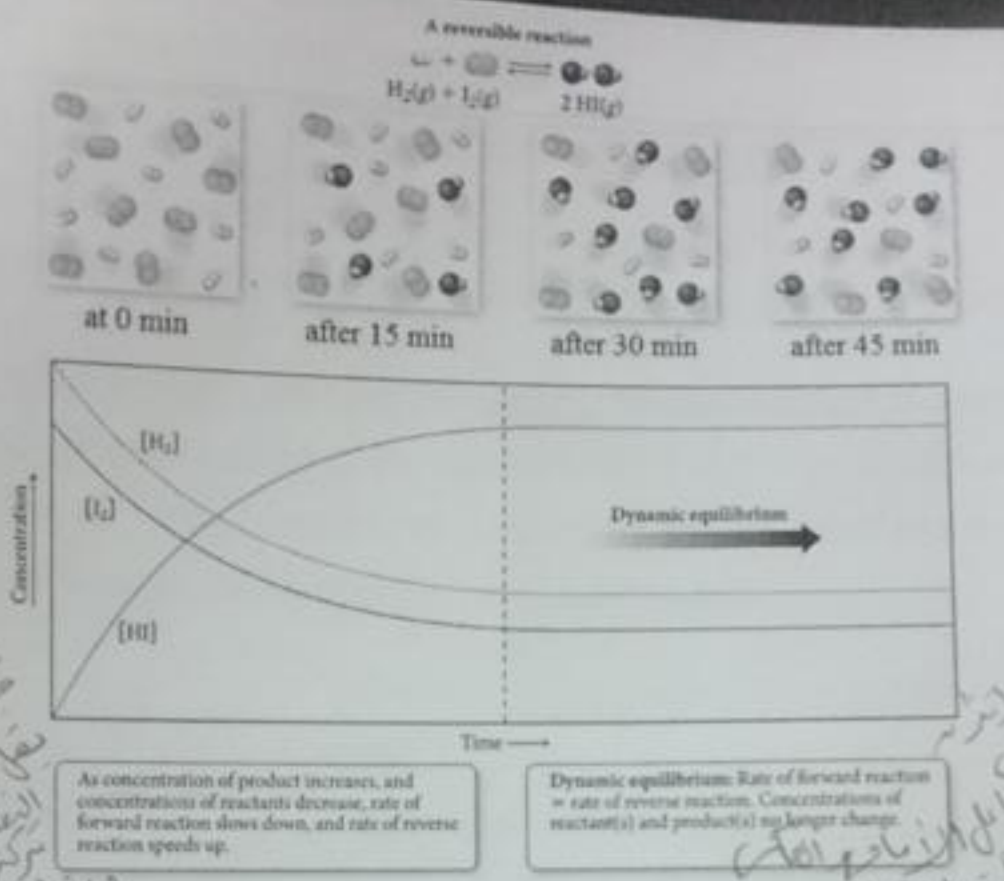
The Concept of Dynamic Equilibrium



Dynamic Equilibrium

Chemical Equilibrium ≠ Equal Concentrations!

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

✓ $R_f = R_r$: <u>DOES NOT</u> mean that the concentrations of reactants and products are equal in value.

- Reactions may reach equilibrium only **after most of the reactant** molecules have been **consumed**. This indicates that the position of **equilibrium favors** the formation of **products**.
- Reactions may reach equilibrium when only a **small percentage** of the **reactant** molecules is **consumed.** This indicates that the position of **equilibrium favors** the formation of **reactants**.

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

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

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

Answer:

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

Expressing Equilibrium Constants (K_{eq}): 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: $K_{eq} =$

Heterogeneous Equilibria: Reactions Involving Solids and 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 <u>solids</u>, you <u>omit</u> them from the equilibrium expression:

$$K_c = [CO_2]$$

5.5 Calculating the Equilibrium Constant 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 equilibrium concentrations are:

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

تعويض مباشر لتعيين ثابت الاتزان

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

Answer:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.78^2}{(0.11)\times(0.11)} = 5.0 \times 10^1 \text{ (products favored, forward)}$$

Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

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

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

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

Solution:

