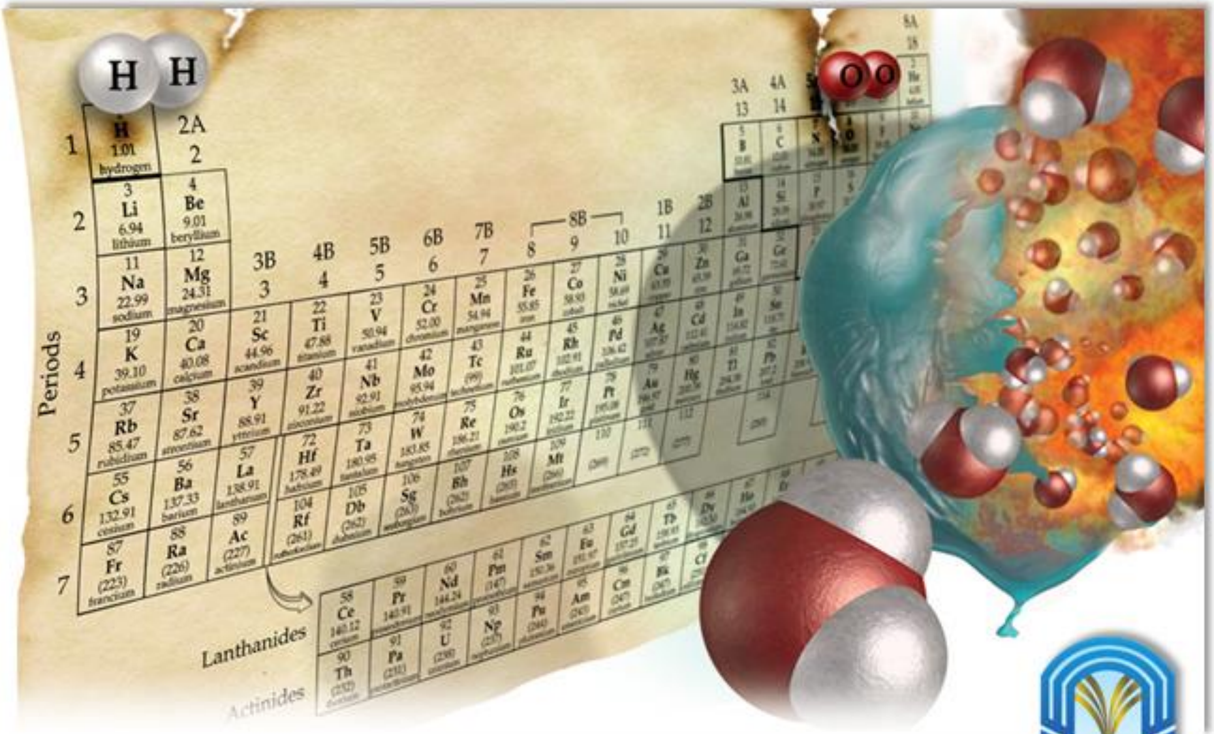
INTRODUCTION TO CHEMISTRY CHEM 101



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Chapter 5

Aqueous Solutions and Acids–Bases Equilibria

Topic 16

- **Chemical Equilibrium**

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Chemical Equilibrium: An Introduction

Dynamic Equilibrium is the condition in which the rate of the forward reaction equals the rate of the reverse reaction:

$$\text{Rate}_{forward} = \text{Rate}_{reverse}$$

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

- ✓ As H_2 and I_2 react, their concentrations decrease, which in turn decreases the rate of the forward reaction.
- ✓ At the same time, the concentration of HI increases, increasing the rate of the reverse reaction.
- ✓ At a certain point, the rate of the reverse reaction, $\mathbf{R_r}$ (*which has been increasing*) equals the rate of the forward reaction, $\mathbf{R_f}$ (*which has been decreasing*). At that point, **dynamic equilibrium** is reached.

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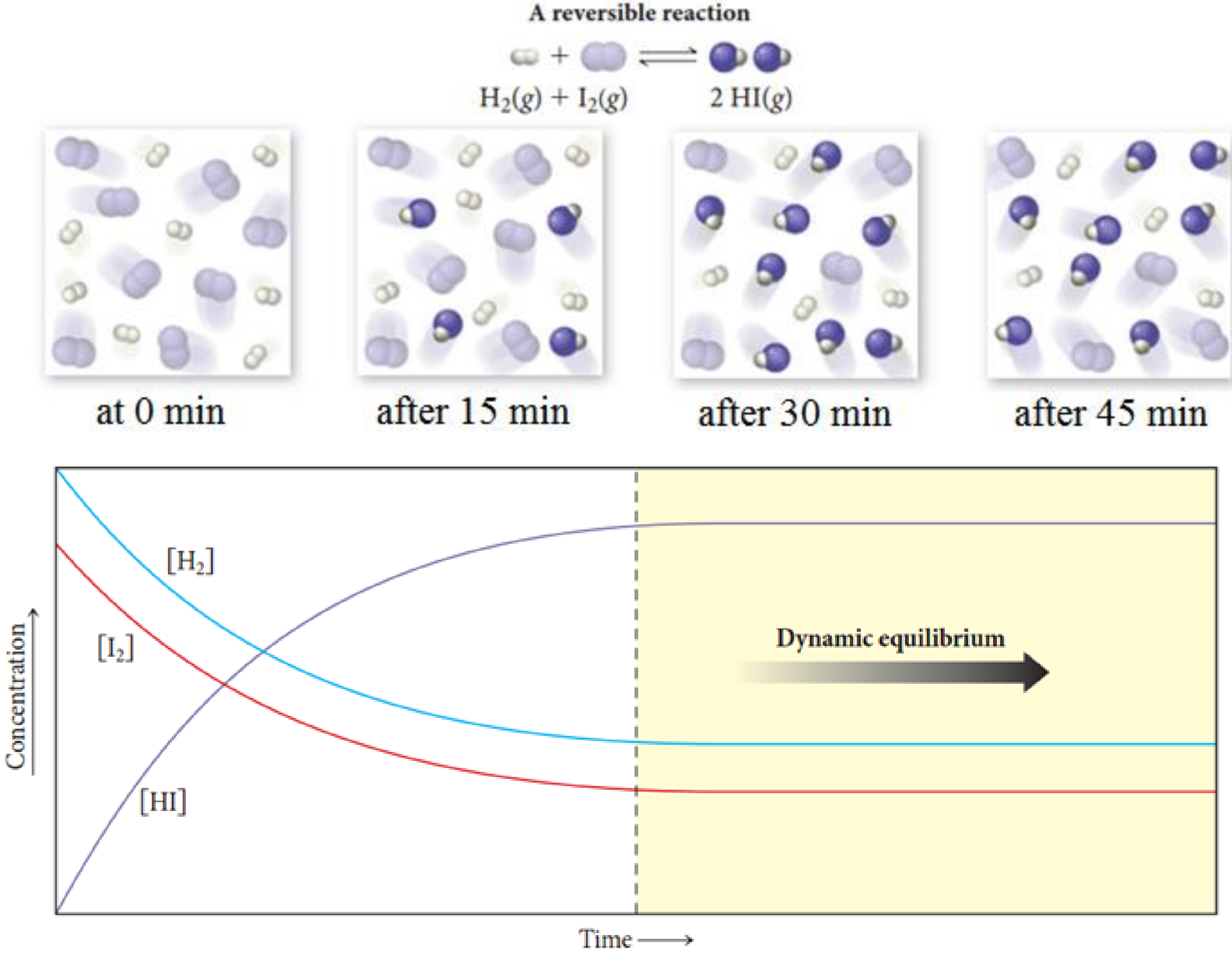
5.1 The Concept of Dynamic Equilibrium



As concentration of product increases, and concentrations of reactants decrease, rate of forward reaction slows down, and rate of reverse reaction speeds up.

Dynamic equilibrium: Rate of forward reaction = rate of reverse reaction. Concentrations of reactant(s) and product(s) no longer change.

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5.1 The Concept of Dynamic Equilibrium

Chemical Equilibrium ≠ Equal Concentrations!

At equilibrium, the rates of the forward **(R_f)** and reverse **(R_r)** reactions are equal:

- ✓ $R_f = R_r$: **DOES NOT** mean that the concentrations of reactants and products are equal in value.

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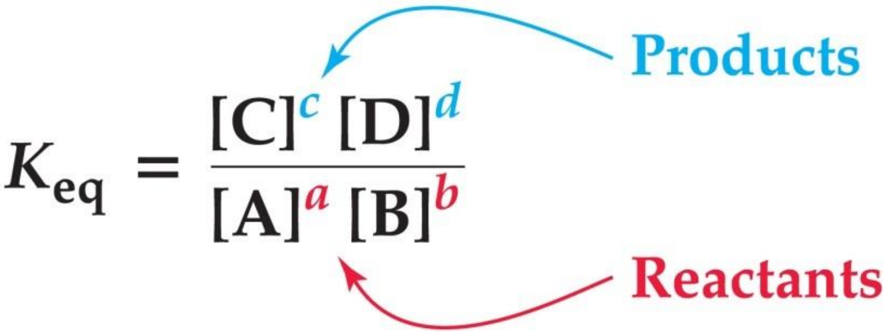
5.2 The Equilibrium Constant: *K_c or K_{eq}*

Chemical Equilibrium in reversible reactions can be numerically expressed by equilibrium constants (K_c or K_{eq}).

- **Expressing K_c or K_{eq}:**

$$aA + bB \rightleftharpoons cC + dD$$

Where A and B are **reactants**, C and D are **products**, and *a*, *b*, *c*, and *d* are the coefficients in the balanced chemical equation:

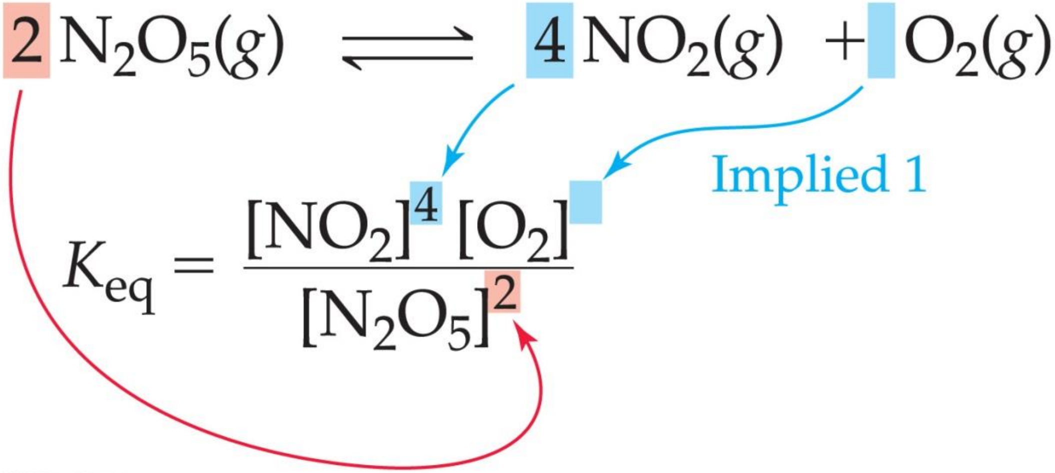


$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Note:
[A] = Molar concentration of "A"
[B] = Molar concentration of "B"
…….. and so on!

Expressing Equilibrium Constants (K_{eq}) for Chemical Reactions: Example 1

Example: write the equilibrium expression for the reaction:



$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

$$K_{eq} = \frac{[NO_2]^4\,[O_2]}{[N_2O_5]^2}$$

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Notice that the coefficients in the chemical equation become exponents in the equilibrium expression.

✓ For this reason, all equations **must be balanced** first!

Expressing Equilibrium Constants (K_{eq}) for Chemical Reactions: Example 2

Example: Express the equilibrium constant for the following chemical equation:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g)$$

Answer:

$$K = \frac{[CO][H_2]^2}{[CH_3OH]}$$

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Expressing Equilibrium Constants (K_{eq}) for Chemical Reactions: Exercises

Write the equilibrium constant expression K_{eq} for the following balanced chemical equations:

a) $C_3H_8(g) + 5\ O_2(g) \rightleftharpoons 3\ CO_2(g) + 4\ H_2O(g)$

Answer: $K_{eq} =$ ……….

b) $2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$

Answer: $K_{eq} =$ ……….

c) $2\ NO(g) \rightleftharpoons N_2(g) + O_2(g)$

Answer: $K_{eq} =$ ……….

