

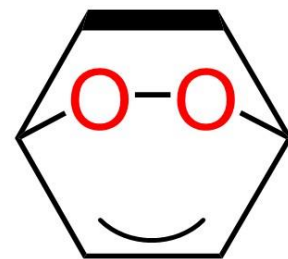
CHEM103

General Chemistry

Chapter 16: Acid–Base Equilibria



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Homeworks 14 & 15

Homework 14

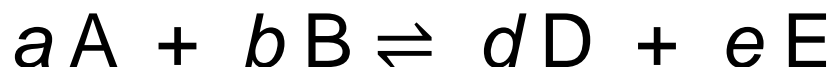
Due date: 5th Dec. (Mon)

Homework 15

Due date: 7th Dec. (Wed)

Review on Chapter 15

Equilibrium constant (K),
Homogeneous equilibria, Heterogeneous equilibria



$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

Reaction quotient

Le Châtelier's Principle

Outline of Chapter 16

Arrhenius/Brønsted/Lewis acids & bases

Conjugate acids and bases

Amphiprotic, autoionization, ion product constant (K_w)

Acid and base strength (pH), acid dissociation constant (K_a or pK_a), base dissociation constant (K_b or pK_b), percent ionization

Polyprotic acids, binary acids, oxyacids, zwitterion



Acids



Orange



Lemon
(Citric acid)



Tomato



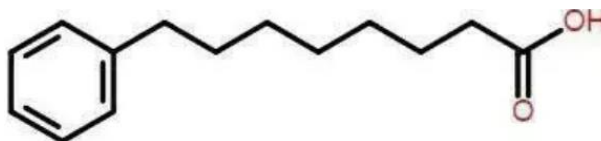
**Grapes &
vinegars**
**(Tartaric &
acetic acids)**



Rhubarb
(Oxalic acid)



(Carbonic acid)



苯宝宝好辛酸

Bases



Soap ($\text{C}_{17}\text{H}_{35}\text{COONa}$)



(NaHCO_3)



Toothpaste (NaF)

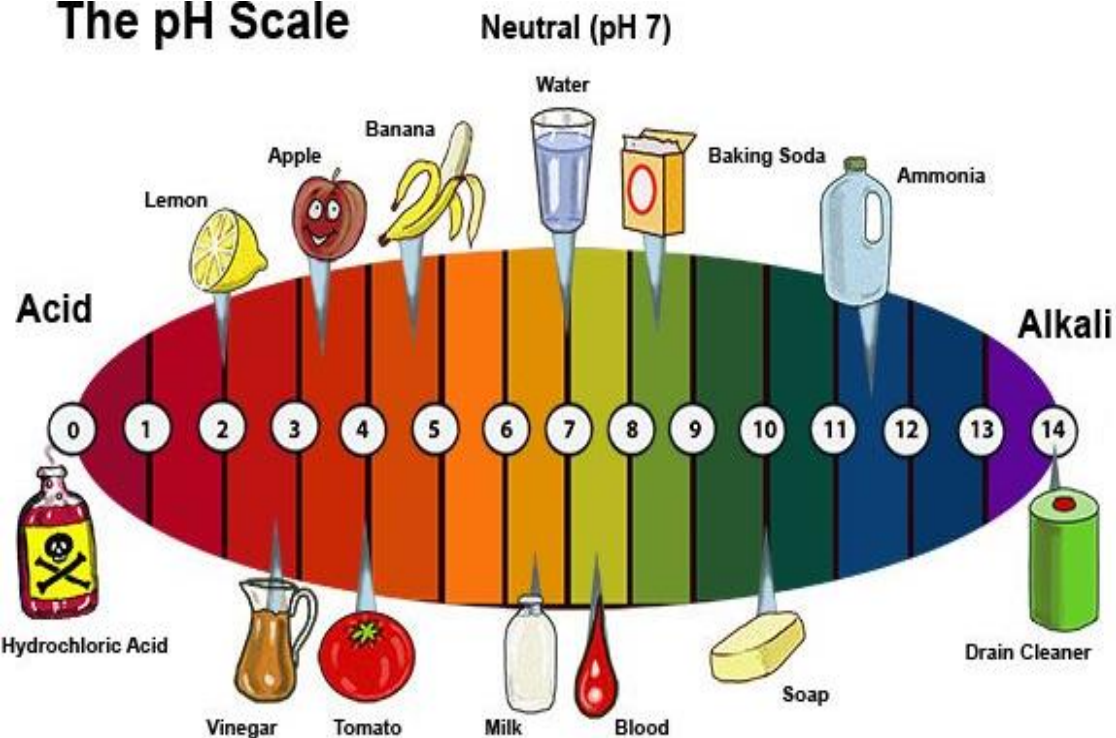


LAS (对十二烷基苯磺酸钠)



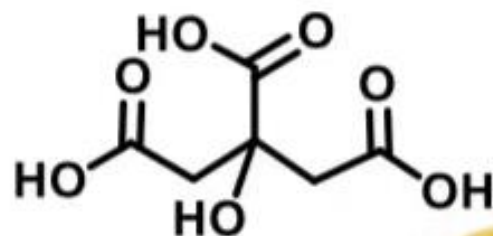
Acids
and
Bases

The pH Scale

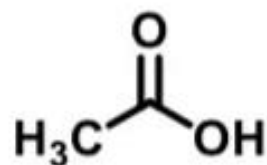


pH	H ⁺ CONCENTRATION (in moles per litre)	OH ⁻ CONCENTRATION (in moles per litre)	EVERYDAY EXAMPLE
14	1×10^{-14}	1	Drain Cleaner
13	1×10^{-13}	0.1	Bleach
12	1×10^{-12}	0.01	Ammonia
11	1×10^{-11}	0.001	Soap
10	1×10^{-10}	1×10^{-4}	Antacid Tablets
9	1×10^{-9}	1×10^{-5}	Baking Soda
8	1×10^{-8}	1×10^{-6}	Seawater
7	1×10^{-7}	1×10^{-7}	Pure Water
6	1×10^{-6}	1×10^{-8}	Urine (average)
5	1×10^{-5}	1×10^{-9}	Black Coffee
4	1×10^{-4}	1×10^{-10}	Tomato Juice
3	0.001	1×10^{-11}	Soda
2	0.01	1×10^{-12}	Lemon Juice
1	0.1	1×10^{-13}	Stomach Acid
0	1	1×10^{-14}	Battery Acid