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

$K_c = \{[0.66]^2\,[0.33]\}\,/\,[1.34]^2$

$K_c = (0.144)/(1.80)$

$K_c = 0.0801$ (reactant favored, reverse)

Expressing The Equilibrium Constant: Assignments

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

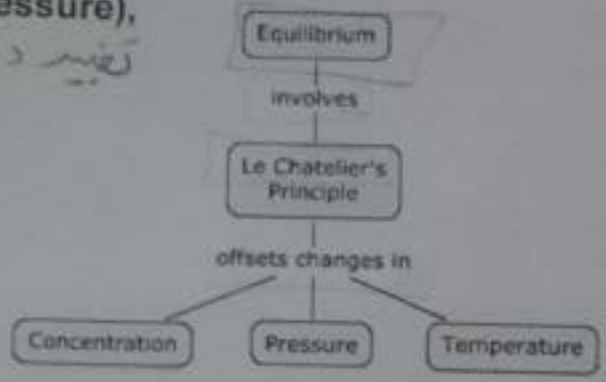
1) $C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$
2) $N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$.
3) $2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$
4) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
5) $2\,KClO_3(s) \rightleftharpoons 2\,KCl(s) + 3\,O_2(g)$
6) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
7) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
8) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

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

أنواع المؤثرات على الاتزان

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

- ✓ Changing the **concentration** of a reactant or product,
  تغير تركيزات المتفاعلات والنواتج
- ✓ Changing the **volume (or pressure)**,
  تغير الحجم او الضغط
- ✓ Changing the **temperature**.
  تغير درجات الحرارة



The Effect of a 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)

عند زيادة النواتج التفاعل يسير فى الاتجاه العكسى لتقليل زيادة النواتج مما يؤدى لتنقص تركيز النواتج

Add NO_2.

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

Reaction shifts left.

The Effect of a Concentration Change on Equilibrium

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 add 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?

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

The Effect of a Volume (or Pressure) Change on Equilibrium

Changing the volume of a gas results in a change in pressure, a decrease in volume causes an increase in pressure (pressure and volume are inversely related), so if the volume of a reaction mixture at chemical equilibrium is changed; the pressure changes and the system shifts in direction to minimize the change.

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

oduction

- If a chemical reaction is at equilibrium and experiences a change in **pressure, temperature,** or **concentration** of products or reactants, the equilibrium shifts in the opposite direction to offset the change.

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

قاعدة لوشاتلية عند حدوث تأثير على تفاعل في حالة اتزان

Le Châtelier's Principle: When a chemical system at equilibrium is disturbed; the system shifts in a direction that minimizes the disturbance. التفاعل يسير في الاتجاه الذي يقلل التأثير

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

...me Common Acids

Table 5.1: Some Common Acids	
Name	Occurrence/Uses
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)	Fertilizer manufacturing, 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**

Some Common Bases

Table 5.2 Some Common Bases	
Name	Occurrence/Uses
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

The Effect of a Temperature Change on Equilibrium

At constant pressure, raising the temperature of an **exothermic reaction** (think of this as adding heat) is similar to adding more product, causing the **reaction to shift left**.

For example, the reaction of nitrogen with hydrogen to form ammonia is **exothermic**.

زيادتها تجعل التفاعل يسير باتجاه العكسي

Add heat

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

Reaction shifts left.
Smaller K

The Effect of a Temperature Change on Equilibrium

Conversely, lowering the temperature of an **exothermic reaction** (think of this as removing heat) is similar to remove more product, causing the **reaction to shift right**.