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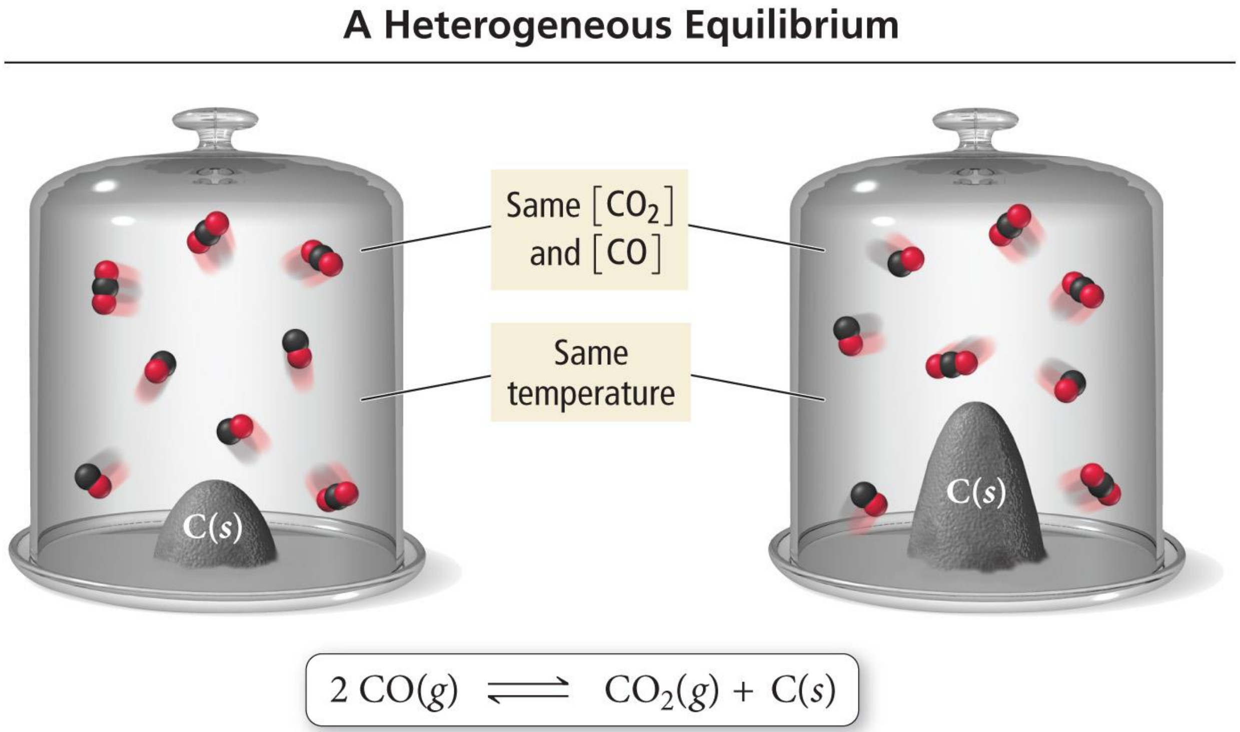
5.4 Heterogeneous Equilibria: Reactions Involving Solids or Liquids

- Many chemical reactions involve pure solids or pure liquids as reactants or products.

Consider the reaction: $2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$



A Heterogeneous Equilibrium

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5.4 Heterogeneous Equilibria: Reactions Involving Solids or Liquids

- For the previous reaction, we might expect the expression for the equilibrium constant to be:

$$K_c = \frac{[CO_2][C]}{[CO]^2} \qquad \text{(incorrect)}$$

The concentration of a solid does not change, because a solid does NOT expand to fill its container. A solid's concentration, therefore, depends only on its density, which is constant.

- The correct equilibrium expression is:

$$K_c = \frac{[CO_2]}{[CO]^2} \qquad \text{(correct)}$$

Similarly, the concentration of a pure liquid does not change. So, pure liquids are also excluded from the equilibrium expression.

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5.4 Heterogeneous Equilibria: Reactions Involving Solids or Liquids

Example:

What is the equilibrium expression K_c for the following reaction?

$$CO_2(g) + H_2O(\ell) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Answer:

Since H_2O is pure liquid, it is omitted from the equilibrium expression:

$$\boxed{K_c = \frac{[H^+][HCO_3^-]}{[CO_2]}}$$

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5.4 Heterogeneous Equilibria: Reactions Involving Solids or Liquids

Example:

What is the equilibrium expression K_c for the following reaction?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Answer:

Since $CaCO_3(s)$ and CaO(s) are both solids, you omit them from the equilibrium expression:

$$\boxed{K_c = [CO_2]}$$

Summarizing The Significance of (K_{eq}) Values

- **$K_{eq} >> 1$:** Forward reaction is favored (the reaction moves right).
  - ✓ The position of equilibrium favors products.
- **$K_{eq} << 1$:** Reverse reaction is favored (the reaction moves left).
  - ✓ The position of equilibrium favors reactants.
- **$K_{eq} \approx 1$:** Neither direction is favored.
  - ✓ Reactants and products are present at equilibrium, i.e. neither reactants nor products are favored.

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5.5 Calculating the K_{eq} from Measured Equilibrium Concentrations

Consider the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

Suppose a mixture of **H_2** and **I_2** is allowed to come to equilibrium at 445 °C.

The measured concentrations at equilibrium were:

$[H_2] = 0.11$ M, $[I_2] = 0.11$ M, $[HI] = 0.78$ M

What is the **value of the equilibrium constant** at this temperature? and predict whether reactants or products will be **favored** at equilibrium.

Answer:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.78^2}{(0.11)\times(0.11)} = 50$$ (Forward, products are favored)

5.5 Calculating the K_{eq} from Measured Equilibrium Concentrations

Example: Determine the K_c value using the following concentrations at equilibrium for the chemical reaction below, and predict whether reactants or products will be favored at equilibrium:

$$2\,\mathrm{NOCl}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g)$$

$[\mathrm{NOCl}]_{eq} = 1.34$ M, $[\mathrm{NO}]_{eq} = 0.66$ M, $[\mathrm{Cl_2}]_{eq} = 0.33$ M

Solution:

$K_c = [\mathrm{NO}]^2\,[\mathrm{Cl_2}]\,/\,[\mathrm{NOCl}]^2$

$K_c = ([0.66]^2\,[0.33])\,/\,[1.34]^2$

$K_c = (0.144)\,/\,(1.80)$

$K_c = 0.0801$ **(Reverse, the reactants are favored)**

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Assessment

Write the correct expression for the equilibrium constant K_{eq} for each chemical equation:

1) $C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$

2) $N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g).$

3) $2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$

4) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$

5) $2\,KClO_3(s) \rightleftharpoons 2\,KCl(s) + 3\,O_2(g)$

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

7) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq)$

8) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

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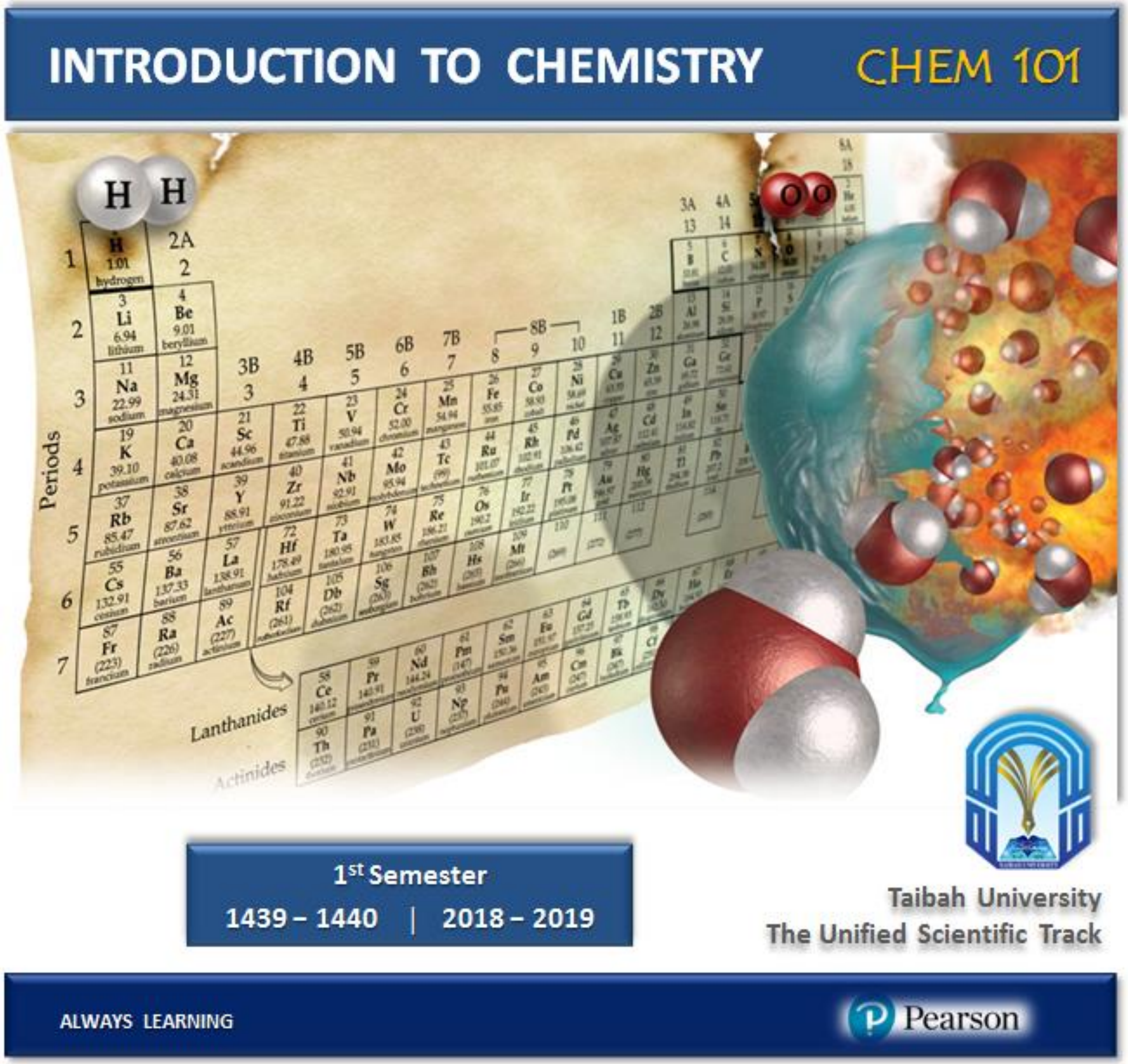

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Chapter 5

Aqueous Solutions and Acids–Bases Equilibria

<u>Topic 17</u>

- **Le Châtelier's Principle**
- **The Nature of Acids and Bases**

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5.6 Le Châtelier’s Principle: How a System at Equilibrium Responds to Disturbances

Le Châtelier’s Principle: When a chemical system at equilibrium is disturbed; the system shifts in a direction that minimizes the disturbance.

In other words, a system at equilibrium tends to maintain equilibrium, it bounces back when disturbed: “Restoring Balance”

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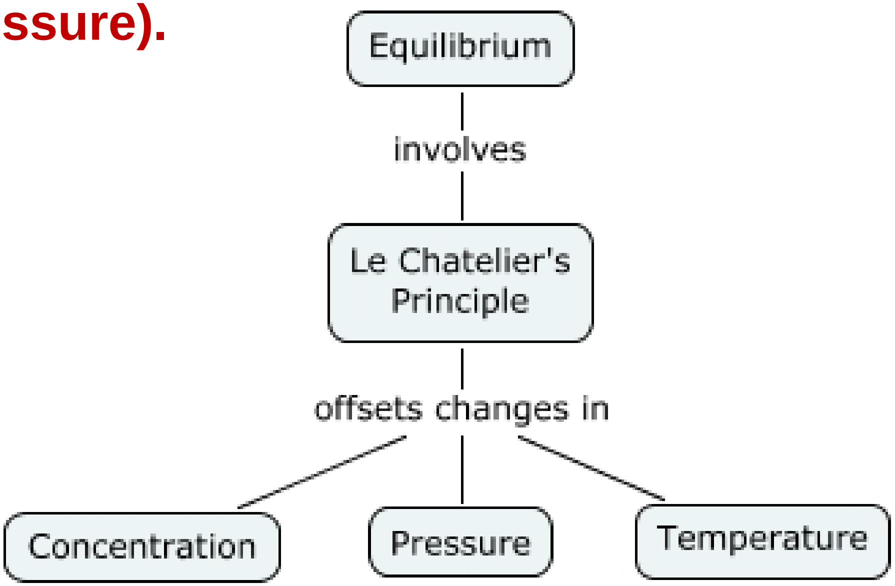
5.6 Le Châtelier’s Principle: Factors Affecting Equilibrium

We can disturb a system in chemical equilibrium in different ways, including:

- ✓ Changing the **concentration** of a reactant or a product.
- ✓ Changing the **volume (or pressure).**
- ✓ Changing the **temperature.**



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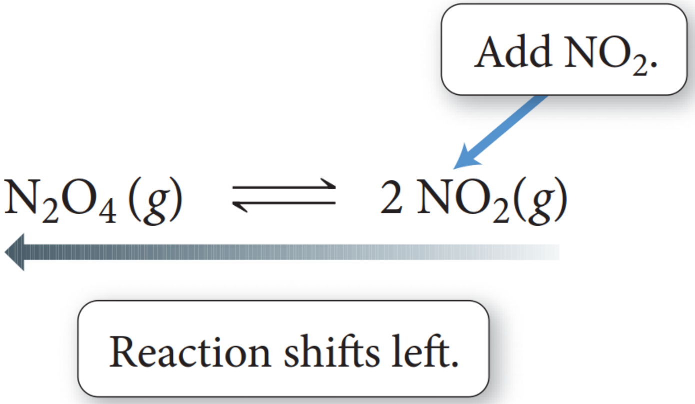
The Effect of Concentration Change on Equilibrium

Consider this reaction in chemical equilibrium:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Suppose we disturb the equilibrium by **adding NO_2** to the equilibrium mixture, What happens? According to Le Châtelier's principle, the system will shift in a direction to minimize the disturbance. The reaction **goes to the left** side (it proceeds in the **reverse** direction)

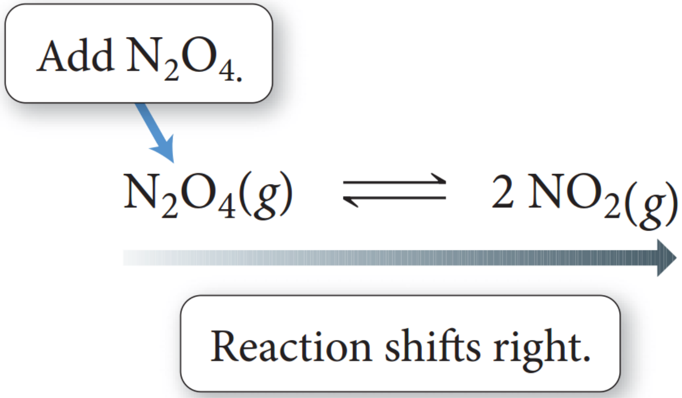

Add NO_2.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Reaction shifts left.