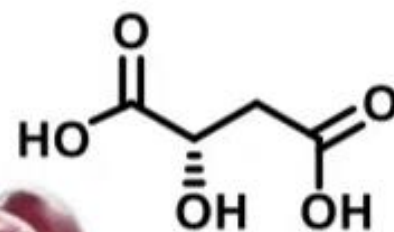
Bases



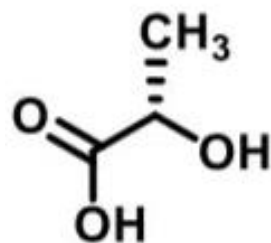
柠檬酸



醋酸



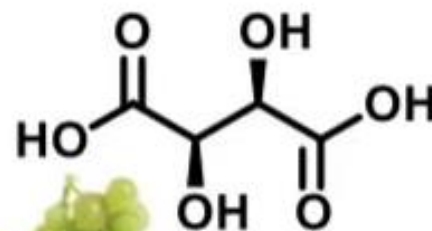
苹果酸



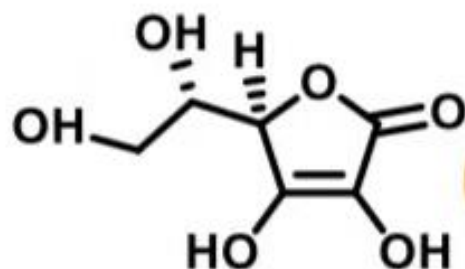
乳酸



酸
S O U R N E S S

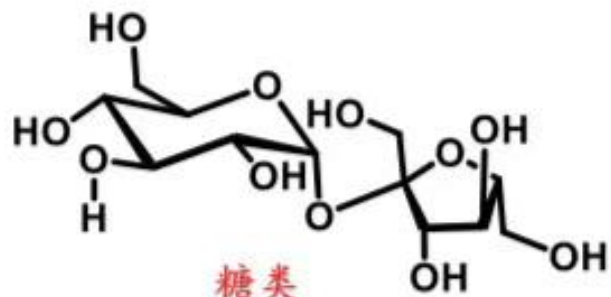


酒石酸

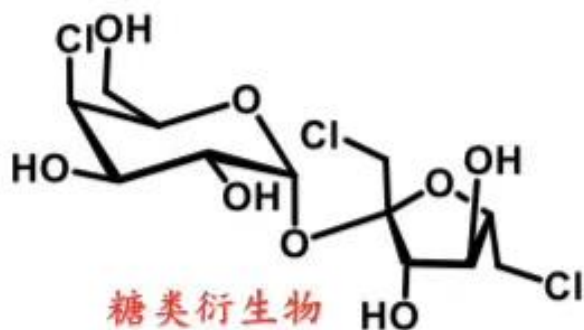


异抗坏血酸

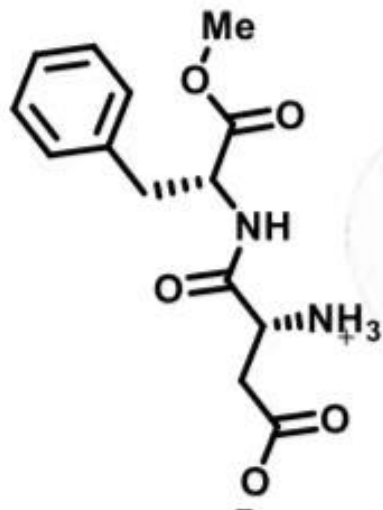




糖类



糖类衍生物

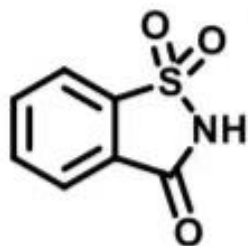


二肽类

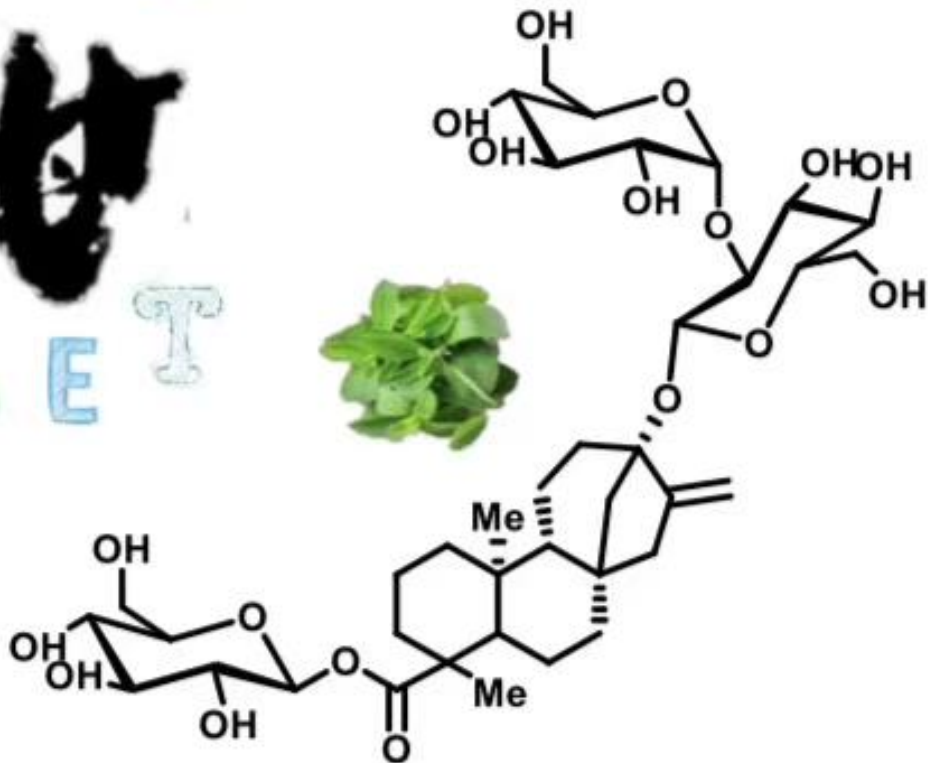


甜

SWEET



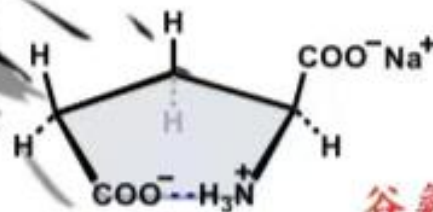
磺酰胺类



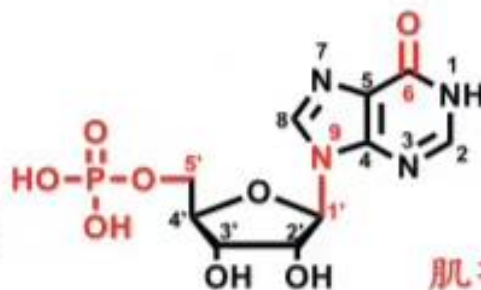
糖苷类

鲜

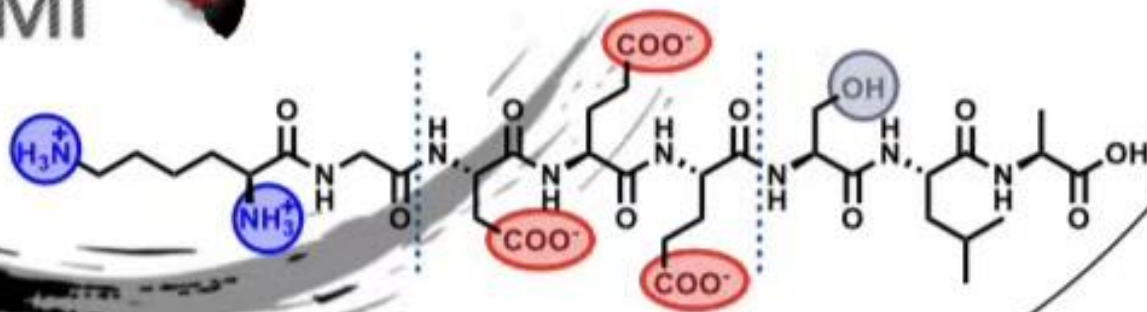
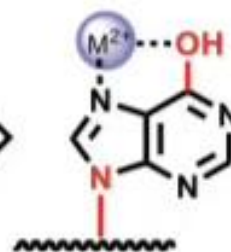
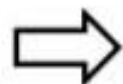
UMAMI



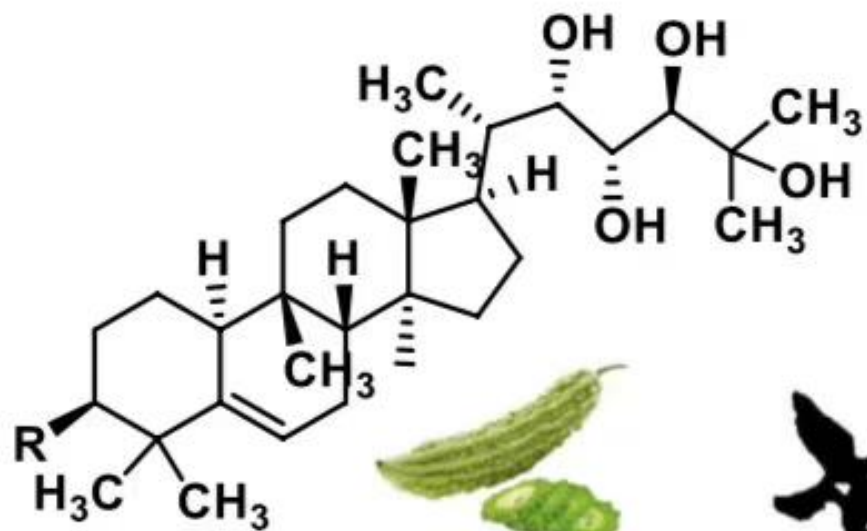
谷氨酸钠



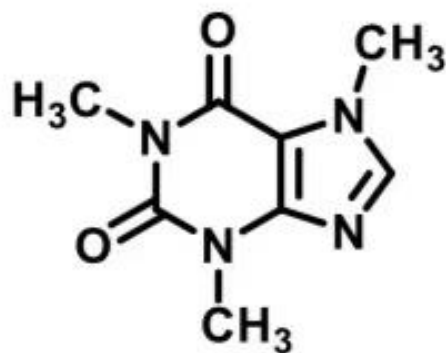
肌苷酸



牛肉八肽



萜类

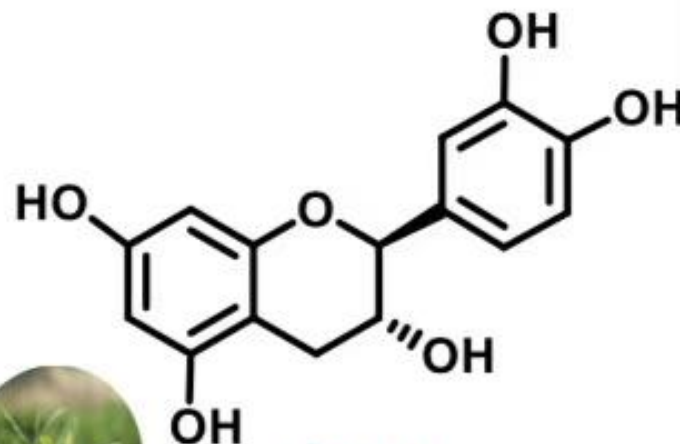


生物碱类

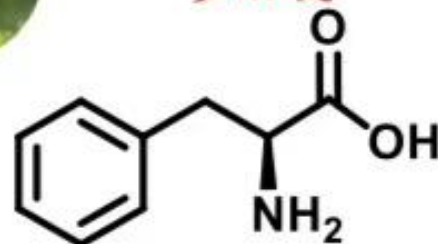
苦

BITTER

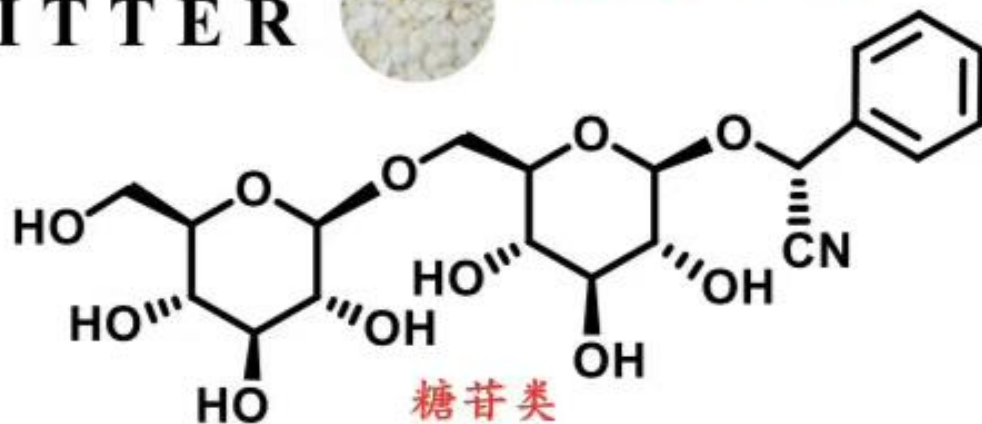
MgCl₂
无机盐类



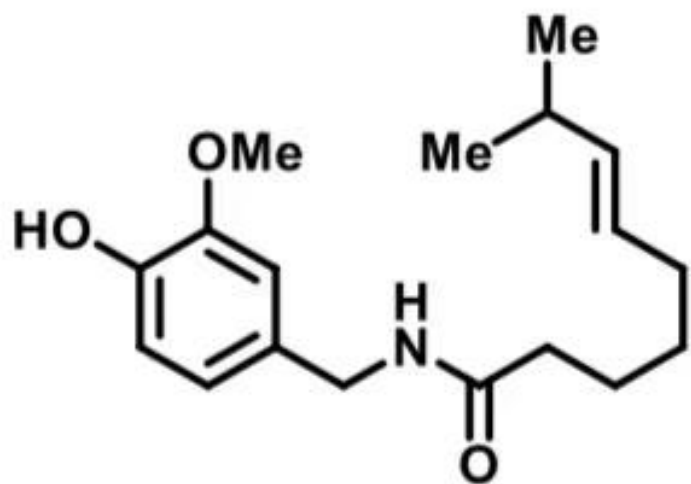
多酚类



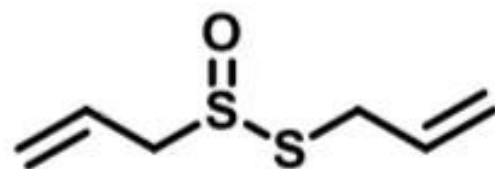
氨基酸及多肽类



糖苷类



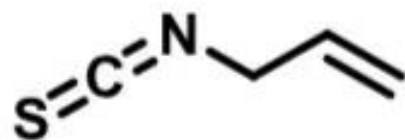
辣椒素



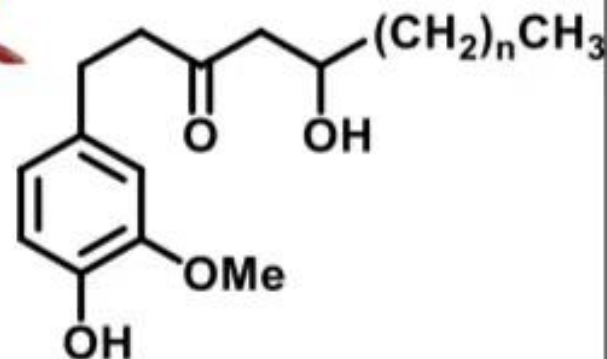
大蒜素 (辛辣)



H O T



烯丙基异硫氰酸酯



姜醇类

Some Definitions

From Chapter 4, we have learned two acid-base theories.

Arrhenius theory:

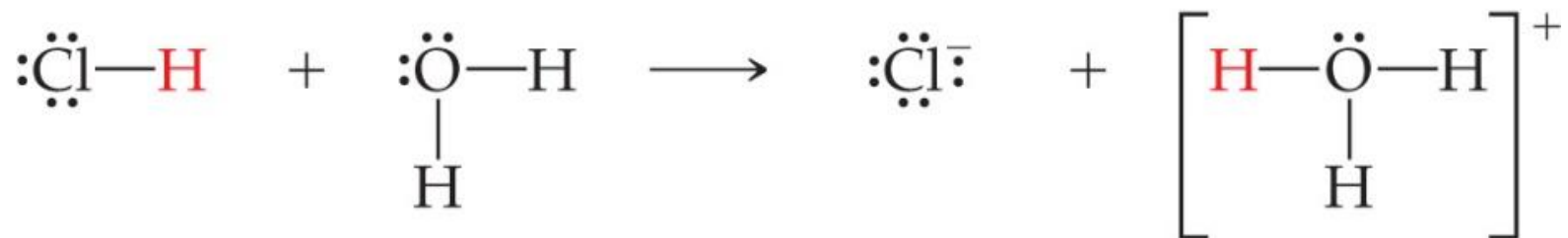
- An **acid** is a substance that, when **dissolved** in water, **increases the concentration of proton (H^+)**.
- A **base** is a substance that, when **dissolved** in water, **increases the concentration of hydroxide ions (OH^-)**.