تقليل الحرارة تجعل التفاعل يسير باتجاه الأمام

Remove heat

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

Reaction shifts right.
Larger K

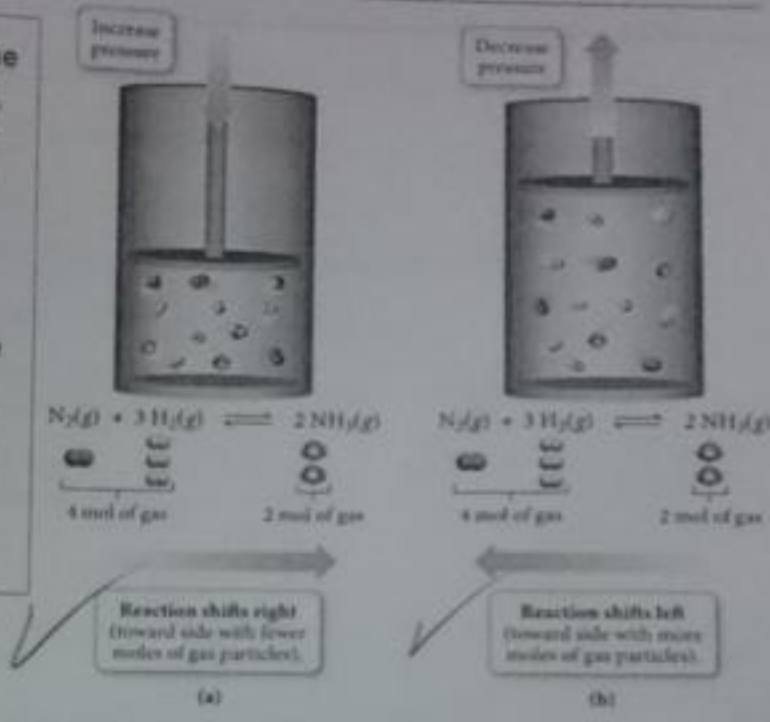
In contrast, for an *endothermic* reaction raising the temperature—think of this as adding heat—is similar to adding more reactant, causing the reaction to shift right. And lowering temperature (removing heat) causes reaction to shift left.

Effect of a Volume (or Pressure) Change on Equilibrium

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

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

Le Châtelier's Principle: Changing Pressure



The Effect of a Temperature Change on Equilibrium

تأثير تغير درجة الحرارة نتعامل مع الحرارة على أنها واحد من المتفاعلات أو النواتج حسب التفاعل

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.

التفاعلات الطاردة للحرارة

An **exothermic reaction** emits heat ($\Delta H = -$). We can think of heat as a product in an exothermic reaction: تعتبر الحرارة واحد من النواتج

$$A + B \rightleftharpoons C + D + heat$$

التفاعلات الماصة للحرارة

An **endothermic reaction** absorbs heat ($\Delta H = +$). We can think of heat as a reactant in an endothermic reaction: تعتبر الحرارة واحد من المتفاعلات

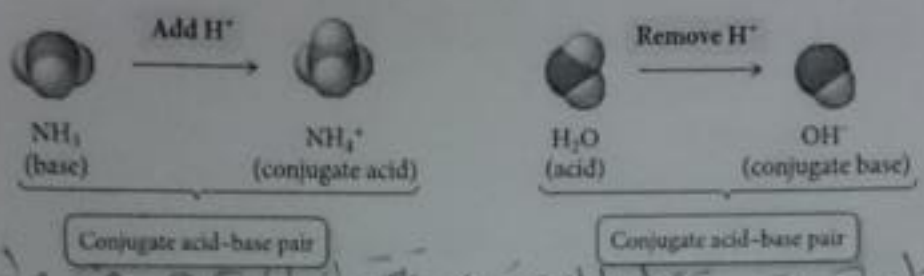
$$A + B + heat \rightleftharpoons C + D$$

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

Base — Acid — Conjugate acid — Conjugate base



القاعدة تستقبل البروتون وتتحول الى حمض مرافق

✓ A base accepts a proton and become a conjugate acid

✓ An acid donates a proton and become a conjugate base.

الحمض يعطي البروتون ويتحول الى قاعدة مرافقة

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.	$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$ $H_2SO_4(aq)$ (Acid) + $H_2O(l)$ (Base) $\longrightarrow$ $HSO_4^-(aq)$ (Conjugate base) + $H_3O^+(aq)$ (Conjugate acid)
(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.	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ $HCO_3^-(aq)$ (Base) + $H_2O(l)$ (Acid) $\rightleftharpoons$ $H_2CO_3(aq)$ (Conjugate acid) + $OH^-(aq)$ (Conjugate base)

The Brønsted-Lowry Definition

Brønsted-Lowry definition of acids and bases: focuses on the *transfer of H+ ion* in an acid-base reaction. Since an H^+ is a proton (hydrogen atom without its electron).