The Effect of Concentration Change on Equilibrium: Example

On the other hand, what happens if we **add more N_2O_4**? In this case, the reaction **shifts to the right** side (it proceeds in the **forward** direction), consuming some of the added N_2O_4 and bringing its concentration back down (restoring equilibrium)



Add N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Reaction shifts right.

Important Note: adding or removing solid (*s*) or pure liquid (*l*) substances does **not** affect the equilibrium position – Because their concentrations are not changed!

- **Example**: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

In this reaction, increasing or decreasing $CaCO_3$ or (CaO) will not cause any change to the equilibrium.

- **Practice**: In the following reaction, what would be the effect of adding more H_2O?

$$4\,HCl(aq) + O_2(g) \rightleftharpoons 2\,H_2O(l) + 2\,Cl_2(g)$$

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The Effect of Volume (or Pressure) Change on Equilibrium

- An increase in pressure (or a decrease in volume) will cause the system to shift to the side with the **fewest gas moles**.
- A decrease in pressure (or a increase in volume) will cause the system to shift to the side with the **most gas moles.**

✓ **Notice that**, changing pressure or volume **does NOT affect** the equilibrium in reactions with no gases included (either in reactants, products, or in both) – **because only gases are compressible.**

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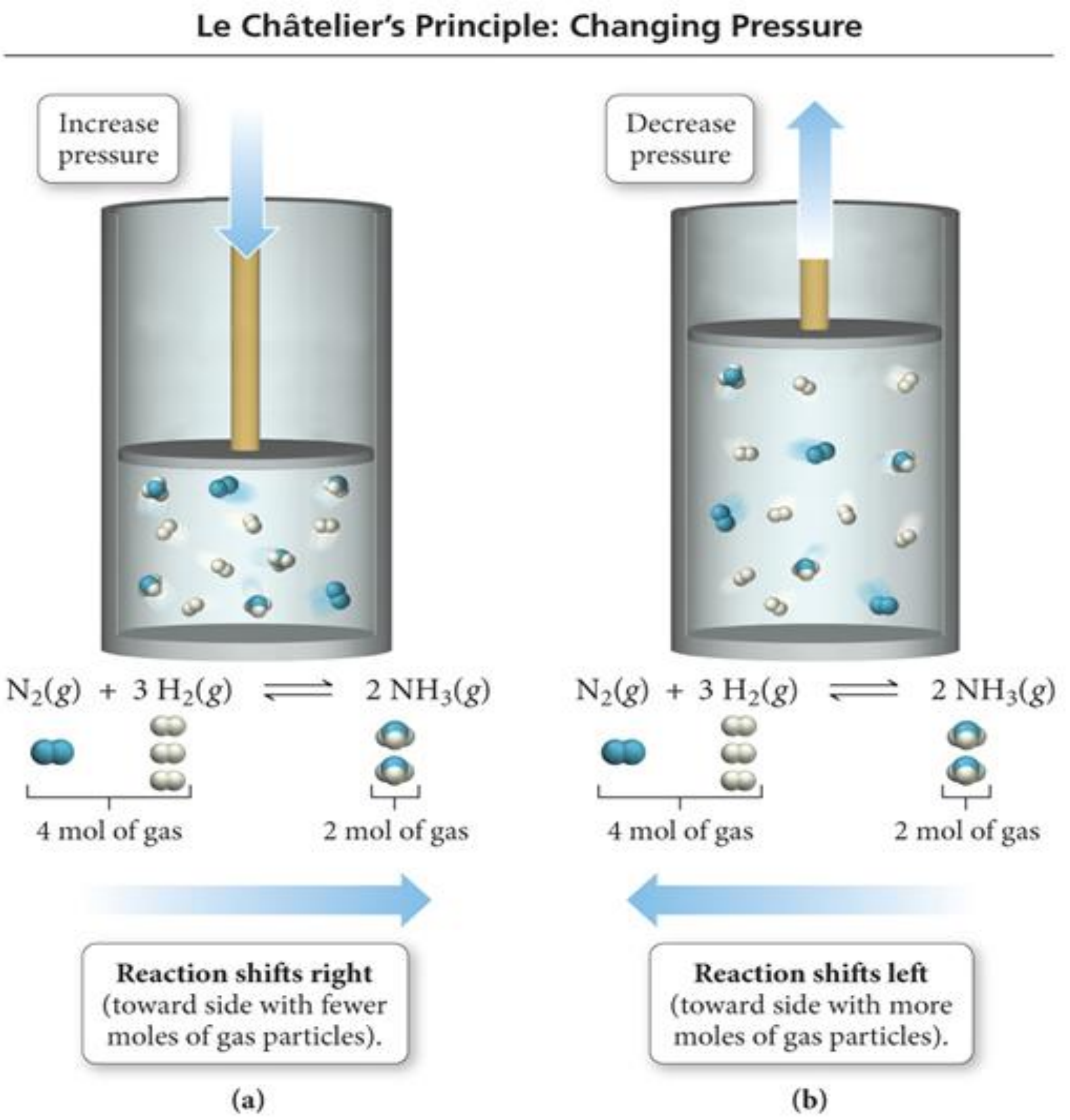
The Effect of Volume (or Pressure) Change on Equilibrium: Example

(a) Decreasing the volume increases the pressure, causing the reaction to shift to the right (**fewer moles of gas)**.

(b) Increasing the volume reduces the pressure, causing the reaction to shift to the left (**more moles of gas)**



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The Effect of Temperature Change on Equilibrium

If the **temperature** at equilibrium changes, the system should shift in the direction to counter that change, so if the temperature at equilibrium increases that tends to decrease the temperature and vice versa.

An **Exothermic Reaction** emits heat ($\Delta H = -$). We can think of heat as a "product":

$$A + B \rightleftharpoons C + D + \text{heat} \qquad (\Delta H = -)$$

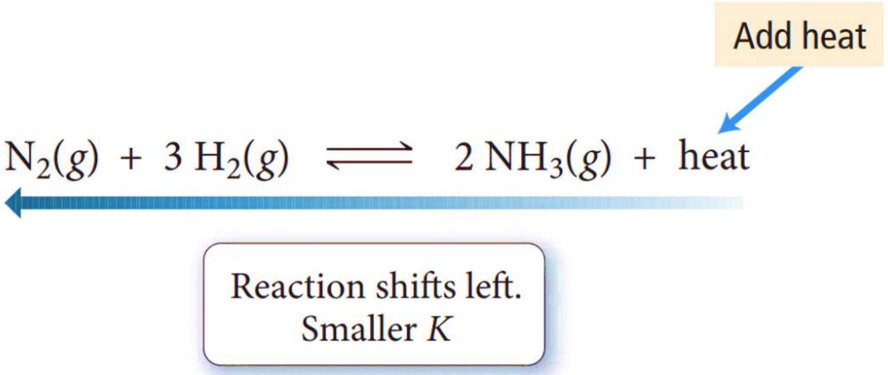
An **Endothermic Reaction** absorbs heat ($\Delta H = +$). We can think of heat as a "reactant":

$$A + B + \text{heat} \rightleftharpoons C + D \qquad (\Delta H = +)$$

The Effect of Temperature Change on Equilibrium: Example

- At constant pressure, raising the temperature of an **exothermic reaction** (think of this as adding heat), causes the **reaction to shift left**.

- Example:



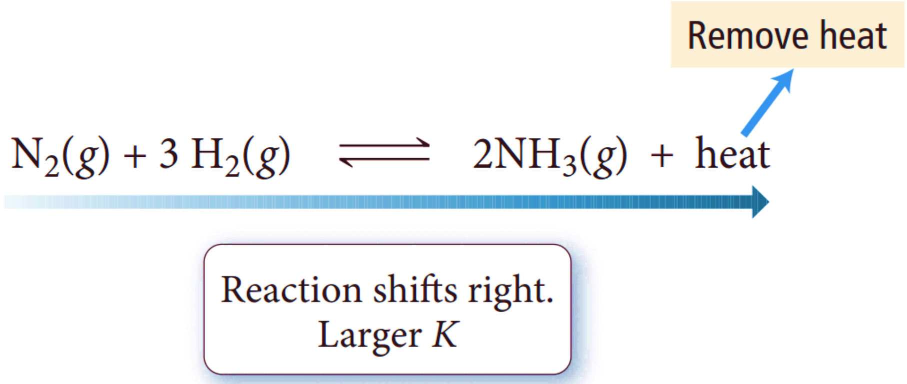
Add heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

Reaction shifts left.
Smaller K

- Conversely, lowering the temperature of an **exothermic reaction** (think of this as removing heat), causes the **reaction to shift right**.

- Example:



Remove heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$$

Reaction shifts right.
Larger K

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Le Châtelier's Principle: Exercises

Answer the following questions:

1. Consider the reaction at equilibrium: $2\ \mathrm{KClO_3}(s) \rightleftharpoons 2\ \mathrm{KCl}(s) + 3\ \mathrm{O_2}(g)$

Predict whether the reaction will shift left, shift right, or remain unchanged upon each disturbance.

a. O_2 is removed **b.** KCl is added **c.** $KClO_3$ is added **d.** O_2 is added

2. This reaction is endothermic. $\mathrm{C}(s) + \mathrm{CO_2}(g) \rightleftharpoons 2\ \mathrm{CO}(g)$

Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature.

3. Each reaction is allowed to come to equilibrium and then the volume is changed as indicated. Predict the effect

a. $\mathrm{I_2}(g) \rightleftharpoons 2\ \mathrm{I}(g)$ (volume is increased)
b. $2\ \mathrm{H_2S}(g) \rightleftharpoons 2\ \mathrm{H_2}(g) + \mathrm{S_2}(g)$ (volume is decreased)
c. $\mathrm{I_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\ \mathrm{ICl}(g)$ (volume is decreased)
d. $\mathrm{C}(s) + \mathrm{CO_2}(g) \rightleftharpoons 2\ \mathrm{CO}(g)$ (volume is increased)

4. Consider the reaction at equilibrium:

$$\mathrm{N_2}(g) + 3\ \mathrm{H_2}(g) \rightleftharpoons 2\ \mathrm{NH_3}(g) + \text{heat}$$

Predict whether the reaction will shift left, shift right, or remain unchanged upon each disturbance.

a. adding N_2 b. decreasing H_2 c. increasing volume
d. increasing pressure e. cooling down f. heating up

5.7 The Nature of Acids and Bases

General Properties of Acids

- Sour taste
- React with “active” metals
  - e.g. Al, Zn, Fe, but not Cu, Ag, or Au
  - Corrosive
- React with carbonates, producing CO_2
  - Marble, baking soda, chalk, limestone

  $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$
- Blue litmus turns red.
- React with bases to form ionic salts:
  - Neutralization Reaction

General Properties of Bases “alkalis”

- Taste bitter
  - e.g. Alkaloids = plant product that is alkaline
- Often poisonous
- Solutions feel slippery to touch.
  - Gelatinous texture
- Red litmus turns blue.
- React with acids to form ionic salts:
  - Neutralization Reaction

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Some Common Acids

Table 5.1: Some Common Acids

Name	Occurrence/Uses (See only, not for memorizing!)
Hydrochloric acid (HCl)	Metal cleaning; main component of stomach acid
Sulfuric acid (H_2SO_4)	Fertilizer; dye and glue; automobile batteries
Nitric acid (HNO_3)	Fertilizer; dye and glue manufacturing
Hydrofluoric acid (HF)	Metal cleaning; glass frosting
Phosphoric acid (H_3PO_4)	Fertilizers, biological buffers, preservatives
Acetic acid (CH_3COOH)	Plastic & rubber; active component of vinegar
Citric acid [$C_3H_5O(COOH)_3$]	Present in citrus food such as lemon and limes
Carbonic acid (H_2CO_3)	Found in carbonated beverage

Occurrence/Uses of those acids are to be seen only, not for memorizing!

