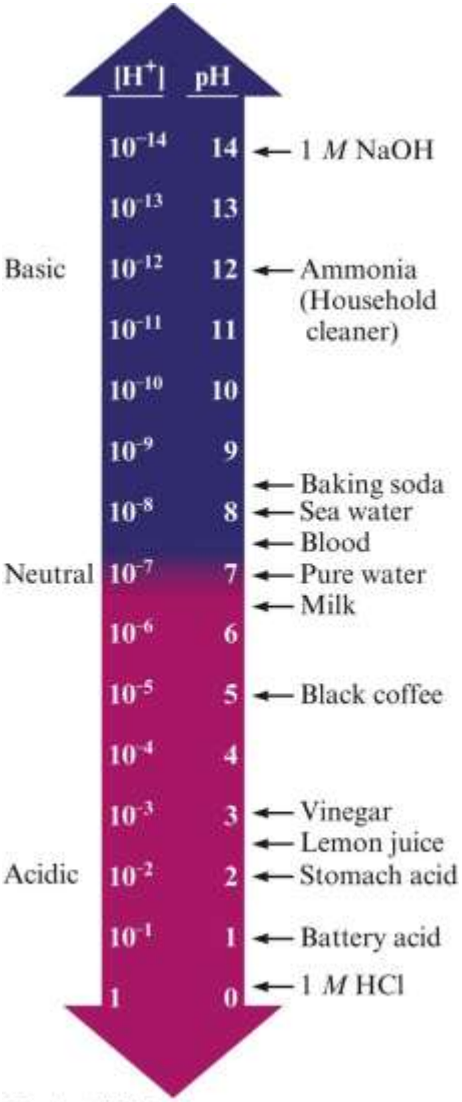
$K = 8.6 \times 10^{-7}$

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

pH Range

- pH = 7; *neutral*
- pH > 7; *basic*
    - Higher the pH, more basic.
- pH < 7; *acidic*
    - Lower the pH, more acidic.

The pH Scale and pH Values of Some Common Substances



EXERCISE!

Calculate the pH for each of the following solutions.

a) 1.0×10^{-4} M H^+

pH = 4.00

b) 0.040 M OH^-

pH = 12.60

EXERCISE!

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

$$[H^+] = 1.4 \times 10^{-6}\ M$$

pH and pOH

- Recall:

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

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

$$pK_w = pH + pOH$$

$$14.00 = pH + pOH$$

EXERCISE!

Calculate the pOH for each of the following solutions.

a) 1.0×10^{-4} *M* H^+

pOH = 10.00

b) 0.040 *M* OH^-

pOH = 1.40

EXERCISE!

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

$$[OH^-] = 7.1 \times 10^{-9}\ M$$

Thinking About Acid–Base Problems

- What are the major species in solution?
- What is the dominant reaction that will take place?
  - Is it an equilibrium reaction or a reaction that will go essentially to completion?
  - React all major species until you are left with an equilibrium reaction.
- Solve for the pH if needed.

CONCEPT CHECK!

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

What are the major species in solution?

H^+, Cl^-, H_2O

What is the pH?

pH = 2.70

CONCEPT CHECK!

Calculate the pH of a 1.5 × 10^{-11} *M* solution of HCl.

pH = 7.00

CONCEPT CHECK!

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

Let's Think About It…

- When HNO_3 is added to water, a reaction takes place immediately:

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

Let's Think About It…

- Why is this reaction not likely?

$$NO_3^-(aq) + H_2O(l) \rightleftharpoons HNO_3(aq) + OH^-(aq)$$

Let's Think About It…

- What reaction controls the pH?
- $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- In aqueous solutions, this reaction is always taking place.
- But is water the major contributor of H^+ (H_3O^+)?

pH = 1.82

Solving Weak Acid Equilibrium Problems

1. List the major species in the solution.
2. Choose the species that can produce H^+, and write balanced equations for the reactions producing H^+.
3. Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+.
4. Write the equilibrium expression for the dominant equilibrium.