Brønsted–Lowry theory:

- An **acid**: a **proton donor**.
- A **base**: a **proton acceptor**.

Brønsted–Lowry Acid and Base

- A Brønsted–Lowry **acid** must have at least one **removable (acidic) proton (H^+)** to **donate**.
- A Brønsted–Lowry **base** must have at least one **nonbonding pair of electrons** to **accept** a proton.

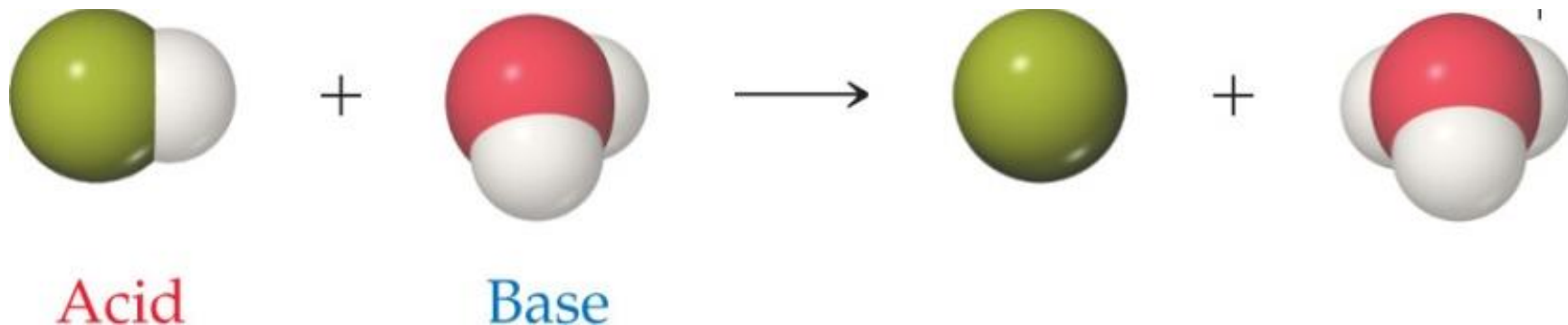


Acid

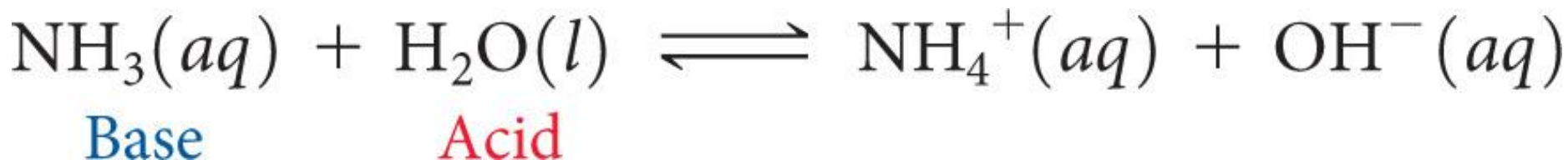
Base

What Is Different about Water?

- Water can act as a Brønsted–Lowry **base** and accept a proton (H^+) from an acid.



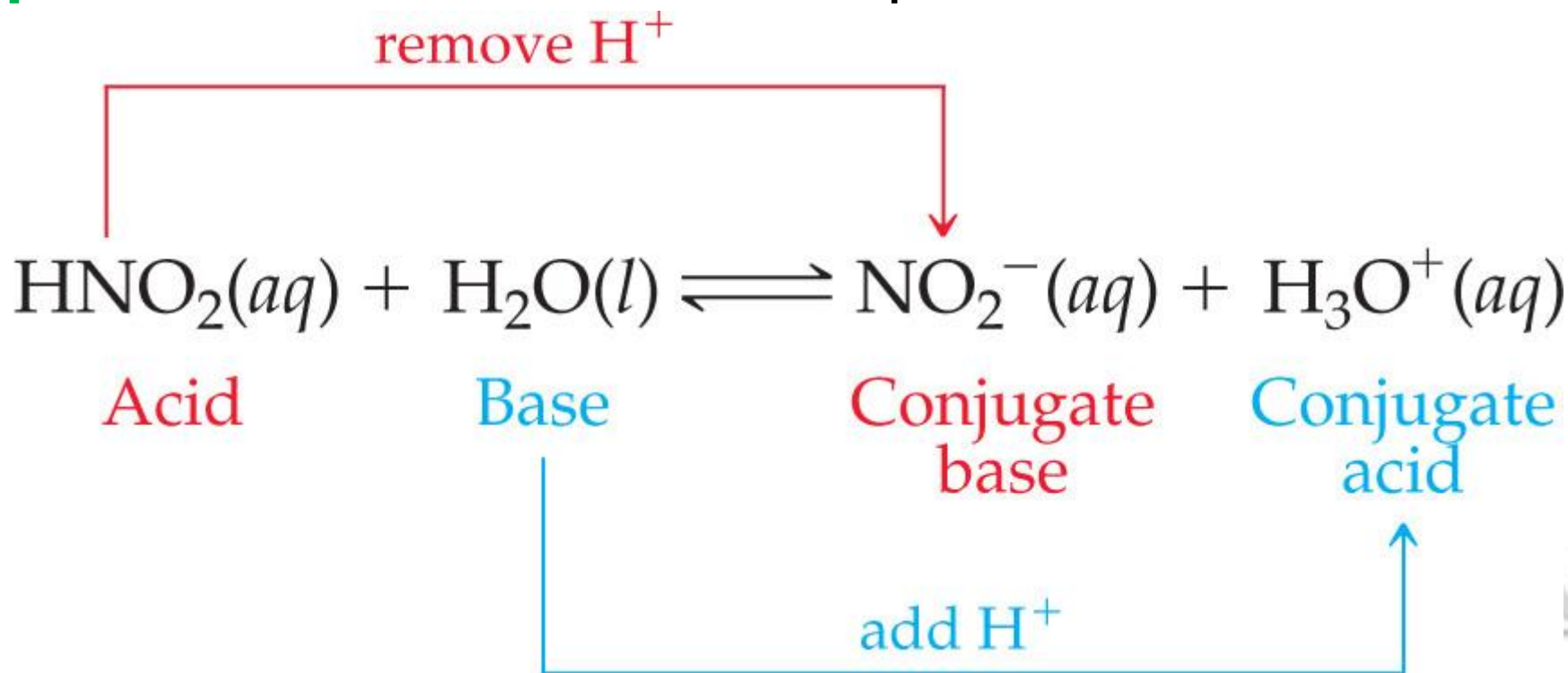
- Water can also donate a proton and act as an **acid**.

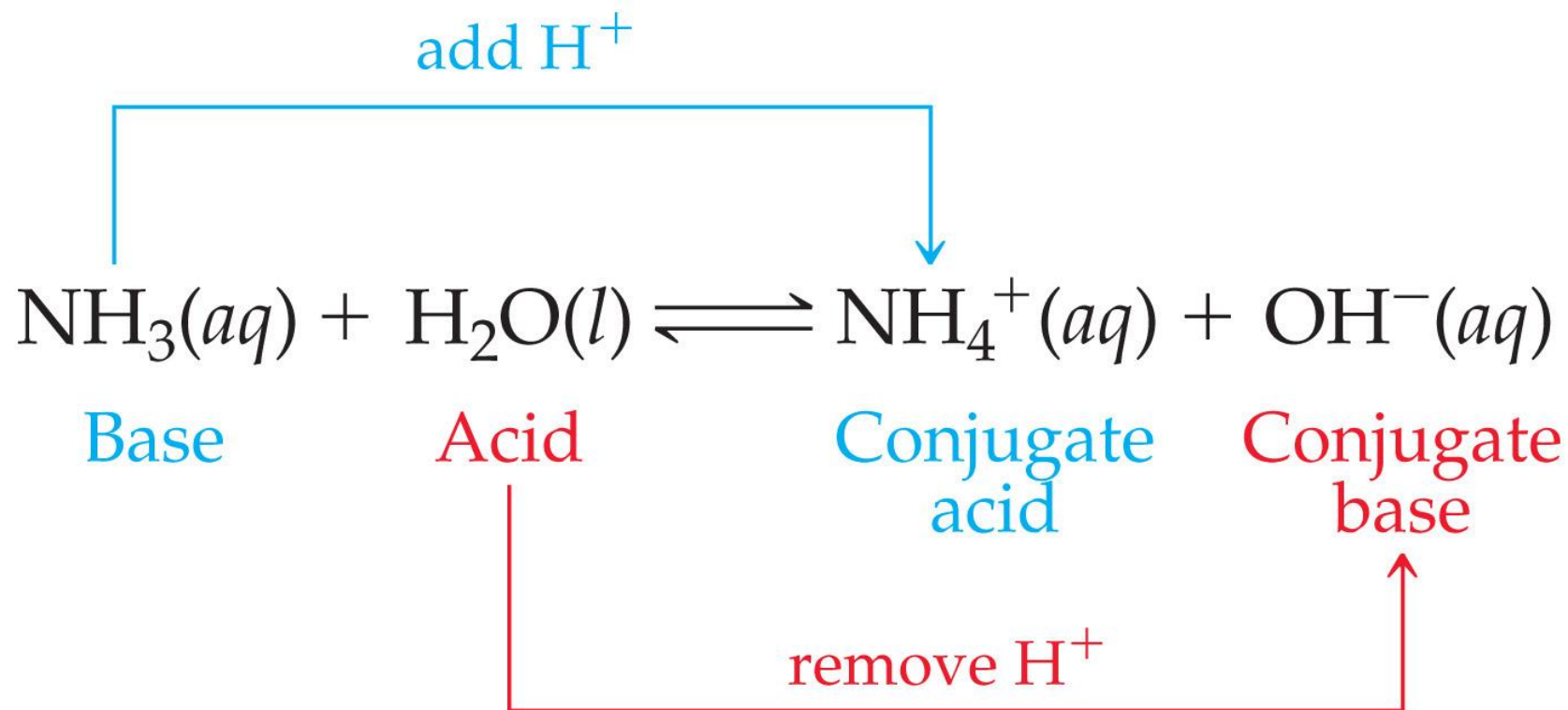


- This makes water **amphiprotic** (两性).
- HCO_3^- and HSO_3^- are also amphiprotic.

Conjugate (共轭) Acids and Bases

- The term **conjugate** means “joined together as a pair”.
- Reactions between acids and bases always yield their **conjugate bases and acids**.
- The **higher stability** the conjugate one is, the **more equilibrium shifts** towards the products.





Relative Strengths of Acids & Bases

	ACID		BASE	
Strong acids	HCl	<div>↑</div> <div>Base strength increasing</div> <div>↓</div> <div>Acid strength increasing</div>	Cl ⁻	Negligible basicity
	H ₂ SO ₄		HSO ₄ ⁻	
	HNO ₃		NO ₃ ⁻	
	H ₃ O ⁺ (aq)		H ₂ O	
			SO ₄ ²⁻	Weak bases
Weak acids	HSO ₄ ⁻		H ₂ PO ₄ ⁻	
	H ₃ PO ₄		F ⁻	
	HF		CH ₃ COO ⁻	
	CH ₃ COOH		HCO ₃ ⁻	
	H ₂ CO ₃		HS ⁻	
	H ₂ S		HPO ₄ ²⁻	Strong bases
	H ₂ PO ₄ ⁻		NH ₃	
	NH ₄ ⁺		CO ₃ ²⁻	
	HCO ₃ ⁻		PO ₄ ³⁻	
	HPO ₄ ²⁻		OH ⁻	
Negligible acidity	H ₂ O		O ²⁻	
	OH ⁻		H ⁻	
	H ₂		CH ₃ ⁻	
	CH ₄			

- The substances between the arrows are conjugate acid–base pairs in water.
- Acids above the line with H₂O as a base are **strong acids**; while their conjugate bases are very weak bases in water.