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Some Common Bases

Table 5.2 Some Common Bases

Name	Occurrence/Uses (See only, not for memorizing!)
Sodium hydroxide ($NaOH$)	Soap and plastic manufacturing
Potassium hydroxide (KOH)	Cotton processing, soap production, batteries
Sodium bicarbonate ($NaHCO_3$)	Antacid, ingredient of baking soda
Sodium carbonate (Na_2CO_3)	Manufacturing of glass and soap, water softener
Ammonia (NH_3)	Detergent, fertilizer & fiber production

Occurrence/Uses of those bases are to be seen only, not for memorizing!

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5.8 Definitions of Acids and Bases

We will examine three definitions of acids and bases:

- **The Arrhenius definition**
- **The Brønsted-Lowry definition**
- **The Lewis definition**

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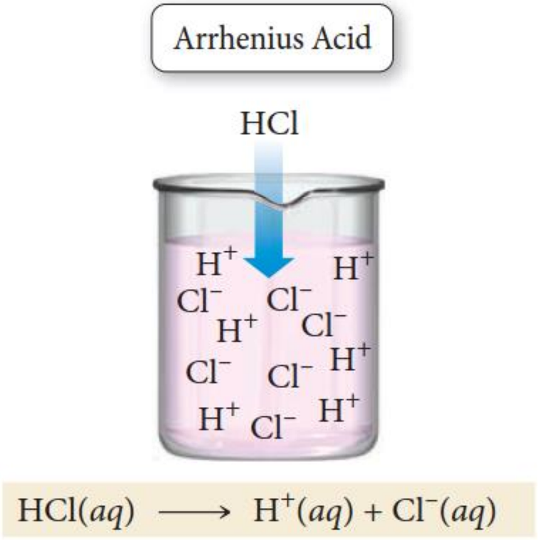
5.8 Definitions of Acids and Bases: The Arrhenius Definition

The Arrhenius Definition

- **Acid**: a substance that dissociates (ionizes) to produce H^+ ions in aqueous solutions.

For example: under the Arrhenius definition HCl is an acid because it produces H^+ ions in solution:

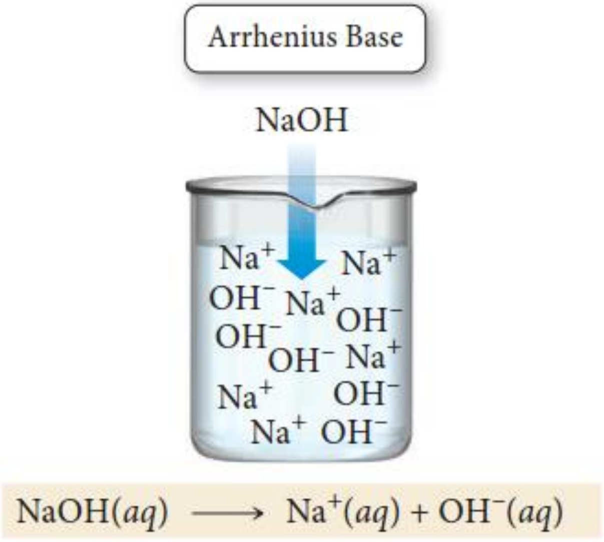
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$



- **Base**: a substance that dissociates (ionizes) to produces OH^- ions in aqueous solutions.

For example: under the Arrhenius definition NaOH is a base because it produces OH^- ions in solution:

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$



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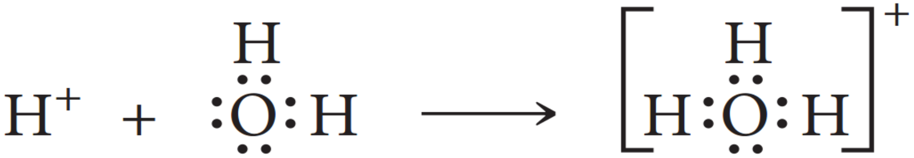
The Hydronium Ion: H_3O^+

- In aqueous solutions, **H^+** ion attaches itself to **H_2O** to form **H_3O^+** or “**hydronium ion”**:



$$H^+ + \overset{H}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{:O:}}}H \longrightarrow \left[H:\overset{H}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}}:H\right]^+$$

Examples:

$$HCl(aq) + H_2O(l) \longrightarrow \mathbf{H_3O^+}(aq) + Cl^-(aq)$$

$$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + \mathbf{H_3O^+}(aq)$$

Notice: $[H^+]$ = $[H_3O^+]$ in aqueous solutions

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Acid – Base Neutralization

Neutralization Reaction:

Under the Arrhenius definition, acid and base react together forming (water + salt), neutralizing each other:

$$\text{Acid} + \text{Base} \rightarrow H_2O + \text{Salt}$$

Examples:

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$$

$$2\ HNO_3(aq) + Ca(OH)_2(aq) \rightarrow 2\ H_2O(l) + Ca(NO_3)_2(aq)$$

$$H_2SO_4(aq) + 2\ KOH(aq) \rightarrow 2\ H_2O(l) + K_2SO_4(aq)$$

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Classifying Acids by The Number of H^+

- **Monoprotic Acids:** contain only one ionizable proton H^+:

✓ For examples, HCl and HNO_3 contain only one ionizable proton, each:

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

- **Polyprotic Acids:** contain more than one ionizable proton H^+ and release them sequentially:

✓ For example H_2SO_4 is a **diprotic acid**: contains two ionizable protons H^+.

✓ Phosphoric acid (H_3PO_4) is a **triprotic acid**: contains three ionizable protons H^+.

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Strong and Weak Acids and bases: Common Examples

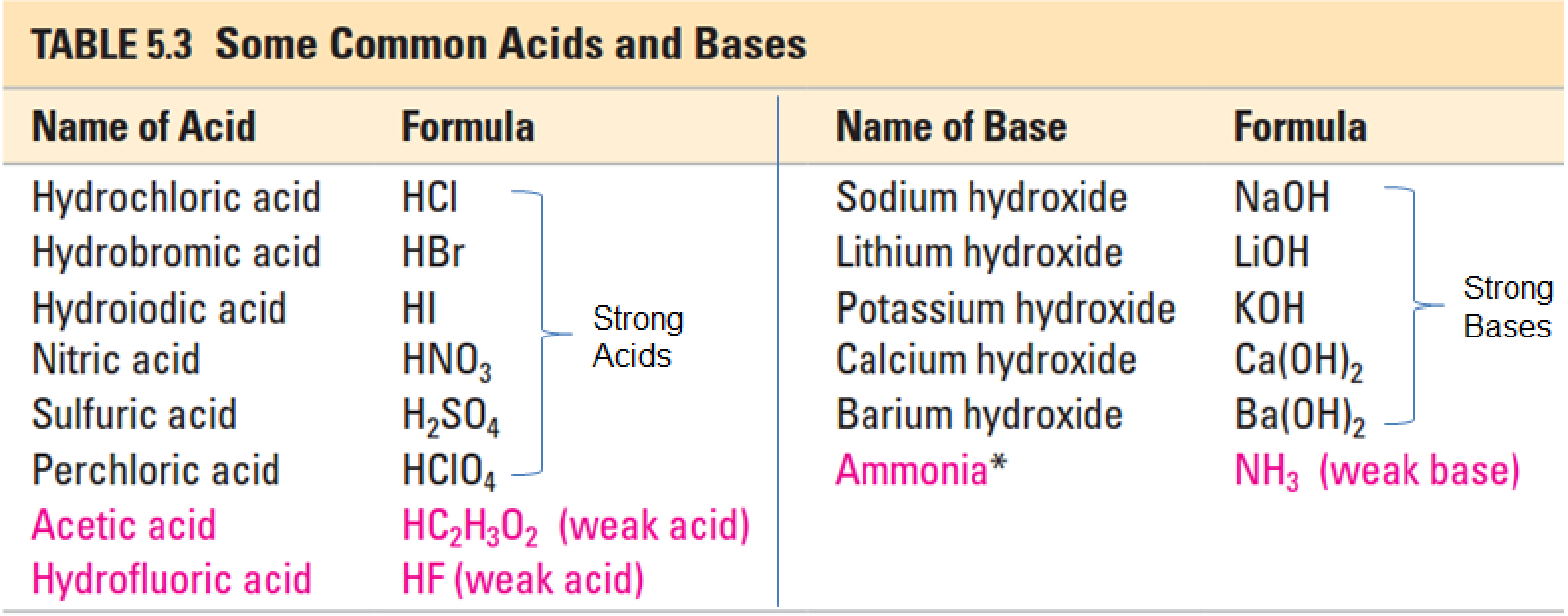
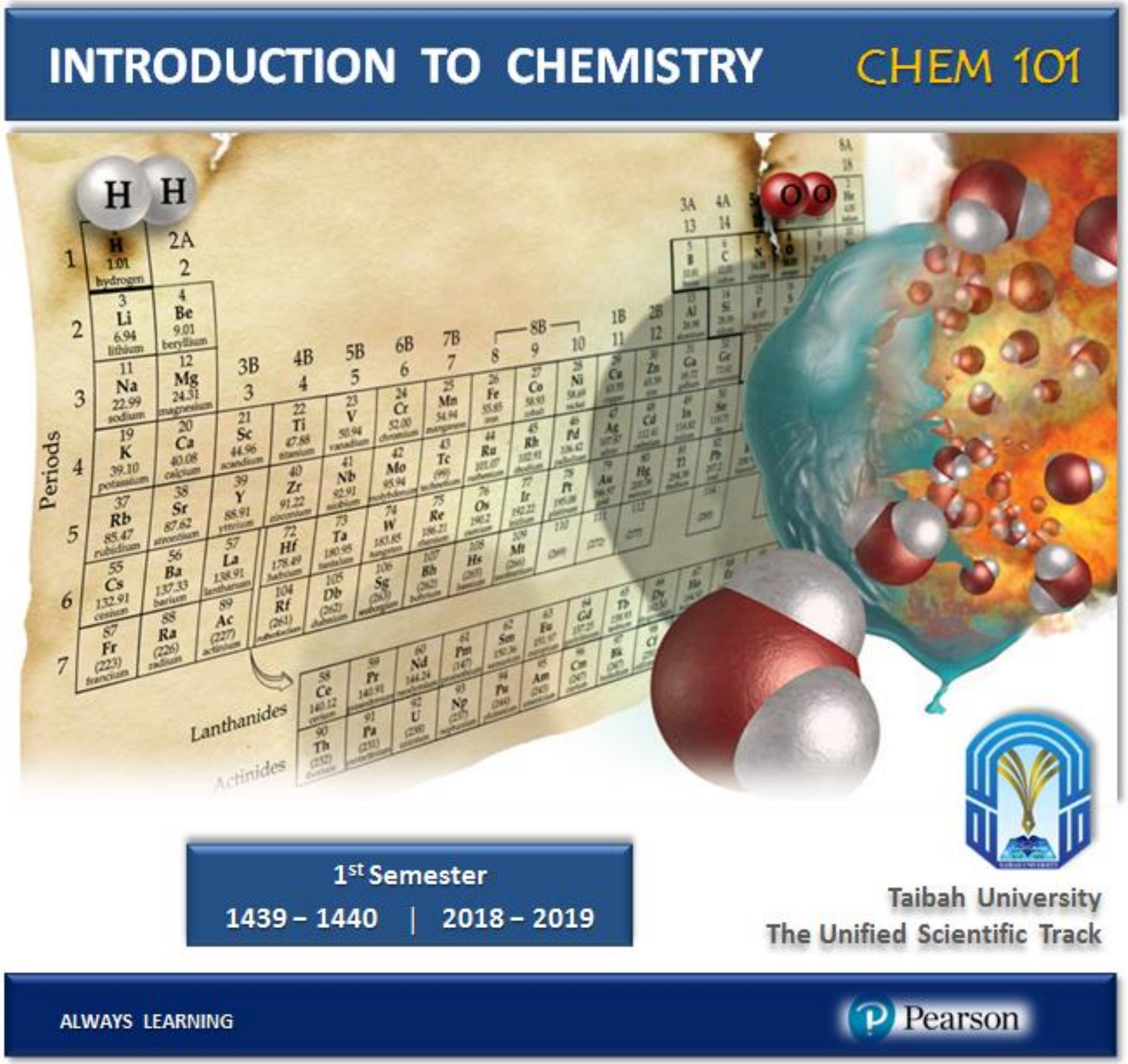


TABLE 5.3 Some Common Acids and Bases

Name of Acid	Formula		Name of Base	Formula	
Hydrochloric acid	HCl	Strong Acids	Sodium hydroxide	NaOH	Strong Bases
Hydrobromic acid	HBr		Lithium hydroxide	LiOH	
Hydroiodic acid	HI		Potassium hydroxide	KOH	
Nitric acid	HNO_3		Calcium hydroxide	$Ca(OH)_2$	
Sulfuric acid	H_2SO_4		Barium hydroxide	$Ba(OH)_2$	
Perchloric acid	$HClO_4$		Ammonia*	NH_3 (weak base)	
Acetic acid	$HC_2H_3O_2$ (weak acid)				
Hydrofluoric acid	HF (weak acid)				

Important: Those examples on strong and weak acids and bases are to be **carefully memorized**!