Solving Weak Acid Equilibrium Problems

5. List the initial concentrations of the species participating in the dominant equilibrium.
6. Define the change needed to achieve equilibrium; that is, define x.
7. Write the equilibrium concentrations in terms of x.
8. Substitute the equilibrium concentrations into the equilibrium expression.

Solving Weak Acid Equilibrium Problems

9. Solve for x the “easy” way, that is, by assuming that $[HA]_0 - x$ about equals $[HA]_0$.
10. Use the 5% rule to verify whether the approximation is valid.
11. Calculate $[H^+]$ and pH.

CONCEPT CHECK!

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

What are the major species in solution?

HCN, H_2O

Let’s Think About It…

- Why aren’t H^+ or CN^- major species?

Consider This

$$\boxed{HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)}$$

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

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

$K_w = 1.0 \times 10^{-14}$

- Which reaction controls the pH? Explain.

Section 14.5

Calculating the pH of Weak Acid Solutions

EXERCISE!

Calculate the pH of a 0.50 *M* aqueous solution of the weak acid HF.

$$(K_a = 7.2 \times 10^{-4})$$

Let’s Think About It…

- What are the major species in solution?

HF, H_2O

- Why aren’t H^+ and F^- major species?

Let's Think About It…

- What are the possibilities for the dominant reaction?

$$\boxed{HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)}$$

$$K_a = 7.2 \times 10^{-4}$$

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

$$K_w = 1.0 \times 10^{-14}$$

- Which reaction controls the pH? Why?

Steps Toward Solving for pH

	$HF(aq) + H_2O$	$\rightleftharpoons$	$H_3O^+(aq)$	$+$	$F^-(aq)$
Initial	0.50 *M*		~ 0		~ 0
Change	–x		+x		+x
Equilibrium	0.50–x		x		x

$$K_a = 7.2 \times 10^{-4}$$

pH = 1.72

Percent Dissociation (Ionization)

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

- For a given weak acid, the percent dissociation increases as the acid becomes more dilute.

EXERCISE!

A solution of 8.00 *M* formic acid ($HCHO_2$) is 0.47% ionized in water.

Calculate the K_a value for formic acid.

$$K_a = 1.8 \times 10^{-4}$$

EXERCISE!

Calculate the pH of an 8.00 *M* solution of formic acid. Use the data from the previous slide to help you solve this problem.

pH = 1.42

EXERCISE!

The value of K_a for a 4.00 M formic acid solution should be:

higher than   lower than   [✓ the same as]

the value of K_a of an 8.00 M formic acid solution.

Explain.

CONCEPT CHECK!

The percent ionization of a 4.00 *M* formic acid solution should be:

[✓ higher than]   lower than   the same as

the percent ionization of an 8.00 *M* formic acid solution.

Explain.

CONCEPT CHECK!

The pH of a 4.00 *M* formic acid solution should be:

[✓ higher than] lower than the same as

the pH of an 8.00 *M* formic acid solution.

Explain.

EXERCISE!

Calculate the percent ionization of a 4.00 *M* formic acid solution in water.

% Ionization = 0.67%

EXERCISE!

Calculate the pH of a 4.00 *M* solution of formic acid.

pH = 1.57

- 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, $Ca(OH)_2$
- $pOH = -\log[OH^-]$
- $pH = 14.00 - pOH$

CONCEPT CHECK!

Calculate the pH of a 1.0×10^{-3} *M* solution of sodium hydroxide.

pH = 11.00

CONCEPT CHECK!

Calculate the pH of a 1.0×10^{-3} *M* solution of calcium hydroxide.

pH = 11.30

- Equilibrium expression for weak bases uses K_b.

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

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

Section 14.6

Bases

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

CONCEPT CHECK!

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

($K_b = 1.8 \times 10^{-5}$)

pH = 11.78

- Acids that can furnish more than one proton.
- Always dissociates in a stepwise manner, one proton at a time.
- The conjugate base of the first dissociation equilibrium becomes the acid in the second step.
- For a typical weak polyprotic acid:

$$K_{a1} > K_{a2} > K_{a3}$$

- For a typical polyprotic acid in water, only the first dissociation step is important to pH.