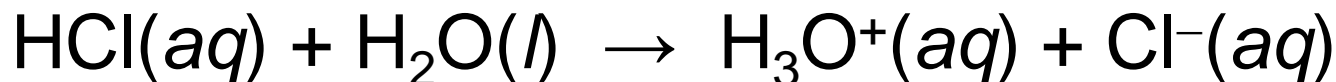
	ACID		BASE	
Strong acids	HCl	<div>↑</div> <div>Base strength increasing</div> <div>↓</div> <div>Acid strength increasing</div>	Cl ⁻	Negligible basicity
	H ₂ SO ₄		HSO ₄ ⁻	
	HNO ₃		NO ₃ ⁻	
	H ₃ O ⁺ (aq)		H ₂ O	
Weak acids	HSO ₄ ⁻		SO ₄ ²⁻	Weak bases
	H ₃ PO ₄		H ₂ PO ₄ ⁻	
	HF		F ⁻	
	CH ₃ COOH		CH ₃ COO ⁻	
	H ₂ CO ₃		HCO ₃ ⁻	
	H ₂ S		HS ⁻	
	H ₂ PO ₄ ⁻		HPO ₄ ²⁻	
	NH ₄ ⁺		NH ₃	
	HCO ₃ ⁻		CO ₃ ²⁻	
	HPO ₄ ²⁻		PO ₄ ³⁻	
Negligible acidity	H ₂ O		OH ⁻	Strong bases
	OH ⁻		O ²⁻	
	H ₂		H ⁻	
	CH ₄		CH ₃ ⁻	

- Bases below the line with H₂O as an acid are **strong bases**; their conjugate acids are **very weak acids** in water.

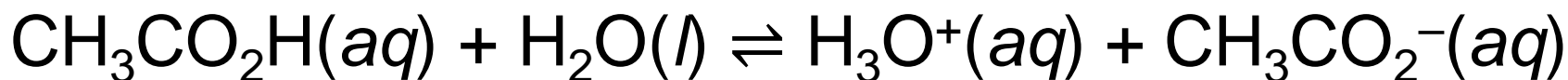
Acid and Base Strength

• In every acid–base reaction, equilibrium favors transfer of the **proton** from the **stronger acid** to the **stronger base** to form the **weaker conjugate acid and base**.

E.g.



➤ H_2O is a much stronger base than Cl^- , so the equilibrium lies far to the right ($K \gg 1$).

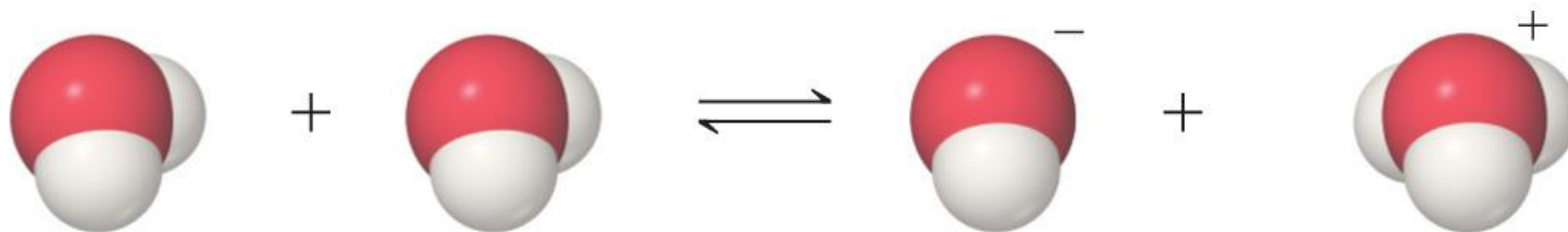
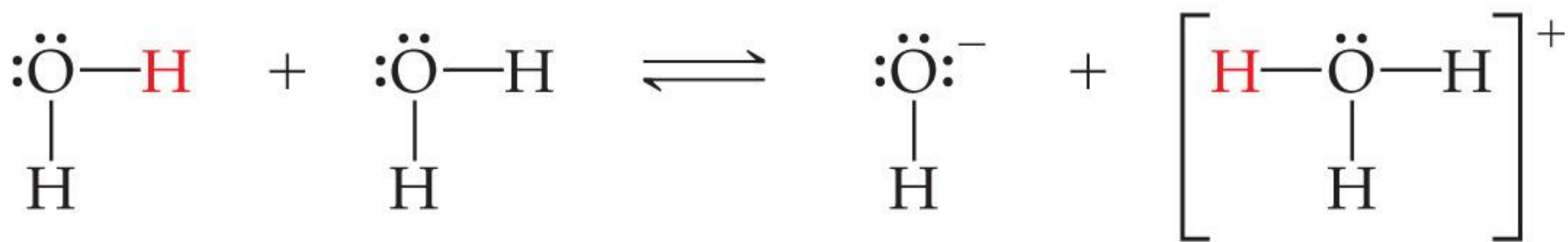


❖ Acetate is a stronger base than H_2O , so the equilibrium favors the left side ($K < 1$).

Acids
and
Bases

Autoionization of Water

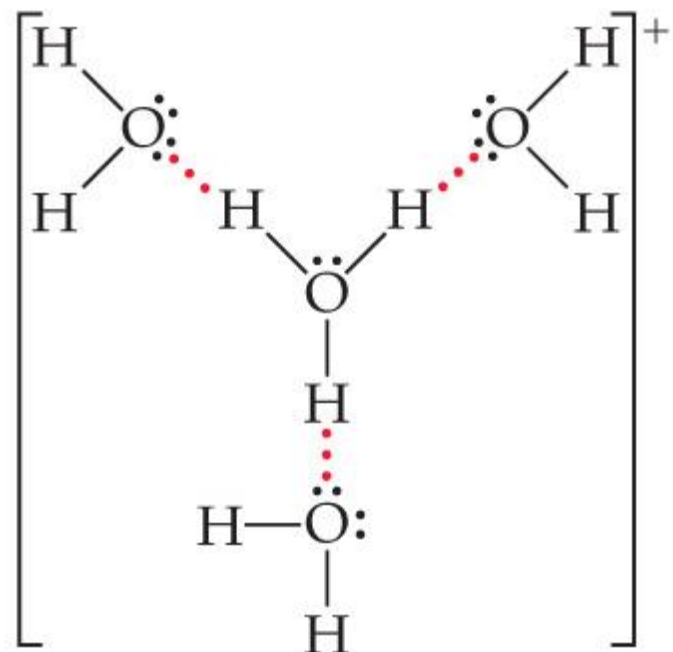
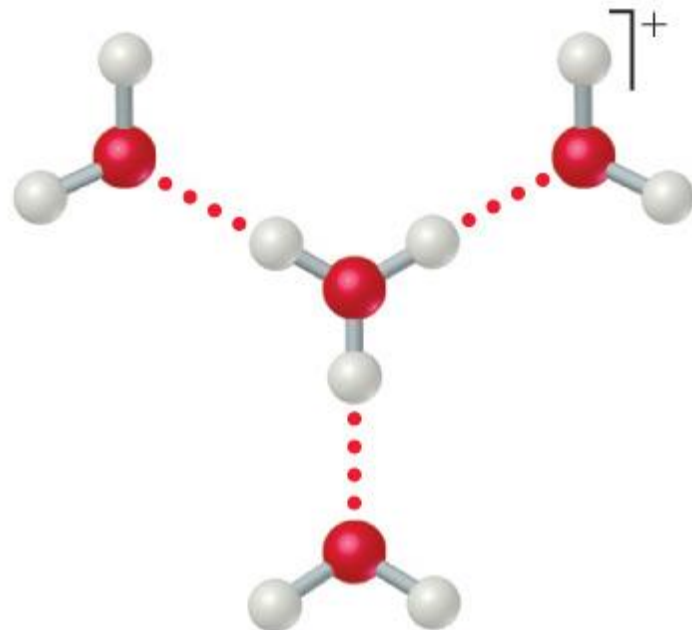
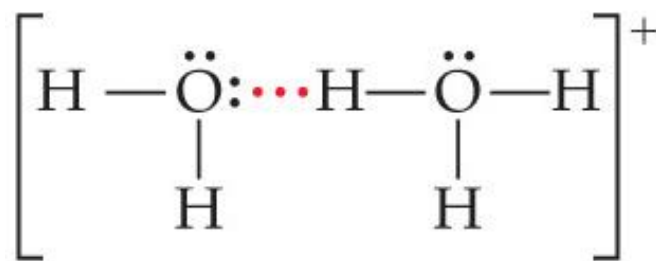
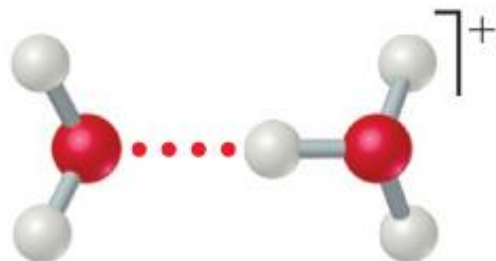
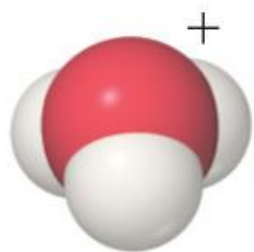
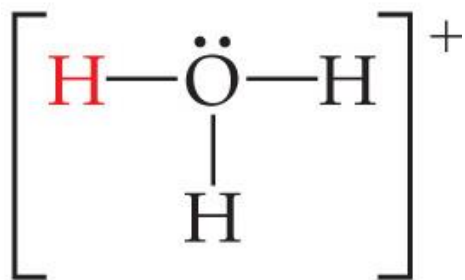
- Water is amphoteric (酸碱两性的).
- In pure water, a few molecules act as bases and a few act as acids. This is referred to as **autoionization**.



Acid

Base

Hydronium ion



Ion Product Constant

- The equilibrium expression for this autoionization process:



$$K_c = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- This special equilibrium constant is referred to as the **ion product constant** for pure water, K_w .

- At 25 °C, $K_w = 1.0 \times 10^{-14}$

- Since in pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$,

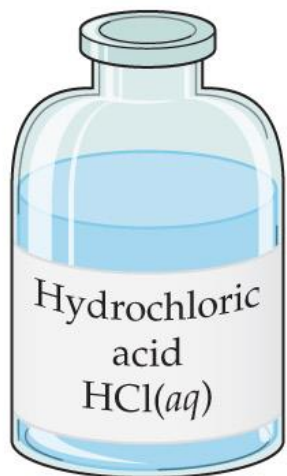
$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log(1.0 \times 10^{-7})$$

$$= 7.00 \text{ (25 °C)}$$

Aqueous Solutions (Acidic, Basic, or Neutral)

- If a solution is **neutral**, $[H^+] = [OH^-]$.
- If a solution is **acidic**, $[H^+] > [OH^-]$.
- If a solution is **basic**, $[H^+] < [OH^-]$.