INTRODUCTION TO CHEMISTRY CHEM 101

1^{st} Semester
1439 – 1440 | 2018 – 2019

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Chapter 5

Aqueous Solutions and Acids–Bases Equilibria

Topic 18

- **Brønsted-Lowry Acids & Bases**
- **Acid Strength and pH Scale**
- **Base Solutions**
- **Buffered Solutions**
- **Lewis Acids & Bases**

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Definitions of Acids and Bases: The Brønsted – Lowry Definition

Brønsted – Lowry definition of acids and bases: focuses on the **transfer of H^+** ion in an acid-base reaction.

According to Brønsted-Lowry:

- **Acid**: is a proton (**H^+**) donor
- **Base**: is a proton (**H^+**) acceptor

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Definitions of Acids and Bases: The Brønsted – Lowry Definition

Under the **Brønsted-Lowry** definition, acids (proton donors) and bases (proton acceptors) always **occur together**:

- **Example 1:**

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

  - ✓ HCl = **acid**, donates H^+ (proton donor)
  - ✓ H_2O = **base**, accepts H^+ (proton accepter)

- **Example 2:**

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

  - ✓ NH_3 = **base**, accepts H^+ (proton accepter)
  - ✓ H_2O = **acid**, donates H^+ (proton donor)

Note: **water** in those two examples acted as an acid and as a base!

- A substance that can act as an acid and as a base is called "**amphoteric substance**".

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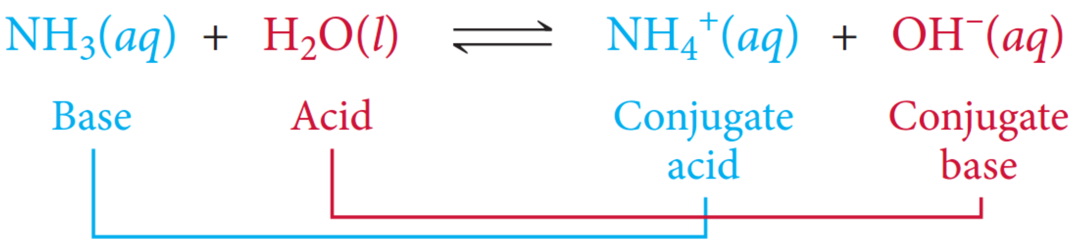
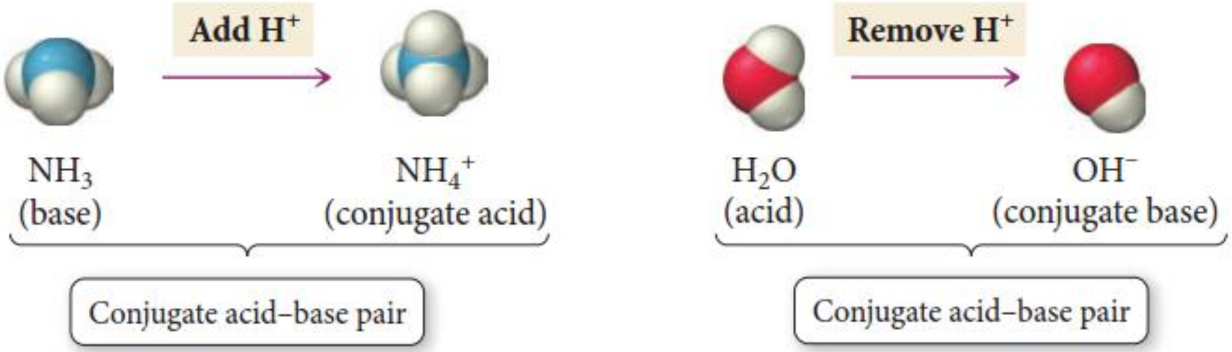
The Brønsted–Lowry Definition: Conjugate Acid – Base Pairs

A conjugate acid–base pair consists of two substances related to each other by the transfer of a proton (H^+):

Example:



$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



- ✓ A base accepts a proton and become a conjugate acid
- ✓ An acid donates a proton and become a conjugate base.

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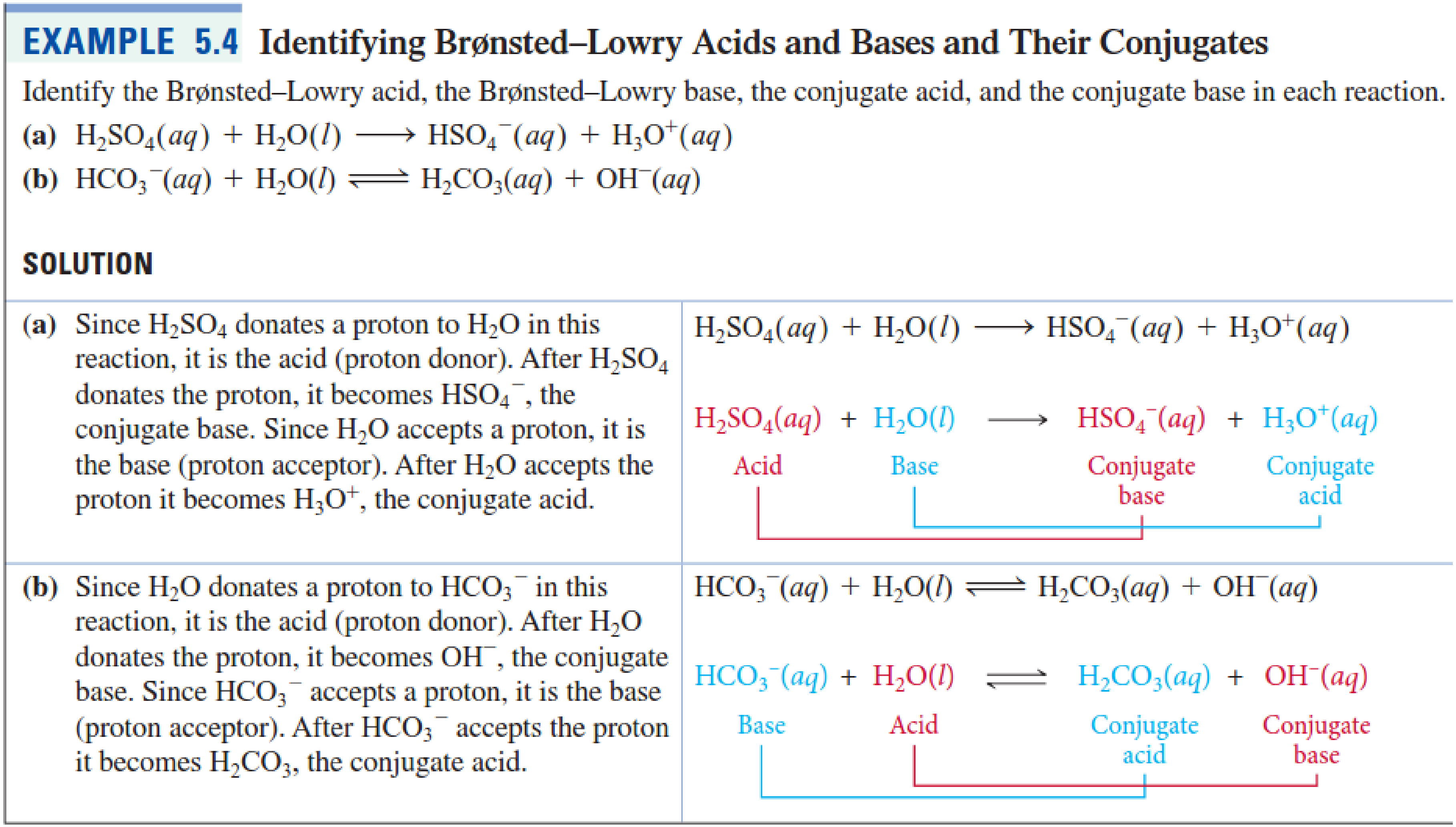
The Brønsted–Lowry Definition: Conjugate Acid – Base Pairs



EXAMPLE 5.4 Identifying Brønsted–Lowry Acids and Bases and Their Conjugates

Identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base in each reaction.

(a) $H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$

(b) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

SOLUTION

(a) Since H_2SO_4 donates a proton to H_2O in this reaction, it is the acid (proton donor). After H_2SO_4 donates the proton, it becomes HSO_4^-, the conjugate base. Since H_2O accepts a proton, it is the base (proton acceptor). After H_2O accepts the proton it becomes H_3O^+, the conjugate acid.	$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$ $\underset{\text{Acid}}{H_2SO_4(aq)} + \underset{\text{Base}}{H_2O(l)} \longrightarrow \underset{\text{Conjugate base}}{HSO_4^-(aq)} + \underset{\text{Conjugate acid}}{H_3O^+(aq)}$
(b) Since H_2O donates a proton to HCO_3^- in this reaction, it is the acid (proton donor). After H_2O donates the proton, it becomes OH^-, the conjugate base. Since HCO_3^- accepts a proton, it is the base (proton acceptor). After HCO_3^- accepts the proton it becomes H_2CO_3, the conjugate acid.	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ $\underset{\text{Base}}{HCO_3^-(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_2CO_3(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$

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5.9 Acid Strength

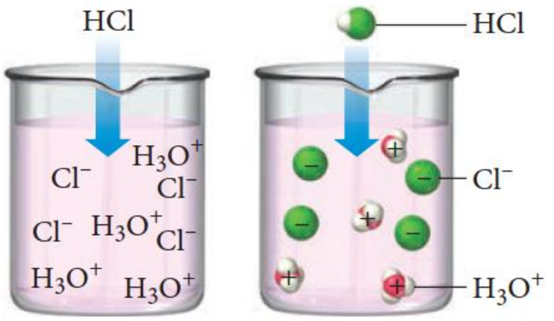
- **A Strong acid:** completely ionizes in the solution.
- **A Weak acid:** partially ionizes in the solution.
- ✓ Example on strong acids: Hydrochloric acid (HCl):

Single arrow indicates complete ionization.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

- **All** HCl molecules have essentially ionized to form $H_3O^+_{(aq)}$ and $Cl^-_{(aq)}$.

A Strong Acid



When HCl dissolves in water, it ionizes completely.

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5.9 Acid Strength

A 1.0 M HCl solution will have an H_3O^+ concentration of 1.0 M

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

1.0 M 1.0 M

we say that 1.0 M HCl solution has $[H_3O^+] = 1.0$ M.

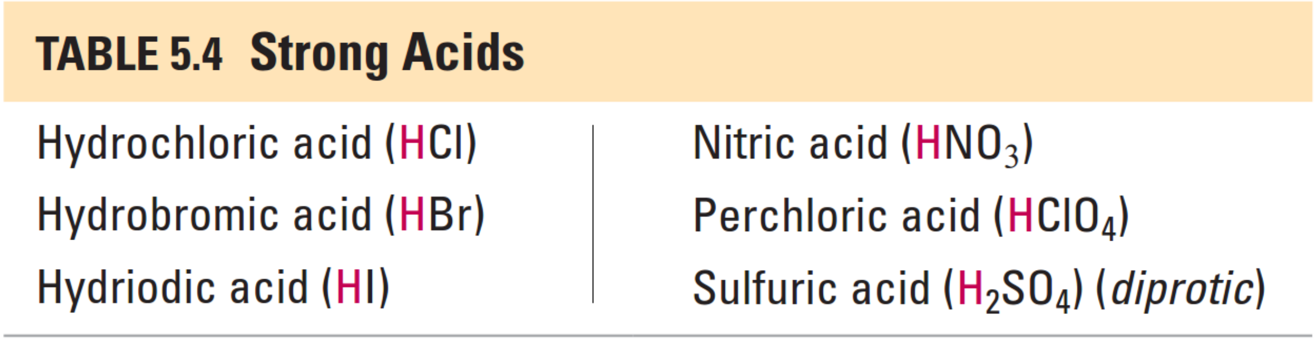

TABLE 5.4 Strong Acids

Hydrochloric acid (HCl)	Nitric acid (HNO_3)
Hydrobromic acid (HBr)	Perchloric acid ($HClO_4$)
Hydriodic acid (HI)	Sulfuric acid (H_2SO_4) (*diprotic*)

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5.9 Acid Strength

Weak acids: in contrast of HCl, **HF** is an example of a weak acid, one that does not completely ionize in solution:

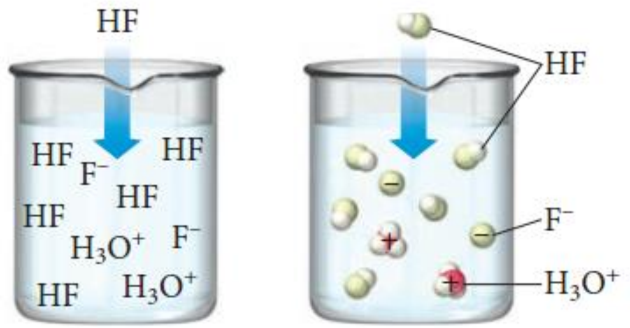
Equilibrium arrow indicates partial ionization.

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

An HF solution contains a lot of intact (un-ionized) HF molecules; it also contains some $H_3O^+{}_{(aq)}$ and $F^-{}_{(aq)}$. In other words, a 1.0 M HF solution has $[H_3O^+]$ that is less than 1.0 M because only some of the HF molecules ionize to form H_3O^+.