EXERCISE!

Calculate the pH of a 1.00 *M* solution of H_3PO_4.

$K_{a1} = 7.5 \times 10^{-3}$

$K_{a2} = 6.2 \times 10^{-8}$

$K_{a3} = 4.8 \times 10^{-13}$

pH = 1.08

CONCEPT CHECK!

Calculate the equilibrium concentration of PO_4^{3-} in a 1.00 *M* solution of H_3PO_4.

$K_{a1} = 7.5 \times 10^{-3}$

$K_{a2} = 6.2 \times 10^{-8}$

$K_{a3} = 4.8 \times 10^{-13}$

$[PO_4^{3-}] = 3.6 \times 10^{-19}\ M$

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

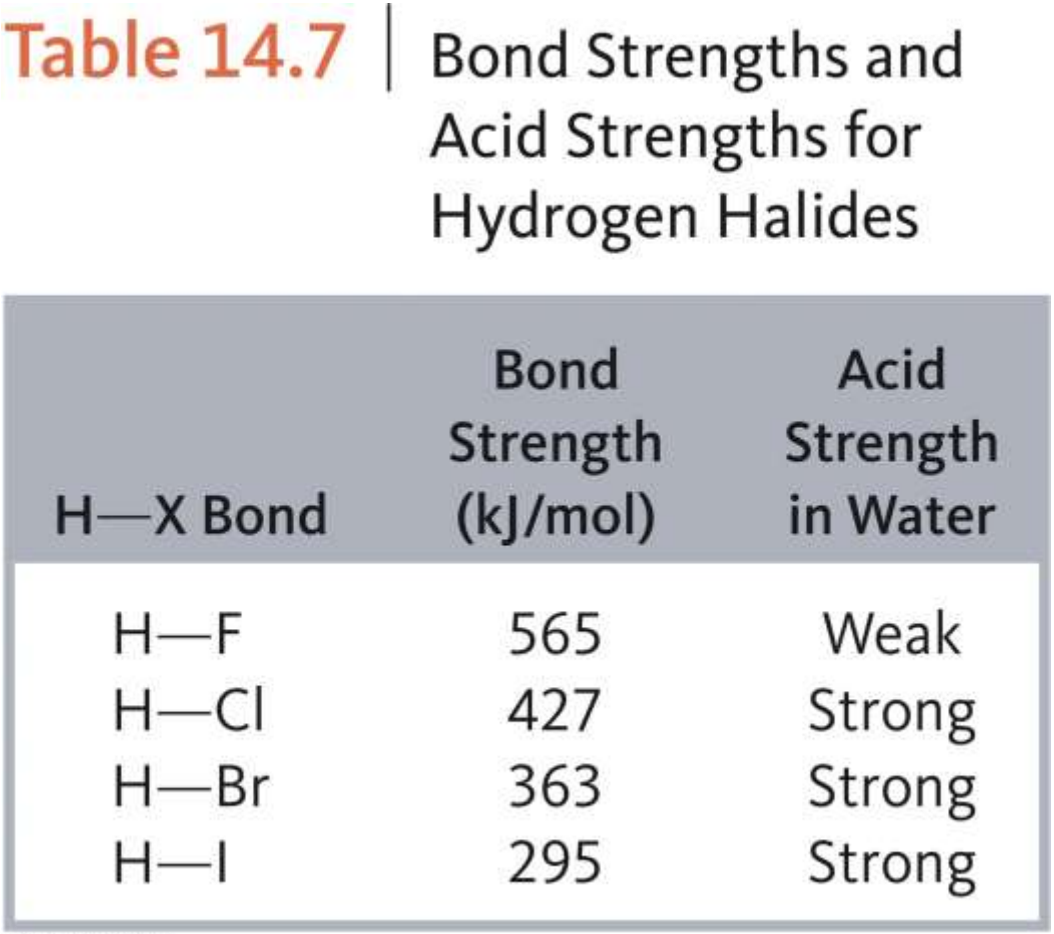


Table 14.7 | Bond Strengths and Acid Strengths for Hydrogen Halides

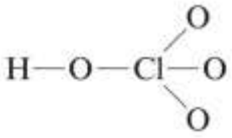
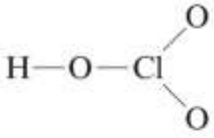
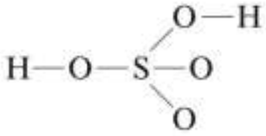
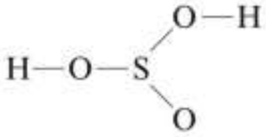
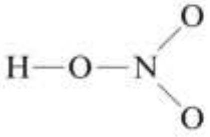
H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