Acidic solution

$$[H^+] > [OH^-]$$

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



Neutral solution

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

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



Basic solution

$$[H^+] < [OH^-]$$

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

pH

Increasing acid strength ↑

	[H ⁺] (M)	pH	pOH	[OH ⁻] (M)	
	1 (1×10 ⁰)	0.0	14.0	1×10 ⁻¹⁴	
Stomach acid	1×10 ⁻¹	1.0	13.0	1×10 ⁻¹³	
Lemon juice	1×10 ⁻²	2.0	12.0	1×10 ⁻¹²	
Cola, vinegar	1×10 ⁻³	3.0	11.0	1×10 ⁻¹¹	
Wine	1×10 ⁻⁴	4.0	10.0	1×10 ⁻¹⁰	
Tomatoes	1×10 ⁻⁵	5.0	9.0	1×10 ⁻⁹	
Black coffee	1×10 ⁻⁶	6.0	8.0	1×10 ⁻⁸	
Rain	1×10 ⁻⁷	7.0	7.0	1×10 ⁻⁷	Human blood
Saliva	1×10 ⁻⁸	8.0	6.0	1×10 ⁻⁶	Seawater
Milk	1×10 ⁻⁹	9.0	5.0	1×10 ⁻⁵	Borax
	1×10 ⁻¹⁰	10.0	4.0	1×10 ⁻⁴	Lime water
	1×10 ⁻¹¹	11.0	3.0	1×10 ⁻³	Household ammonia
	1×10 ⁻¹²	12.0	2.0	1×10 ⁻²	Household bleach
	1×10 ⁻¹³	13.0	1.0	1×10 ⁻¹	
	1×10 ⁻¹⁴	14.0	0.0	1 (1×10 ⁰)	

Increasing base strength ↓

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

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

- A method of reporting proton concentration.
- **pH = -log[H⁺]**
- Neutral pH is 7.00;
- Acidic pH is <7.00; Basic pH is >7.00.

Other “p” Scales

- The “p” in pH tells us to take the $-\log$ of a quantity (in this case, hydronium ions).

- Some other “p” systems are:

$$\text{pOH: } -\log[\text{OH}^-]$$

$$\text{p}K_w: -\log K_w$$

$$\text{p}K_a: -\log K_a$$

$$\text{p}K_b: -\log K_b$$

Relating pH and pOH

Because

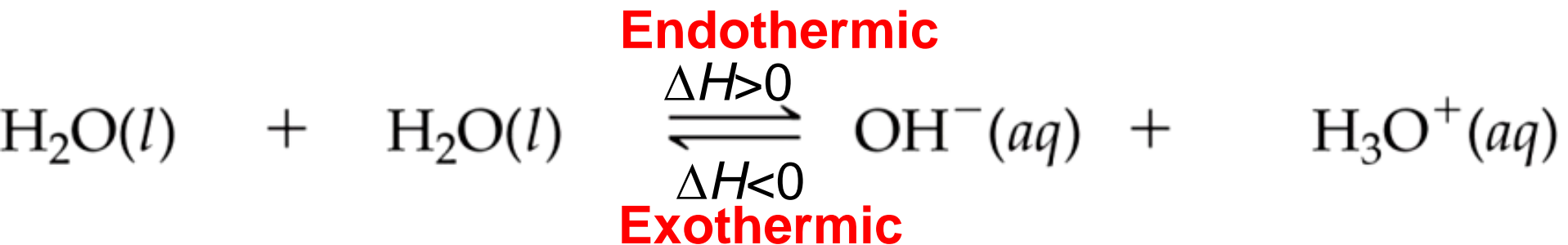
$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

we can take the $-\log$ of the equation:

$$-\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-] = -\log K_w = 14.00$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00 \text{ (298.15 K)}$$

pH Values of Pure Water at Various Temperature



- According to Le Châtelier's Principle, the chemical equilibrium shifts to the right at higher temperature.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] > 1.0 \times 10^{-14} \quad T > 298 \text{ K}$$

In pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, therefore $\text{pH} < 7$.

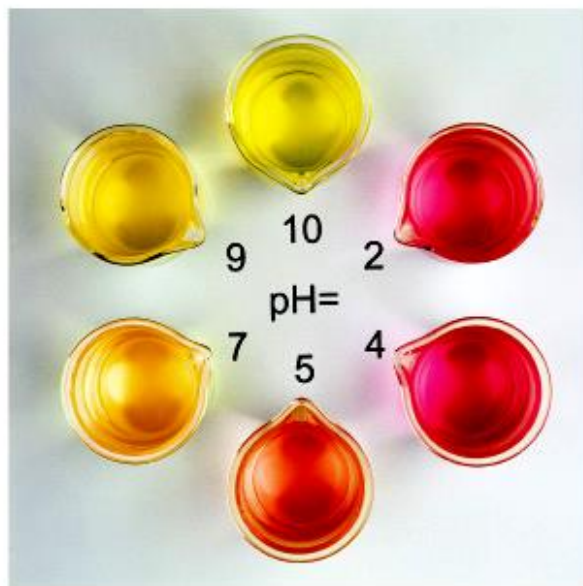
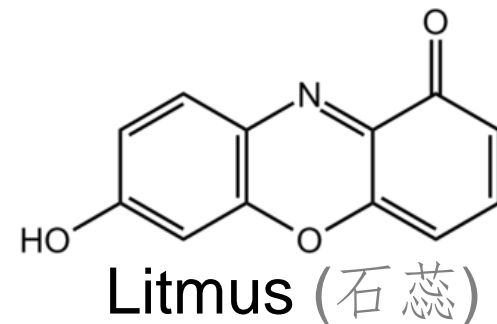
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] < 1.0 \times 10^{-14} \quad T < 298 \text{ K}$$

In pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, therefore $\text{pH} > 7$.

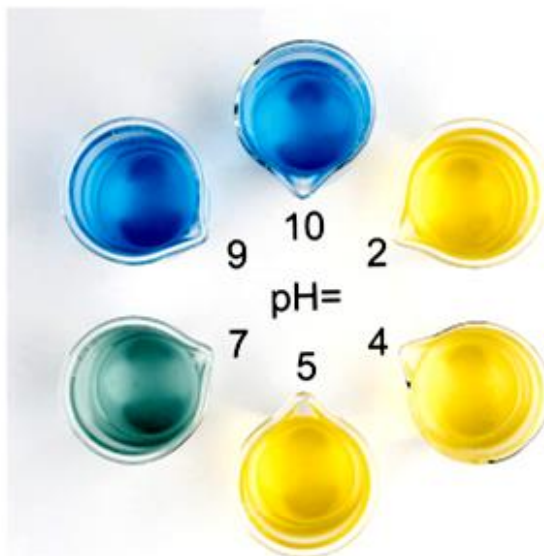
T (°C)	K_w	$[H^+]$ (M)	pH	Acidity
0	0.114×10^{-14}	3.376×10^{-8}	7.47	neutral
10	0.293×10^{-14}	5.413×10^{-8}	7.27	neutral
20	0.681×10^{-14}	8.252×10^{-8}	7.08	neutral
25	1.008×10^{-14}	1.004×10^{-7}	7.00	neutral
30	1.471×10^{-14}	1.213×10^{-7}	6.92	neutral
40	2.916×10^{-14}	1.708×10^{-7}	6.77	neutral
50	5.476×10^{-14}	2.340×10^{-7}	6.63	neutral

How Do We Measure pH?

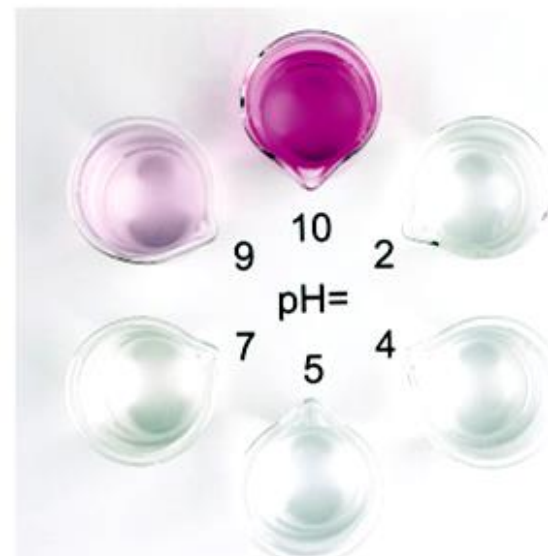
- **Indicators**, including litmus paper, are used for less accurate measurements; an indicator is one color in its acid form and another color in its basic form.



Methyl red

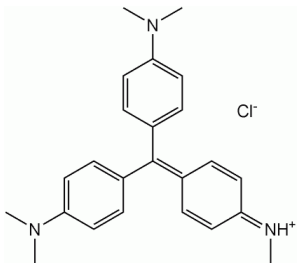


Bromthymol blue

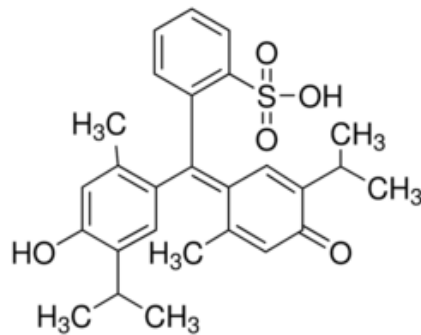


Phenolphthalein

Common indicators' structure

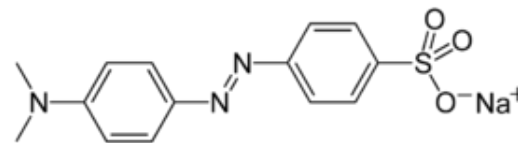


Methyl violet
(甲基紫)

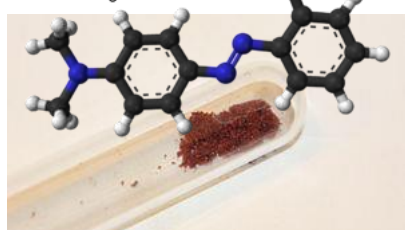


Thymol blue

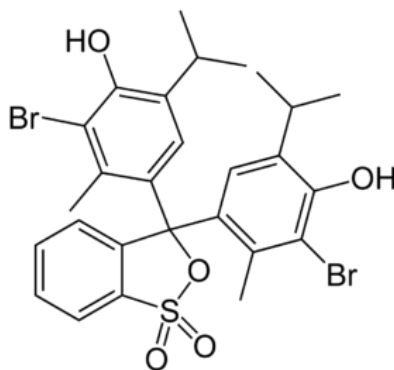
(百里酚蓝)



Methyl orange
(甲基橙)

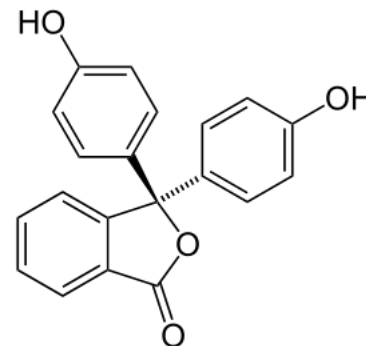


Methyl red
(甲基红)

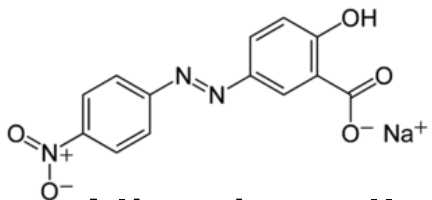


Bromthymol blue

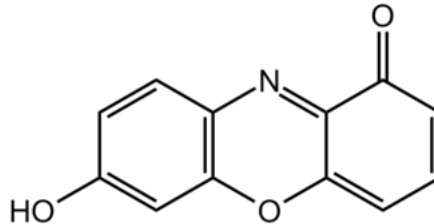
(溴百里酚蓝)





Phenolphthalein (酚酞)