A Weak Acid

When HF dissolves in water, only a fraction of the molecules ionize.



5.9 Acid Strength

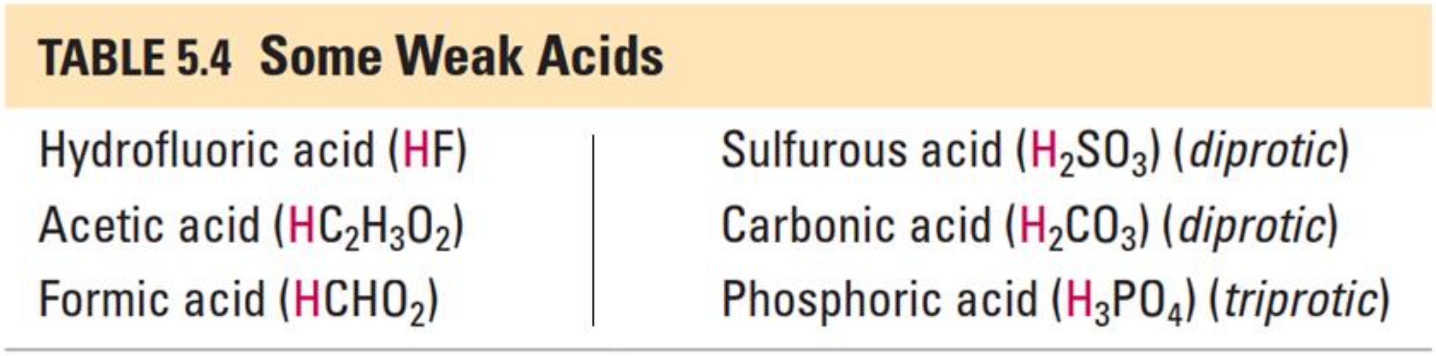


TABLE 5.4 Some Weak Acids

Hydrofluoric acid (HF)
Acetic acid ($HC_2H_3O_2$)
Formic acid ($HCHO_2$)
Sulfurous acid (H_2SO_3) (*diprotic*)
Carbonic acid (H_2CO_3) (*diprotic*)
Phosphoric acid (H_3PO_4) (*triprotic*)

Two of the weak acids above are **diprotic**, meaning they have two ionizable protons, and one is **triprotic** (three ionizable protons).

Notice that: although acetic acid (CH_3COOH) contains 4 hydrogen atoms in its formula, it’s a **monoprotic** acid, because only one of the four hydrogens is “**ionizable**”

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The pH Scale: A Way to Quantify Acidity and Basicity

The pH scale: is a compact way to specify the acidity of a solution. We define pH as:

$$\text{pH} = -\log\left[\text{H}^+\right] \quad \textit{or} \quad \text{pH} = -\log\left[\text{H}_3\text{O}^+\right]$$

For example, a solution with $[H_3O^+] = 1.0 \times 10^{-3}$ M

has a pH of $-\log 1.0 \times 10^{-3} = -(-3.0) = 3.0$ (Acidic)

- **In general:**

pH < 7.0	**Solution is acidic**	$[H_3O^+] > [OH^-]$
pH = 7.0	**Solution is neutral**	$[H_3O^+] = [OH^-]$
pH > 7.0	**Solution is basic**	$[H_3O^+] < [OH^-]$

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Self-Ionization of Water

Self-Ionization of Water:

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

- Since **$[H_3O^+] = [H^+]$**
- Product of $[H_3O^+]$ and $[OH^-]$ equals ***K_w***

$$\boxed{K_w = [H_3O^+] \times [OH^-] = 1.0 \times 10^{-14}}$$

Example:

In a sample of juice at 25 °C, $[H^+] = 4.6 \times 10^{-4}$ M. Find $[OH^-]$:

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}}{4.6\times10^{-4}} = 2.17\times10^{-11}\,\text{M}$$

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The pH Values of Some Common Substances

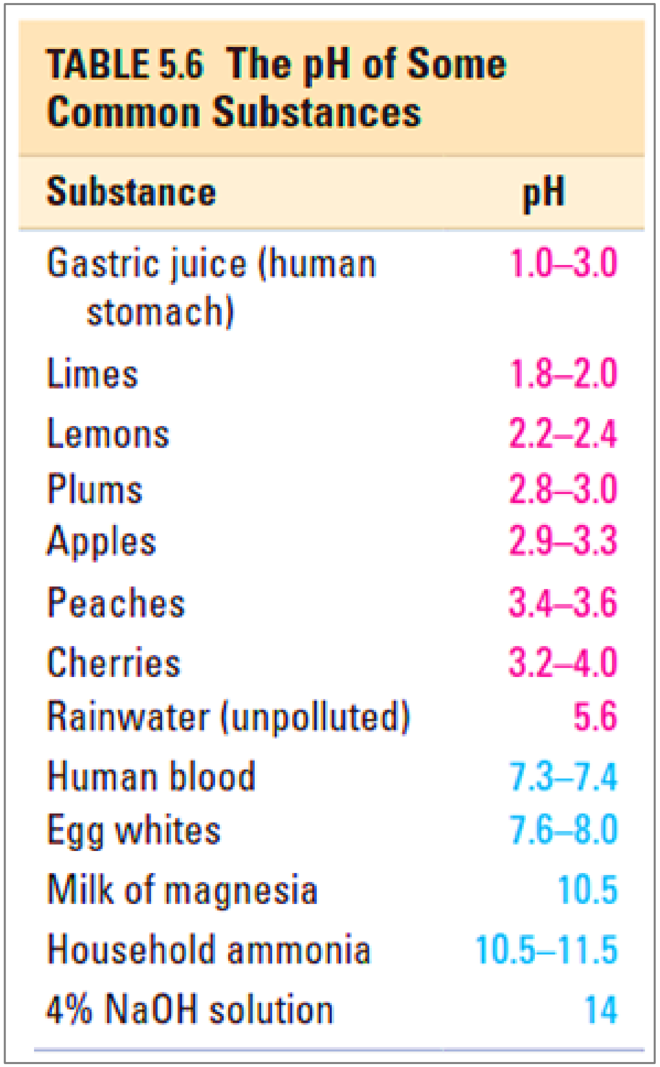

TABLE 5.6 The pH of Some Common Substances

Substance	pH
Gastric juice (human stomach)	1.0–3.0
Limes	1.8–2.0
Lemons	2.2–2.4
Plums	2.8–3.0
Apples	2.9–3.3
Peaches	3.4–3.6
Cherries	3.2–4.0
Rainwater (unpolluted)	5.6
Human blood	7.3–7.4
Egg whites	7.6–8.0
Milk of magnesia	10.5
Household ammonia	10.5–11.5
4% NaOH solution	14

(See only, not for memorizing!)

Notes

- **Since the pH scale is a logarithmic scale, a change of 1 pH unit corresponds to a 10 fold change in H_3O^+ concentration:**

  - For example, a lime with a pH of 2.0 is 10 times more acidic than a plum with a pH of 3.0

- **Highly concentrated acid solutions can have a negative pH:**

  - Example: if $[H_3O^+] = 2\ M \rightarrow pH = -\log(2) = -0.3$

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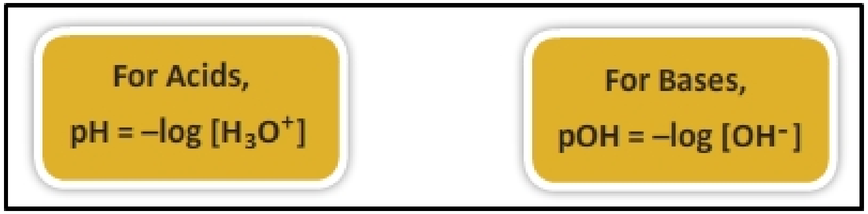
The pH Scale: pH and pOH scales

- As mentioned before, **The pH** values are calculated using the equation:

$$pH = -\log [H_3O^+]$$

- There is also **a pOH scale,** based upon the hydroxide ion concentration **$[OH^-]$** with the equation:

$$pOH = -\log [OH^-]$$



For Acids,
$pH = -\log [H_3O^+]$

For Bases,
$pOH = -\log [OH^-]$

- **pH and pOH** are related by:

$$\boxed{pH + pOH = 14}$$

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The pH Scale: Practice

Example 5.5: Calculating pH from $[H_3O^+]$ or $[OH^-]$:

Calculate the pH of a solution at 25°C and indicate whether the solution is acidic or basic, if:

(a) $[H_3O^+] = 1.8 \times 10^{-4}$ M (b) $[OH^-] = 1.3 \times 10^{-2}$ M

Solution:

(a) $[H_3O^+] = 1.8 \times 10^{-4}$ M:

$pH = -\log[H_3O] = -\log(1.8 \times 10^{-4}) = -(-3.74) = \mathbf{3.74}$

Since pH < 7, the solution is **acidic**.

(b) $[OH^-] = 1.3 \times 10^{-2}$ M:

$pOH = -\log[OH] = -\log(1.3 \times 10^{-2}) = 1.88$

Using pH + pOH = 14, we get pH = 14 – pOH

Then (14.0) – (1.88) = **12.12**

Since pH > 7, the solution is **basic**.

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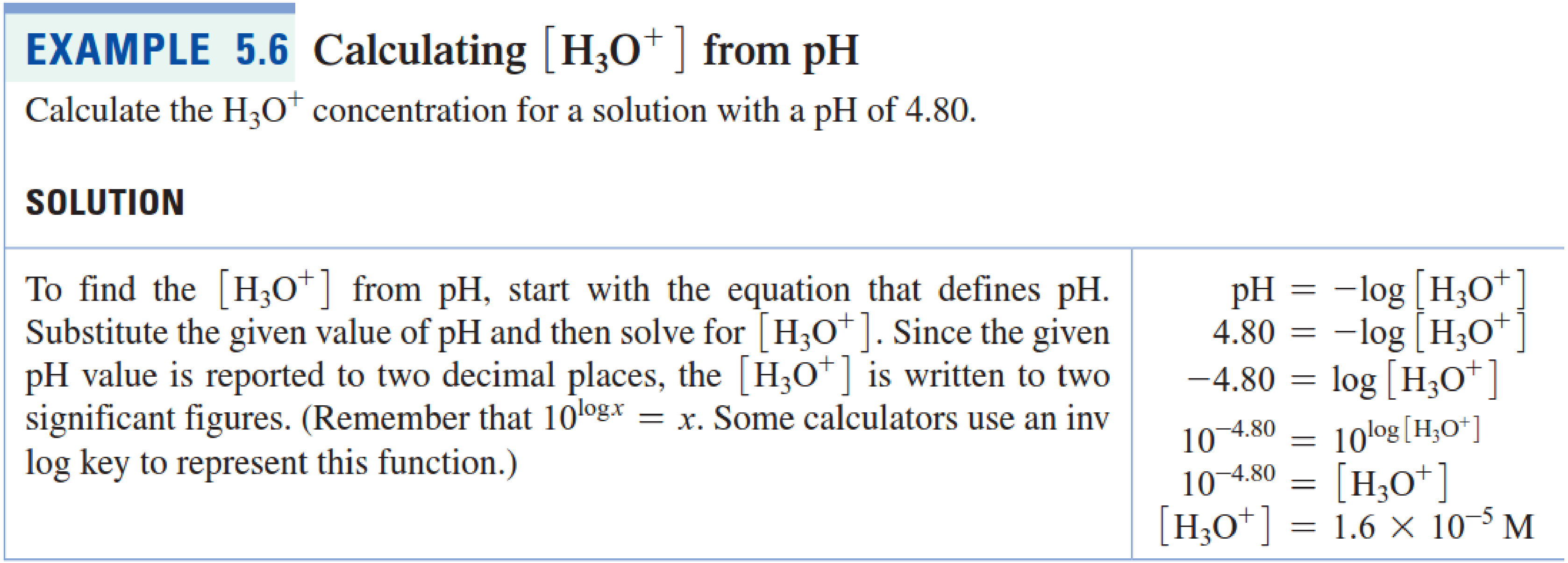
The pH Scale: Practice



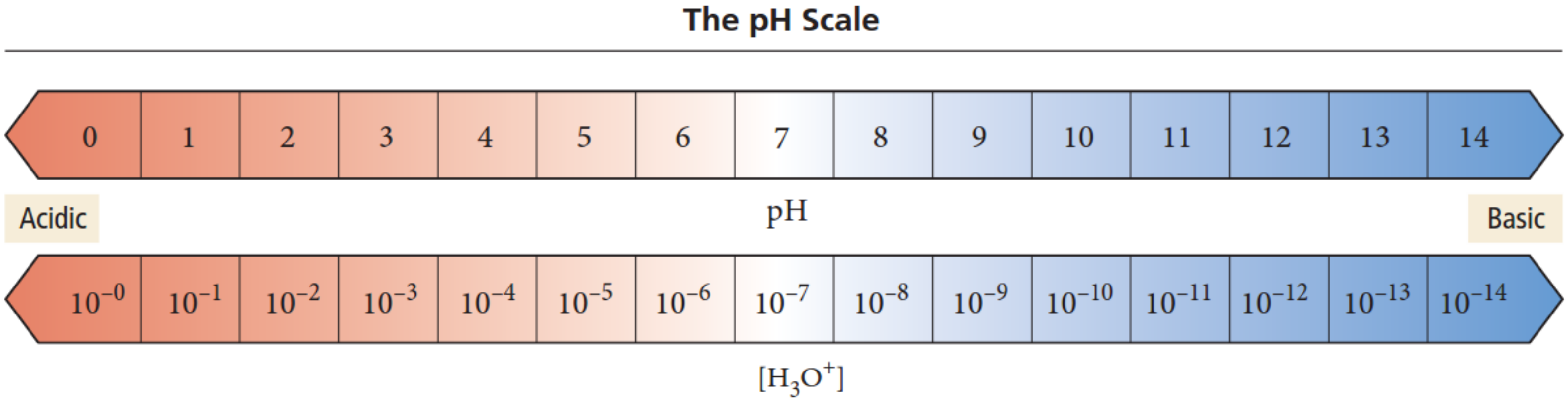
EXAMPLE 5.6 Calculating $[H_3O^+]$ from pH

Calculate the H_3O^+ concentration for a solution with a pH of 4.80.