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

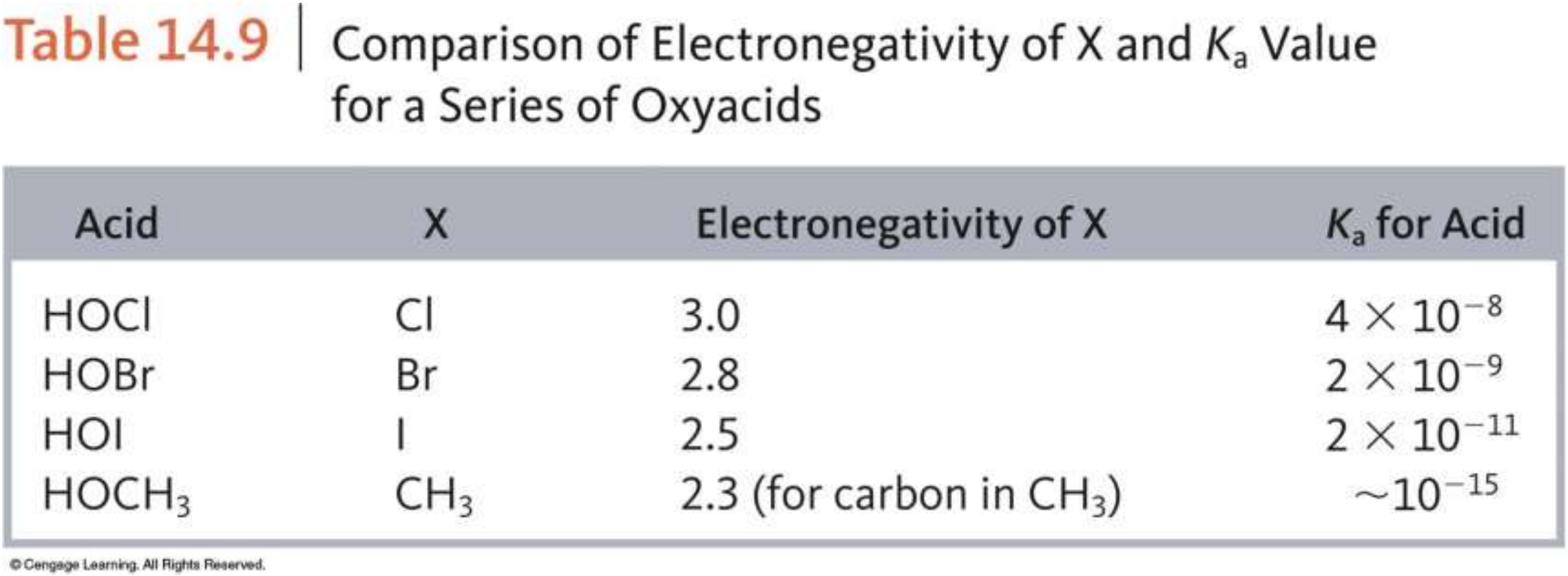


Table 14.9 | Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

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

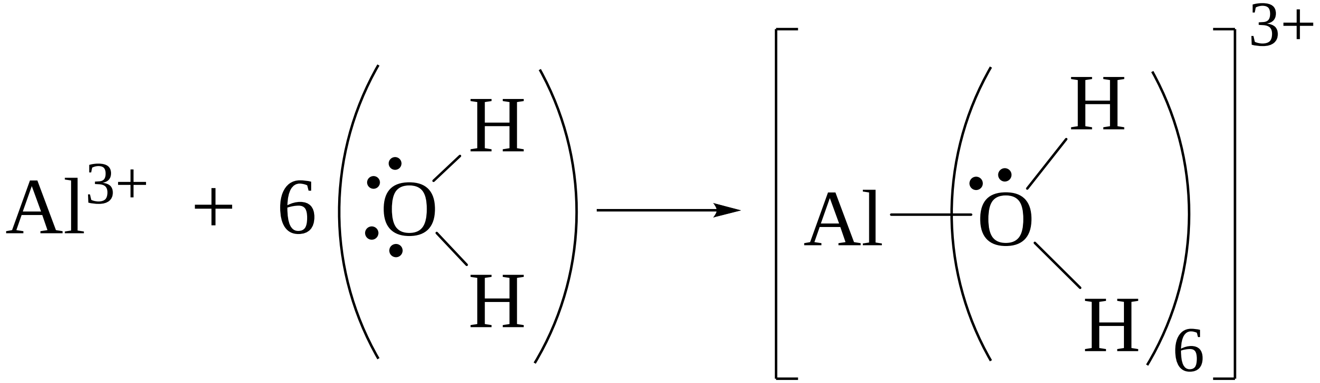
- Basic Oxides (Basic Anhydrides):