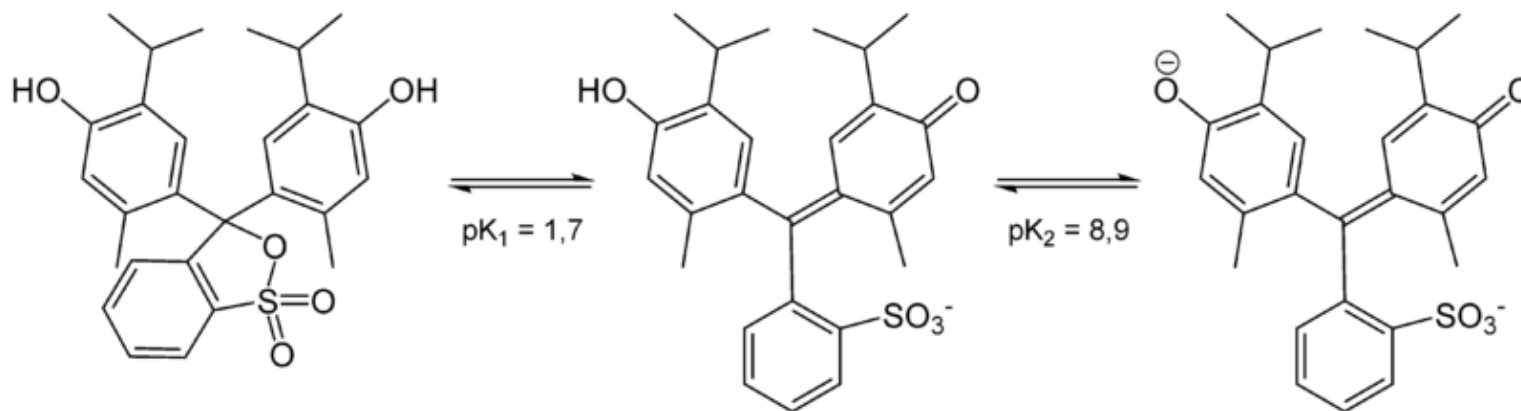


Alizarin yellow R
(茜素黃)



Litmus (石蕊)

	pH range for color change									
	0	2	4	6	8	10	12	14		
Thymol blue	Red		Yellow		Yellow		Blue			



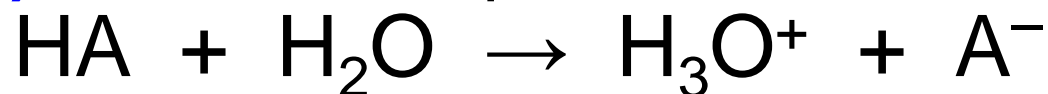


- **pH meters** are used for accurate measurement of pH; electrodes indicate small changes in voltage to detect pH.

Strong Acids

- Chapter 4: seven strong acids are HCl, HBr, HI, HNO₃, H₂SO₄, HClO₃, and HClO₄.

- These are **strong electrolytes** and exist **totally (or essentially) as ions** in aqueous solution; e.g.,



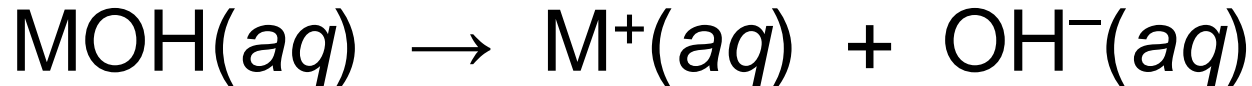
- So, for the monoprotic strong acids,

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{acid}] \\ \text{pH} &= -\log([\text{acid}]) \end{aligned}$$

Strong Bases

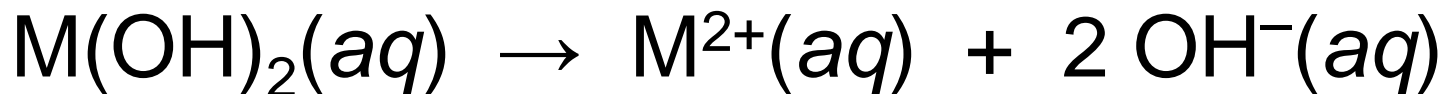
- Strong bases are the soluble hydroxides, which are the alkali metal and heavier alkaline earth metal hydroxides (Ca^{2+} , Sr^{2+} , and Ba^{2+}).

- Again, these substances dissociate **completely (or essentially) into ions** in aqueous solution; e.g.,



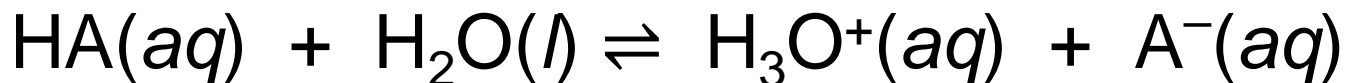
$$\begin{aligned} [\text{OH}^-] &= [\text{base}] \\ \text{pOH} &= -\log([\text{base}]) \end{aligned}$$

or



Acids
and
Bases

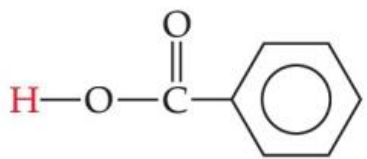
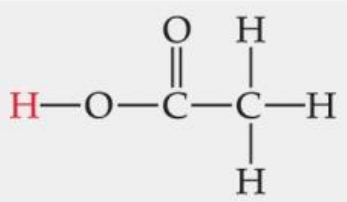
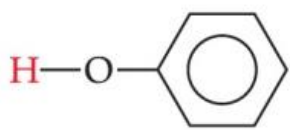
Weak Acids



- Since it is an **equilibrium**, there is an related equilibrium constant, **acid dissociation constant** (K_a).

$$K_a = [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$$

Table 16.2 Some Weak Acids in Water at 25 °C

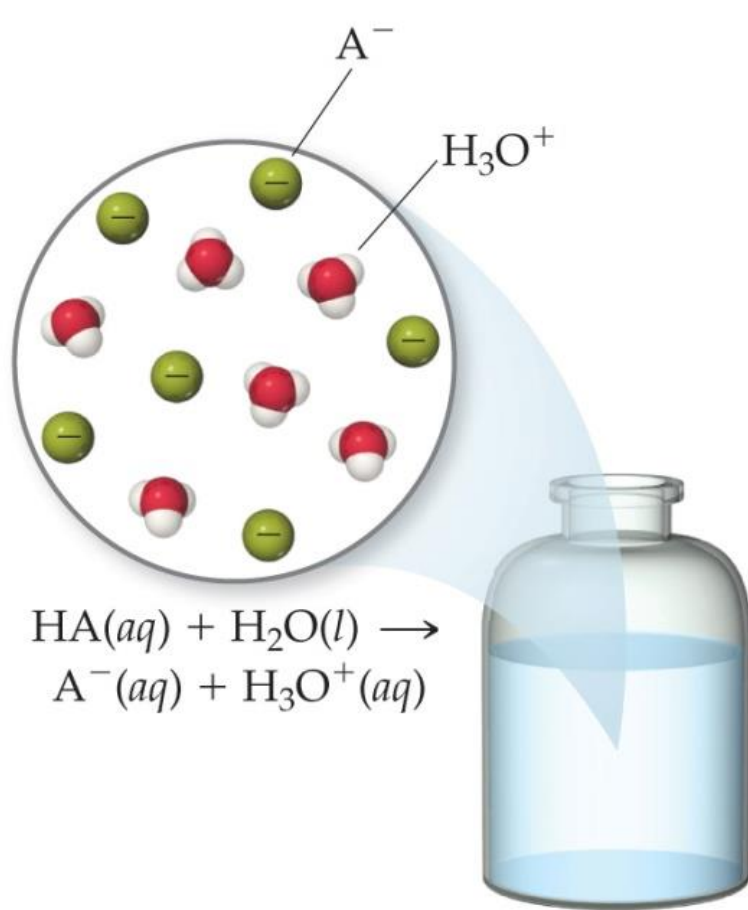
Acid	Structural Formula*	Conjugate Base	K_a
Chlorous (HClO_2)	$\text{H}-\text{O}-\text{Cl}-\text{O}$	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	$\text{H}-\text{F}$	F^-	6.8×10^{-4}
Nitrous (HNO_2)	$\text{H}-\text{O}-\text{N}=\text{O}$	NO_2^-	4.5×10^{-4}
Benzoic ($\text{C}_6\text{H}_5\text{COOH}$)		$\text{C}_6\text{H}_5\text{COO}^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	$\text{H}-\text{O}-\text{Cl}$	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	$\text{H}-\text{C}\equiv\text{N}$	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$\text{C}_6\text{H}_5\text{O}^-$	1.3×10^{-10}

- The **greater** the K_a value, the **stronger** the acid.

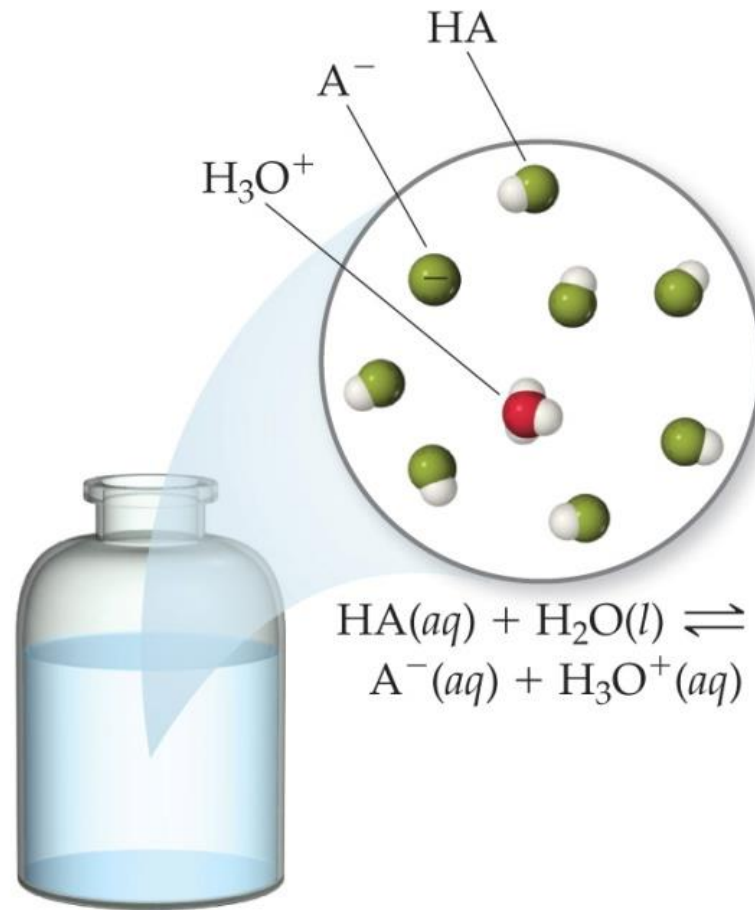
- $\text{p}K_a$: $\text{MeO}-\text{H}$ (15.5)

Comparing Strong and Weak Acids

- Strong acids **completely** dissociate to ions.
- Weak acids only **partially** dissociate to ions.



Strong acid
HA molecules
completely dissociate



Weak acid
HA molecules
partially dissociate

Calculating K_a from the pH

- The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25 °C is 2.38. Calculate K_a for formic acid at this temperature.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

- To calculate K_a , we need **the equilibrium concentrations** of all three things.
- We can find $[\text{H}_3\text{O}^+]$, which is the same as $[\text{HCOO}^-]$, from the pH.
- $[\text{H}_3\text{O}^+] = [\text{HCOO}^-] = 10^{-2.38} = 4.2 \times 10^{-3}$

- We can **set up a below table** for equilibrium concentrations. We know initial HCOOH (**0.10 M**) and ion concentrations (**0 M**);
- We found equilibrium ion concentrations (**4.2×10^{-3} M**); so we calculate the change, then the equilibrium HCOOH concentration.