SOLUTION

To find the $[H_3O^+]$ from pH, start with the equation that defines pH. Substitute the given value of pH and then solve for $[H_3O^+]$. Since the given pH value is reported to two decimal places, the $[H_3O^+]$ is written to two significant figures. (Remember that $10^{\log x} = x$. Some calculators use an inv log key to represent this function.)

$$
\begin{aligned}
\text{pH} &= -\log[H_3O^+] \\
4.80 &= -\log[H_3O^+] \\
-4.80 &= \log[H_3O^+] \\
10^{-4.80} &= 10^{\log[H_3O^+]} \\
10^{-4.80} &= [H_3O^+] \\
[H_3O^+] &= 1.6 \times 10^{-5}\ \text{M}
\end{aligned}
$$



▲ **Figure 5.11 The pH Scale** An increase of 1 on the pH scale corresponds to a decrease in $[H_3O^+]$ by a factor of 10.

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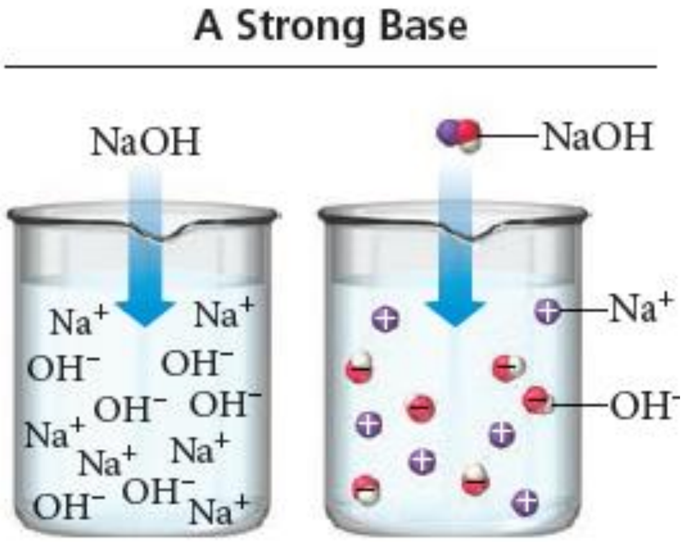
5.10 Base Solutions

- **A Strong Base** is one that completely dissociates in aqueous solutions releasing OH^-
- NaOH, is a strong base:

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

✓ The NaOH solution contains no intact NaOH. It all has dissociated to form $Na^+_{(aq)}$ and $OH^-_{(aq)}$



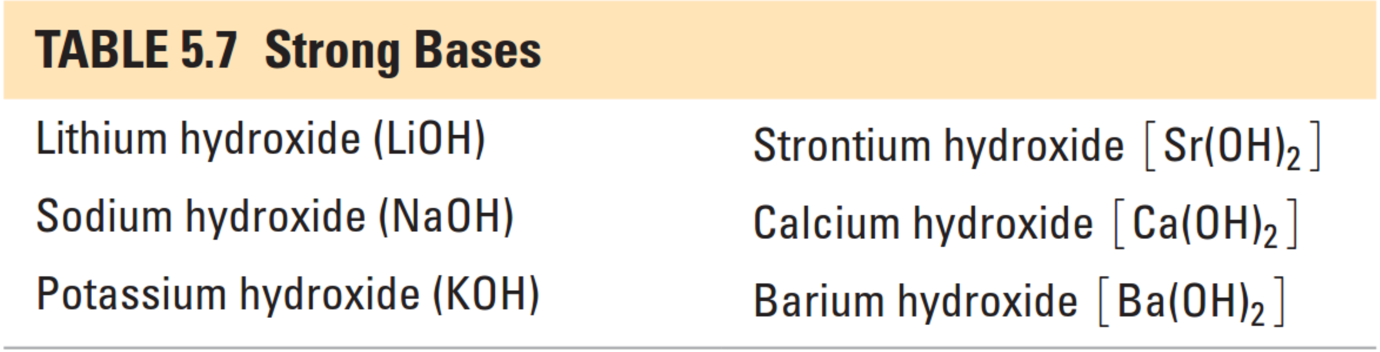


TABLE 5.7 Strong Bases

Lithium hydroxide (LiOH)	Strontium hydroxide [$Sr(OH)_2$]
Sodium hydroxide (NaOH)	Calcium hydroxide [$Ca(OH)_2$]
Potassium hydroxide (KOH)	Barium hydroxide [$Ba(OH)_2$]

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5.10 Base Solutions

Bases containing two OH^- ions dissociate in one step. For example, $Sr(OH)_2$ dissociates as follows:

$$Sr(OH)_2(aq) \longrightarrow Sr^{2+}(aq) + 2\,OH^-(aq)$$

Calculate the pH of 0.011 M $Ca(OH)_2$:

$$Ca(OH)_2(s) + H_2O \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

- $\mathbf{[OH^-]} = 2\times[Ca(OH)_2] = 2\times0.011\,M = 0.022$ M

  $\mathbf{pOH} = -\log(0.022) = 1.66$

  $\mathbf{pH} = 14 - \mathbf{pOH} = 14 - 1.66 = \mathbf{12.34}$

- **Calculate $[H^+]$ in the solution?**

  $\mathbf{[H^+]} = 10^{-pH} = 10^{-12.34} = 4.6 \times 10^{-13}$ M

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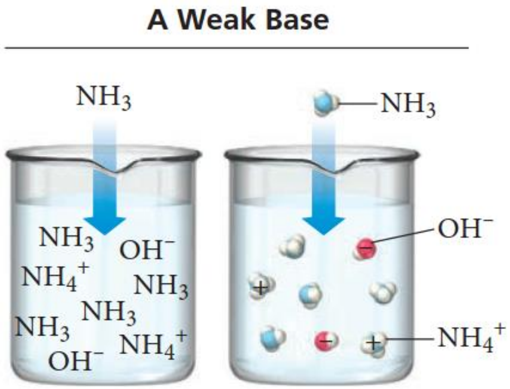
5.10 Base Solutions

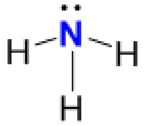
A Weak Base: a substance that produces OH^- by accepting a proton from water (i.e. ionizing water to form OH^-).

- **Ammonia**, for example, ionizes water as follows:

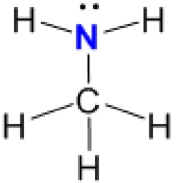
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



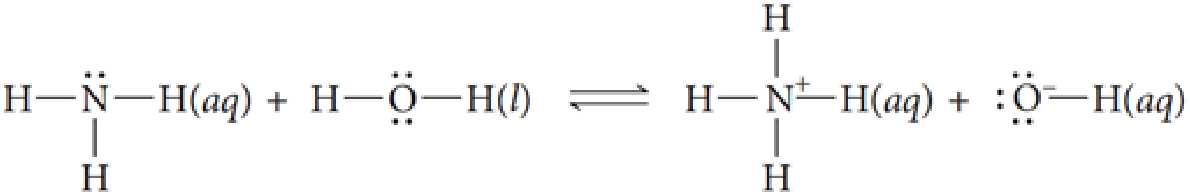
- ✓ The common element in most weak bases is a **"N atom"** with a lone pair of electrons.
- ✓ The lone pair accepts a proton and makes the substance a base.
- ✓ As shown in the reactions of ammonia (NH_3):



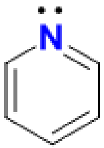
ammonia



methylamine



$$H-\underset{\substack{\mid\\ H}}{\ddot{N}}-H(aq) + H-\underset{\cdot\cdot}{\ddot{O}}-H(l) \rightleftharpoons H-\overset{\substack{H\\ \mid}}{\underset{\substack{\mid\\ H}}{N^+}}-H(aq) + :\underset{\cdot\cdot}{\ddot{O}}^- -H(aq)$$



pyridine

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Buffers (or Buffered Solutions)

- **Buffers (or buffered solutions)** are solutions that resist drastic changes in their pH when small amounts of strong acids or bases are added to them.
  - ✓ Buffers contain weak conjugate acid-base pairs.
  - ✓ Human blood, for example, is a complex buffered solution that maintain the blood pH at about 7.4.

- Buffers are often prepared by mixing a weak acid (or a weak base) with a salt of that acid or base:

- **Examples on buffers** **(See only, not for memorizing!):**
  - CH_3COOH + CH_3COONa (weak acid + its salt) = buffer
  - HF + NaF (weak acid + its salt) = buffer
  - NH_3 + NH_4Cl (weak base + its salt) = buffer

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5.12 Definitions of Acids and Bases: Lewis Acids and Bases

Lewis defined acids and bases as:

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

✓ The product of a Lewis acid-base reaction is sometimes called: **adduct**):

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{adduct}}{F_3B:NH_3}$$

✓ A Lewis acid has an empty orbital (or can rearrange electrons to create an empty orbital) that can accept an electron pair.

✓ **Examples on Lewis acids (to be memorized): BF_3, $AlCl_3$ and CO_2**

✓ **Examples on Lewis bases (to be memorized): NH_3, F^-, OH^- and H_2O**

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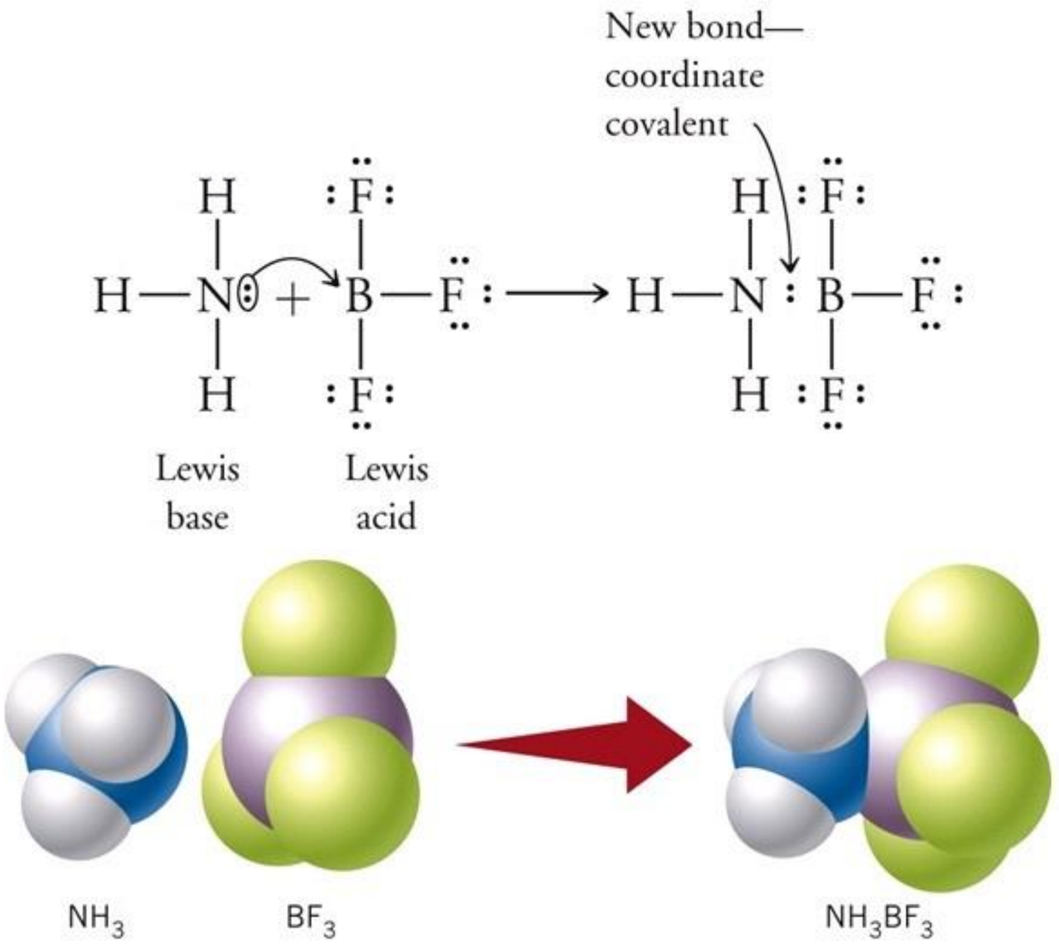
5.12 Lewis Acids and Bases: Example