    - O—X bond is ionic.

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

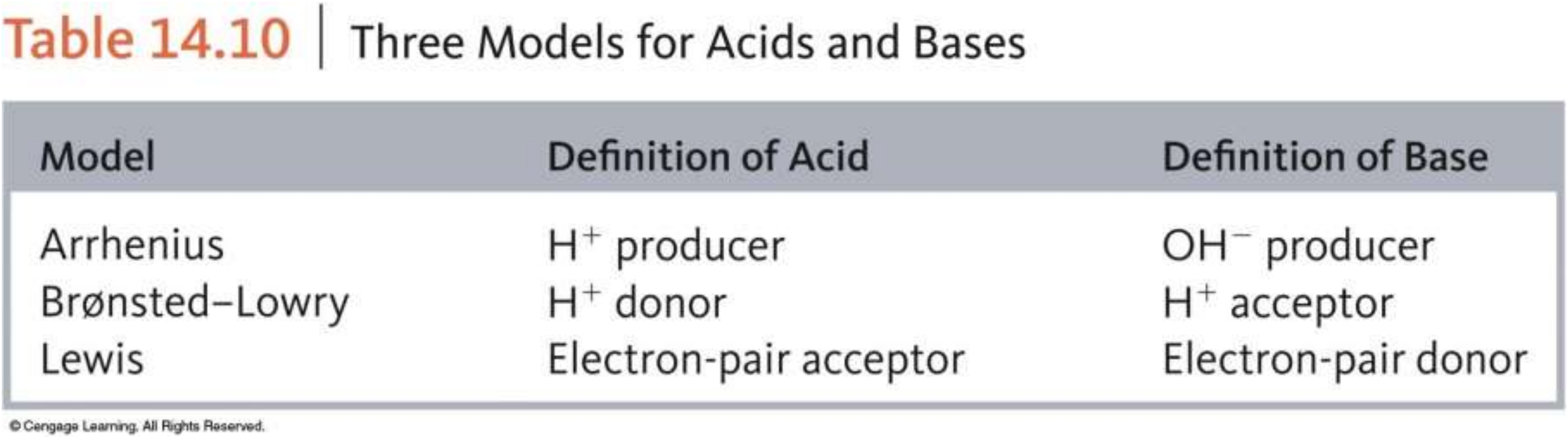


Table 14.10 | Three Models for Acids and Bases

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

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.*