Initial concentration (M)	0.10	0	0
Change in concentration (M)	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equilibrium concentration (M)	$(0.10 - 4.2 \times 10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

$$\begin{aligned}
 K_a &= \frac{[4.2 \times 10^{-3}][4.2 \times 10^{-3}]}{[0.10]} \\
 &= 1.8 \times 10^{-4}
 \end{aligned}$$

Calculating Percent Ionization

- Percent ionization = $\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_{\text{initial}}} \times 100\%$
 $= \frac{\text{concentration of ionized HA}}{\text{original concentration of HA}} \times 100\%$

- In this previous example,

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 4.2 \times 10^{-3} \text{ M}$$

$$[\text{HCOOH}]_{\text{initial}} = 0.10 \text{ M}$$

$$\begin{aligned}\text{Percent ionization} &= \frac{4.2 \times 10^{-3}}{0.10} \times 100\% \\ &= 4.2\%\end{aligned}$$

Method to Follow to Calculate pH Using K_a

- 1) Write the ***chemical equation*** for the ***ionization equilibrium***.
- 2) Write the ***equilibrium constant expression***.
- 3) Set up a table for Initial/Change in/Equilibrium Concentration to ***determine equilibrium concentrations*** as a function of change (x).
- 4) ***Substitute equilibrium concentrations into the equilibrium constant expression and solve for x .***
(Make assumptions if you can!)

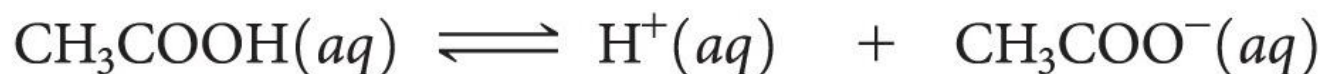
Example

- Calculate the pH of a 0.30 *M* solution of acetic acid, CH₃CO₂H, at 25 °C, in which its *K_a* is 1.8 × 10⁻⁵.



2) $K_a = [\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}]$

3)



Initial concentration (<i>M</i>)	0.30	0	0
Change in concentration (<i>M</i>)	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium concentration (<i>M</i>)	(0.30 - <i>x</i>)	<i>x</i>	<i>x</i>

$$\begin{aligned} 4) K_a &= [\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}] \\ &= (x)(x)/(0.30 - x) \end{aligned}$$

If we assume that $x \ll 0.30$, then $0.30 - x$ becomes 0.30. The problem becomes easier, since we don't have to use the quadratic formula to solve it.

$$\begin{aligned} K_a &= 1.8 \times 10^{-5} = x^2/0.30, \\ \text{so } x &= 2.3 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} x &= [\text{H}_3\text{O}^+], \\ \text{so pH} &= -\log(2.3 \times 10^{-3}) = 2.64 \text{ (or 2.6)} \end{aligned}$$

Strong vs. Weak Acids - Another Comparison

- **Strong** Acid: $[\text{H}^+]_{\text{eq}} = [\text{HA}]_{\text{init}}$
- **Weak** Acid: $[\text{H}^+]_{\text{eq}} < [\text{HA}]_{\text{init}}$
- This creates a difference in conductivity and in rates of chemical reactions.

Reaction proceeds more rapidly in strong acid, leading to formation of larger H_2 bubbles and rapid disappearance of metal

Reaction complete in strong acid

H_2 bubbles show reaction still in progress in weak acid

Reaction eventually goes to completion in both acids

1 M $\text{HCl}(\text{aq})$
 $[\text{H}^+] = 1 \text{ M}$

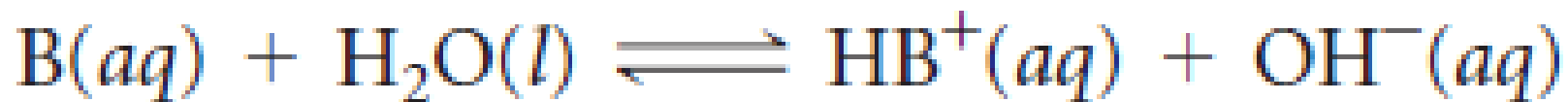
1 M $\text{CH}_3\text{COOH}(\text{aq})$
 $[\text{H}^+] = 0.004 \text{ M}$

Polyprotic Acids

- Polyprotic acids have **more than one acidic proton**.
- It is always **easier to remove the first proton** than any successive proton.
- If the factor in the K_a values for the first and second dissociation has a difference of 3 or greater, the pH generally depends *only* on the first dissociation.

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$\text{HOOC} - \text{COOH}$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$\text{C}_2\text{H}_2\text{O}_2(\text{COOH})_2$	1.0×10^{-3}	4.6×10^{-5}	

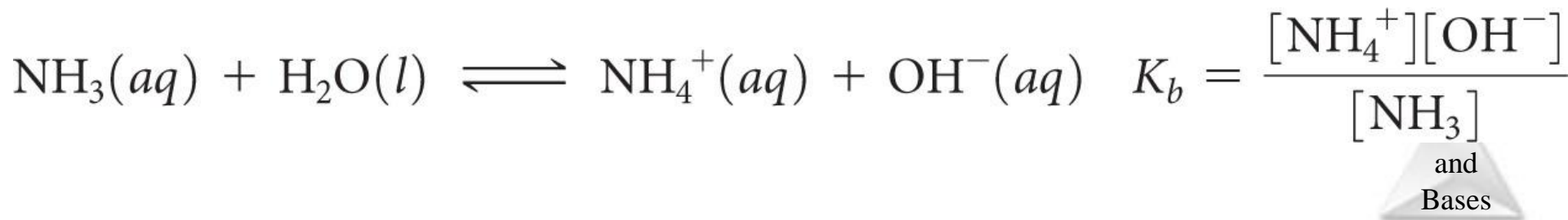
Weak Bases



- Ammonia, NH_3 , is a weak base.
- Like weak acids, weak bases have an equilibrium constant called the **base dissociation constant (K_b)**.

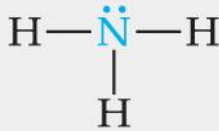

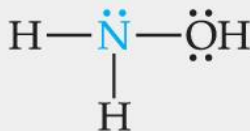
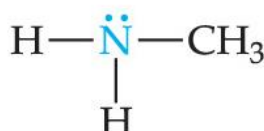

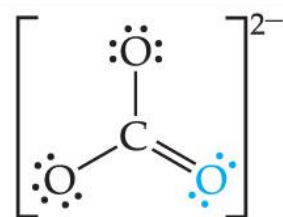

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

- Equilibrium calculations work the *same* as for acids, using the base dissociation constant instead.



Base Dissociation Constants

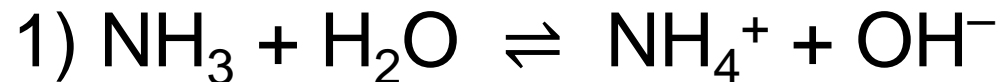
Table 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine ($\text{C}_5\text{H}_5\text{N}$)		$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}
Hydroxylamine (HONH_2)		HONH_3^+	1.1×10^{-8}
Methylamine (CH_3NH_2)		CH_3NH_3^+	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.3×10^{-7}

• The greater the K_b value, the stronger the base.

Example

- What is the pH of 0.15 M NH_3 ?



2) $K_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] = 1.8 \times 10^{-5}$

3)



Initial concentration (M)	0.15	—	0	0
Change in concentration (M)	$-x$	—	$+x$	$+x$
Equilibrium concentration (M)	$(0.15 - x)$	—	x	x

$$4) \quad 1.8 \times 10^{-5} = x^2/(0.15 - x)$$

If we assume that $x \ll 0.15$, $0.15 - x \sim 0.15$.

Then:

$$1.8 \times 10^{-5} = x^2/0.15$$

&

$$x = 1.6 \times 10^{-3}$$

Note: x is the molarity of OH^- ,

so $\text{pOH} = -\log(x)$

$$= 2.80$$

&

$$\text{pH} = 14.00 - \text{pOH}$$

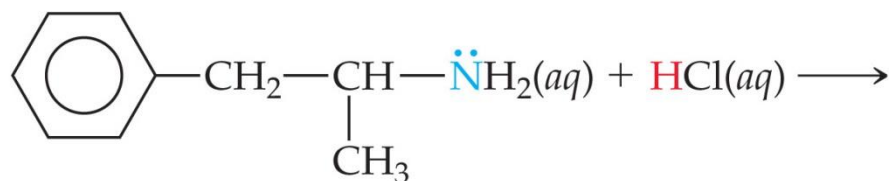
$$= 11.20 \text{ (or } 11.2)$$

Types of Weak Bases

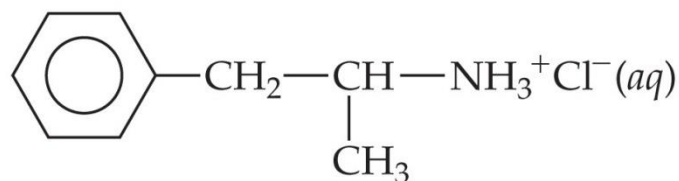
- Two main categories

1) **Neutral** substances with an atom that has a **nonbonding pair of electrons** that can **accept H^+** (like ammonia (NH_3) and the **amines**).

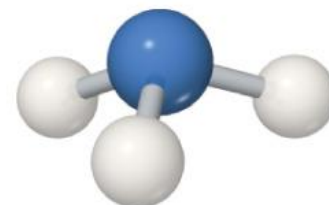
2) **Anions** of **weak acids**: e.g., CO_3^{2-} , HS^- , ClO^-).



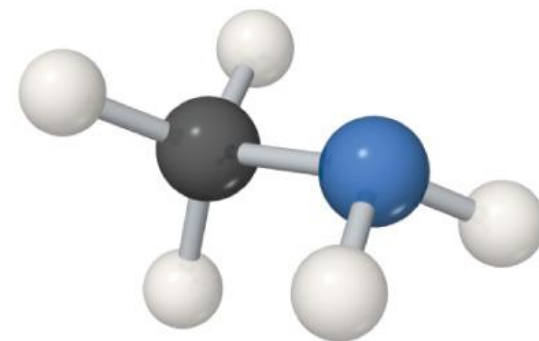
Amphetamine



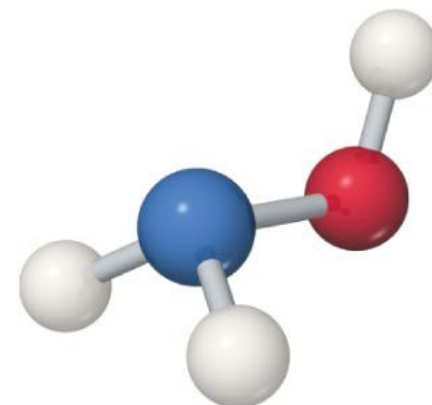
Amphetamine hydrochloride



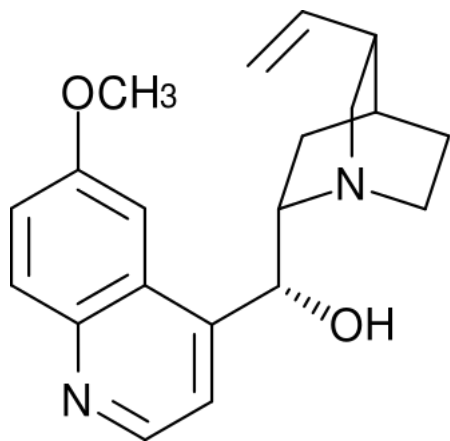
Ammonia
 NH_3



Methylamine
 CH_3NH_2

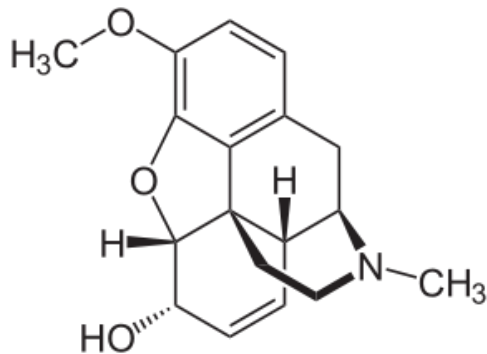


Hydroxylamine
 NH_2OH



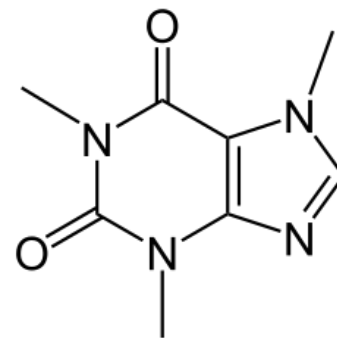
Quinine

(antimalarial, antipyretic: 退热药)