Example: NH_3 (Lewis base) + BF_3 (Lewis acid)



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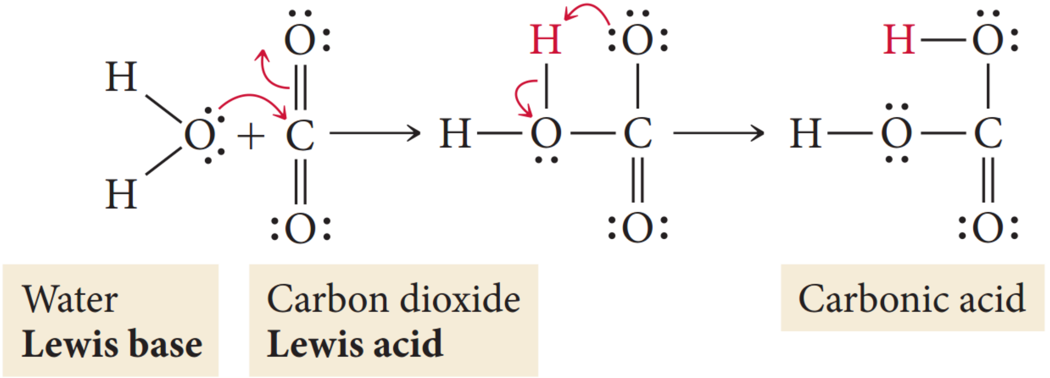
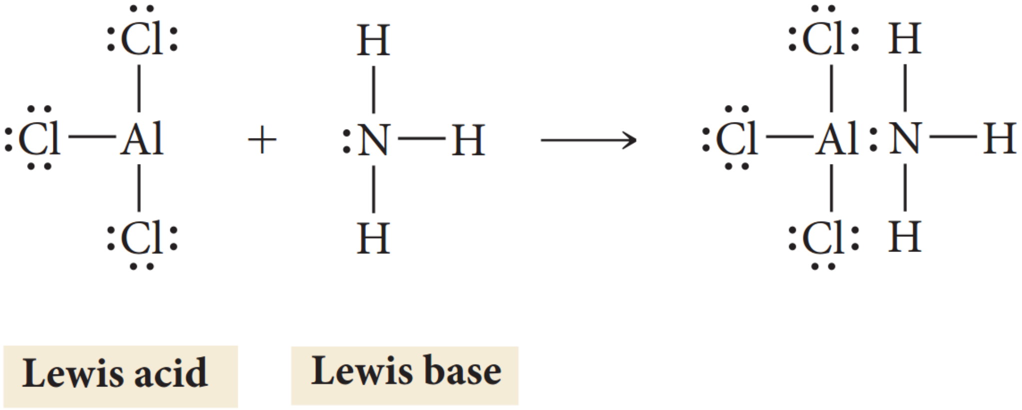
5.12 Lewis Acids and Bases: Examples

Example: H_2O (Lewis base) + CO_2 (Lewis acid)



Example: $AlCl_3$ (Lewis acid) + NH_3 (Lewis base)



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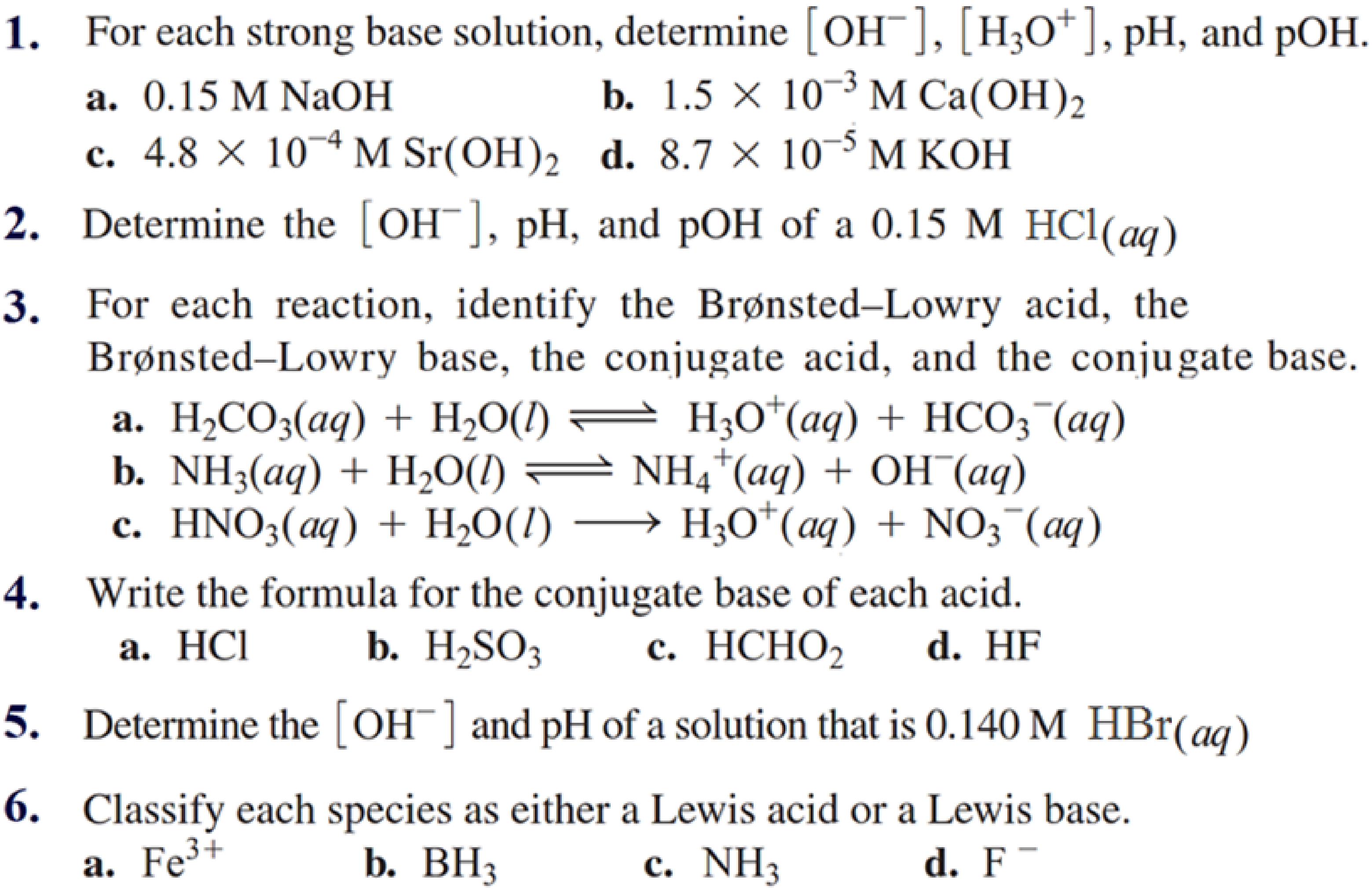
Assessment

Answer the following questions:



1. For each strong base solution, determine $[OH^-]$, $[H_3O^+]$, pH, and pOH.

a. 0.15 M NaOH **b.** 1.5×10^{-3} M $Ca(OH)_2$
c. 4.8×10^{-4} M $Sr(OH)_2$ **d.** 8.7×10^{-5} M KOH

2. Determine the $[OH^-]$, pH, and pOH of a 0.15 M $HCl(aq)$

3. For each reaction, identify the Brønsted–Lowry acid, the Brønsted–Lowry base, the conjugate acid, and the conjugate base.

a. $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$
b. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
c. $HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$

4. Write the formula for the conjugate base of each acid.

a. HCl **b.** H_2SO_3 **c.** $HCHO_2$ **d.** HF

5. Determine the $[OH^-]$ and pH of a solution that is 0.140 M $HBr(aq)$

6. Classify each species as either a Lewis acid or a Lewis base.

a. Fe^{3+} **b.** BH_3 **c.** NH_3 **d.** F^-

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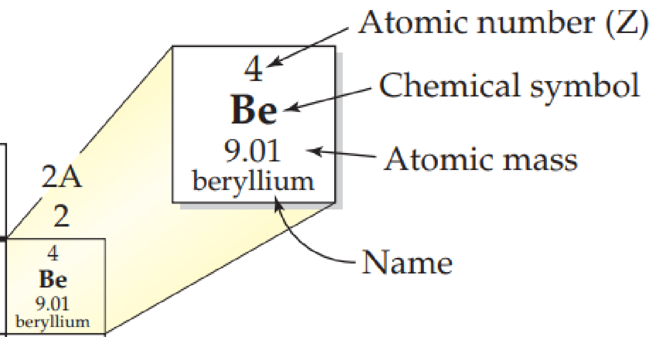
The periodic table of the elements



Periods	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.01 hydrogen																	2 **He** 4.00 helium
2	3 **Li** 6.94 lithium	4 **Be** 9.01 beryllium											5 **B** 10.81 boron	6 **C** 12.01 carbon	7 **N** 14.01 nitrogen	8 **O** 16.00 oxygen	9 **F** 19.00 fluorine	10 **Ne** 20.18 neon
3	11 **Na** 22.99 sodium	12 **Mg** 24.31 magnesium											13 **Al** 26.98 aluminum	14 **Si** 28.09 silicon	15 **P** 30.97 phosphorus	16 **S** 32.07 sulfur	17 **Cl** 35.45 chlorine	18 **Ar** 39.95 argon
4	19 **K** 39.10 potassium	20 **Ca** 40.08 calcium	21 **Sc** 44.96 scandium	22 **Ti** 47.88 titanium	23 **V** 50.94 vanadium	24 **Cr** 52.00 chromium	25 **Mn** 54.94 manganese	26 **Fe** 55.85 iron	27 **Co** 58.93 cobalt	28 **Ni** 58.69 nickel	29 **Cu** 63.55 copper	30 **Zn** 65.39 zinc	31 **Ga** 69.72 gallium	32 **Ge** 72.61 germanium	33 **As** 74.92 arsenic	34 **Se** 78.96 selenium	35 **Br** 79.90 bromine	36 **Kr** 83.80 krypton
5	37 **Rb** 85.47 rubidium	38 **Sr** 87.62 strontium	39 **Y** 88.91 yttrium	40 **Zr** 91.22 zirconium	41 **Nb** 92.91 niobium	42 **Mo** 95.94 molybdenum	43 **Tc** (99) technetium	44 **Ru** 101.07 ruthenium	45 **Rh** 102.91 rhodium	46 **Pd** 106.42 palladium	47 **Ag** 107.87 silver	48 **Cd** 112.41 cadmium	49 **In** 114.82 indium	50 **Sn** 118.71 tin	51 **Sb** 121.75 antimony	52 **Te** 127.60 tellurium	53 **I** 126.90 iodine	54 **Xe** 131.29 xenon
6	55 **Cs** 132.91 cesium	56 **Ba** 137.33 barium	57 **La** 138.91 lanthanum	72 **Hf** 178.49 hafnium	73 **Ta** 180.95 tantalum	74 **W** 183.85 tungsten	75 **Re** 186.21 rhenium	76 **Os** 190.2 osmium	77 **Ir** 192.22 iridium	78 **Pt** 195.08 platinum	79 **Au** 196.97 gold	80 **Hg** 200.59 mercury	81 **Tl** 204.38 thallium	82 **Pb** 207.2 lead	83 **Bi** 208.98 bismuth	84 **Po** (209) polonium	85 **At** (210) astatine	86 **Rn** (222) radon
7	87 **Fr** (223) francium	88 **Ra** (226) radium	89 **Ac** (227) actinium	104 **Rf** (261) rutherfordium	105 **Db** (262) dubnium	106 **Sg** (263) seaborgium	107 **Bh** (262) bohrium	108 **Hs** (265) hassium	109 **Mt** (266) meitnerium	110 **Ds** (281) darmstadtium	111 **Rg** (280) roentgenium	112 **Cn** (285)	113 — (284)	114 — (289)	115 — (288)	116 — (292)	117 ** (292)	118 — (294)

Lanthanides	58 **Ce** 140.12 cerium	59 **Pr** 140.91 praseodymium	60 **Nd** 144.24 neodymium	61 **Pm** (147) promethium	62 **Sm** 150.36 samarium	63 **Eu** 151.97 europium	64 **Gd** 157.25 gadolinium	65 **Tb** 158.93 terbium	66 **Dy** 162.50 dysprosium	67 **Ho** 164.93 holmium	68 **Er** 167.26 erbium	69 **Tm** 168.93 thulium	70 **Yb** 173.04 ytterbium	71 **Lu** 174.97 lutetium
Actinides	90 **Th** (232) thorium	91 **Pa** (231) protactinium	92 **U** (238) uranium	93 **Np** (237) neptunium	94 **Pu** (244) plutonium	95 **Am** (243) americium	96 **Cm** (247) curium	97 **Bk** (247) berkelium	98 **Cf** (251) californium	99 **Es** (252) einsteinium	100 **Fm** (257) fermium	101 **Md** (258) mendelevium	102 **No** (259) nobelium	103 **Lr** (260) lawrencium

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