According to Brønsted-Lowry:

- **Acid**: is a proton (H^+) donor الحمض معطي البروتون
- **Base**: is a proton (H^+) acceptor القاعدة مستقبلة البروتون

The Brønsted-Lowry Definition

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

- Example:

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

✓ **HCl = acid,** Donates H^+ (proton donor) حمض لأنه أعطى البروتون

✓ **H_2O = base,** Accepts H^+ (proton accepter) قاعدة لأنها استقبلت البروتون

- Example:

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

✓ **NH_3 = base,** Accepts H^+ (proton accepter) قاعدة

✓ **H_2O = acid,** Donates H^+ (proton donor) حمض

الماء يسمى متردد لأنه تفاعل كحمض أو كقاعدة

Note: Water in the two examples above, acted as an acid and as a base.

- Substance that can act as acids or bases are termed "**amphoteric**".

he 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,	For Bases,
$pH = -\log [H_3O^+]$	$pOH = -\log [OH^-]$

- pH and pOH are related by:

$$pH + pOH = 14$$

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.

Solution:

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

Since pH < 7, the solution is acidic.

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

Solution:

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

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

Then (14.0) – (1.88) = 12.12

Since pH > 7, the solution is basic.

12 Lewis Acids and Bases

G.N. Lewis, the American chemist defined acids and bases as:

- Lewis acid: electron pair acceptor الحمض مستقبل لزوج الالكترونات
- Lewis base: electron pair donor القاعدة مانح لزوج الالكترونات

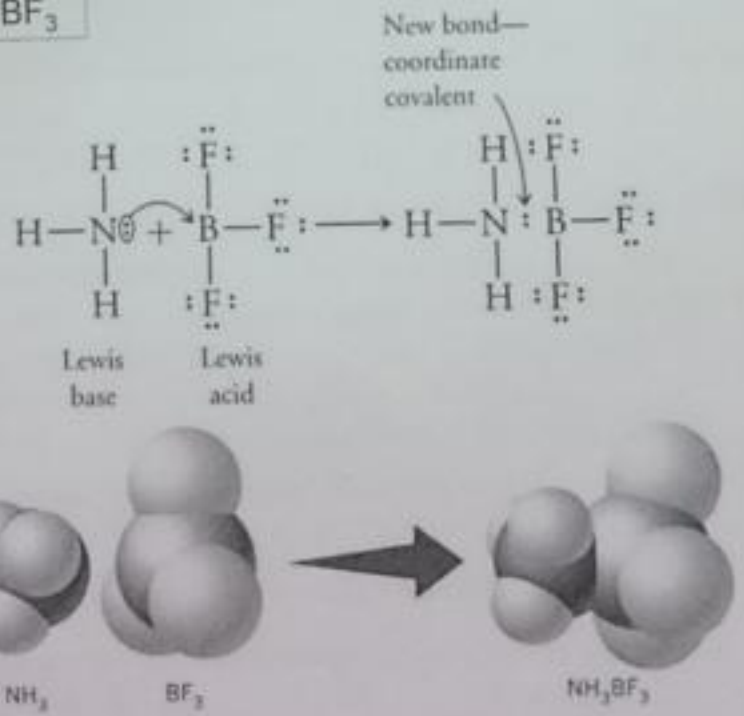
✓ Boron trifluoride has an empty orbital that can accept the electron pair from ammonia and form the product (the product of a Lewis acid-base reaction is sometimes called an *adduct*).

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

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

5.12 Lewis Acids and Bases: An Example

Example: $NH_3 + BF_3$



Acid Strength

أحماض ضعيفة

TABLE 5.4 Some Weak Acids

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

الرقم الهيدروجيني (pH)

The pH Scale: A way to quantify acidity and basicity

هو طريقة للتعبير عن درجة حموضة المحلول

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

$$pH = -\log[H^+] \quad \text{or} \quad pH = -\log[H_3O^+]$$

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, at 25 °C:

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

Lewis acid	Lewis bases
⊛ H^+, Cu^{2+}, Fe^{2+}	⊛ $\ddot{N}H_3$, amines
⊛ BF_3, BCl_3, $AlCl_3$	⊛ $H_2\ddot{O}:$, ethers
⊛ CO_2	⊛ $C_2O_4^{2-}$, OH^-