Codeine

(analgesic, antidiarrhoeal)



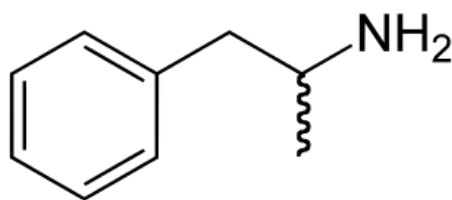
Caffeine

(stimulant)



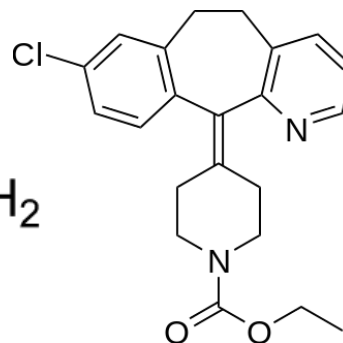
Diphenhydramine

Benadryl



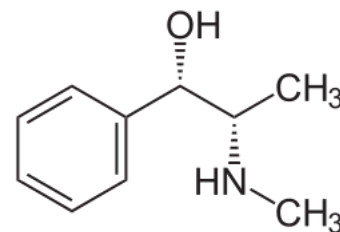
Amphetamine

(stimulant)



Loratadine

Claritin-D



Acids
and
Bases

Relationship between K_a and K_b

Table 16.5 Some Conjugate Acid–Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

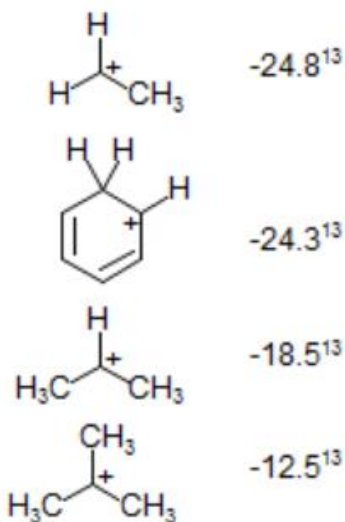
- For a conjugate acid–base pair, K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

- If you know one of them, you can calculate the other.
- K_a and K_b values are depended on solvent & temperature.

(Extra info.) Superacids

J. Org. Chem.
2011, 391



HClO₄

CF₂(CF₂SO₂)₂NH

4-NO₂-C₆H₄SO(=NTf)₂NHTf

HB(CN)₄

(FSO₂)₃CH

Tf₂CH(CN)

2,3,4,5-tetracyanocyclopentadiene

CN-TCNP


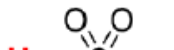
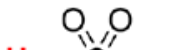
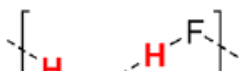
Tf₃CH^g

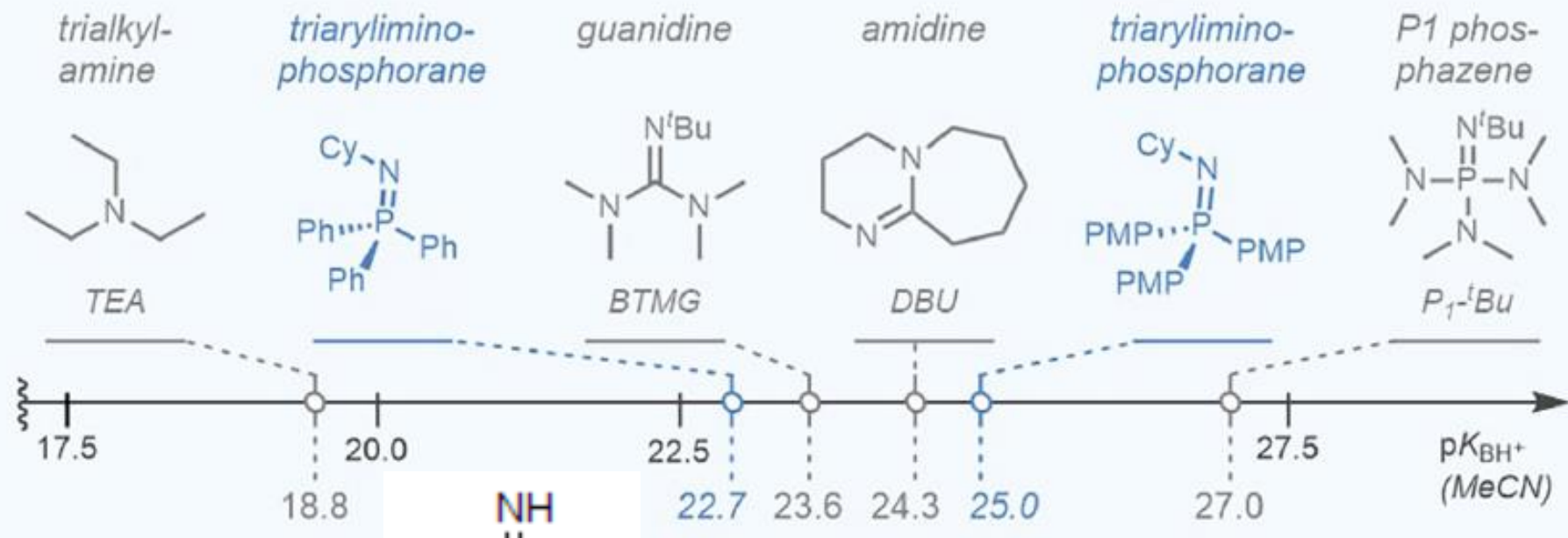
CF₃SO(=NTf)₂NHTf^g

Acid	pK _a (DCE)	Directly measured ΔpK _{ip} values in DCE ^a	pK _a (MeCN) ^b
Picric acid ^c	0.0		11.0
HCl	-0.4	-0.73, 0.71, 1.48, 0.36, 1.09	10.6
2,3,4,6-(CF ₃) ₅ -C ₆ H-CH(CN) ₂	-0.7	0.77, 0.74, 2.08, 1.00	10.3
4-NO ₂ -C ₆ H ₄ SO ₂ NHTos ^d	-1.5	0.28, 1.78	9.6
HNO ₃	-1.7	1.01	9.4
4-NO ₂ -C ₆ H ₄ SO ₂ NHSO ₂ C ₆ H ₄ -4-Cl	-2.4	-1.13, 0.88, 0.08	8.8
H ₂ SO ₄	-2.5	0.12, 1.26	8.7
C ₆ (CF ₃) ₅ CH(CN) ₂	-2.6	1.02, 1.02, 1.05	8.6
(4-NO ₂ -C ₆ H ₄ -SO ₂) ₂ NH	-3.7	1.48, 0.47	7.7
3-NO ₂ -4-Cl-C ₆ H ₃ SO ₂ NHSO ₂ C ₆ H ₄ -4-NO ₂	-4.1	0.36, 0.80	7.3
(3-NO ₂ -4-Cl-C ₆ H ₃ SO ₂) ₂ NH	-4.5	0.39, 1.35, 0.93	7.0
HBr	-4.9	0.40, 0.62	6.6
[C ₆ H ₅ SO(=NTf)] ₂ NH	-11.1	0.84, 0.84	1.0
[(C ₂ F ₅) ₂ PO] ₂ NH	-11.3	-0.89, 0.29, 0.84, 0.91, 0.93	0.8
2,4,6-(NO ₂) ₃ -C ₆ H ₂ SO ₂ OH	-11.3	0.28	0.8
[C(CN) ₂ =C(CN)] ₂ CH ₂	-11.4	0.44, 0.10	0.8
TfOH	-11.4	0.04, 0.12, 0.07, 0.09, 0.47, 0.49	0.7
C ₆ H ₅ SO(=NTf) ₂ NHTf	-11.5	0.40, 0.32, 0.47	0.7
TfCH(CN) ₂	-11.6		0.6
	-13.0	0.80, 0.40, 0.56, 1.04	-0.7
	-13.1	0.89, 0.11, 0.86, 0.07	-0.8
	-13.1	0.19	-0.8
	-13.3	1.76, 0.44	-1.0
	-13.6	1.92, 2.16	-1.2
	-14.9	1.46, 1.73, 0.22	-2.4
	-15.1	-0.40, 0.21, 0.23	-2.6
	-15.3		-2.8
	-16.4		-3.7
	-18		-5

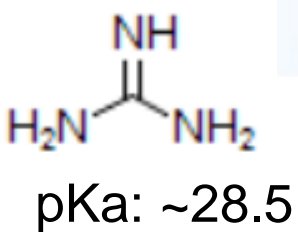
(Extra info.) Super acid, Magic acid ($\text{HSO}_3\text{F}-\text{SbF}_5$)



Reference	A Primary Superacids			B Conjugate Brønsted–Lewis Superacids		
				$[\text{H}(\text{HSO}_3\text{F})]^+[\text{FSO}_3(\text{SbF}_5)_n]^-$ "magic acid"	$[\text{H}(\text{HF})_x]^+[\text{F}(\text{SbF}_5)_n]^-$ fluoroantimonic acid	
H_2SO_4	HOTf	HSO_3F	HF	$\text{HSO}_3\text{F} \cdot \text{SbF}_5$ (1:1)	$\text{HF} \cdot \text{SbF}_5$ (10:1)	
$H_0 = -12$	$H_0 = -14.1$	$H_0 = -15.1$	$H_0 = -15.1$	$H_0 \approx -22$ to -23	$H_0 \approx -23$	

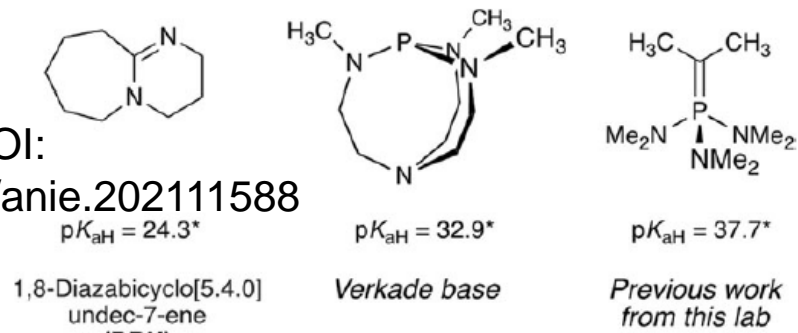


pK_a: ~10.8
(Extra info.)
Super bases



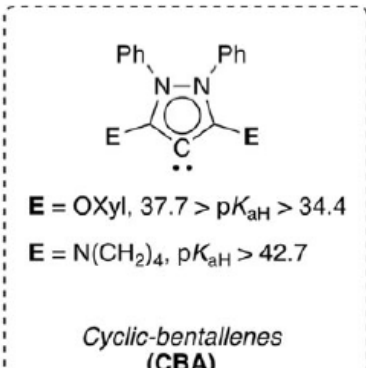
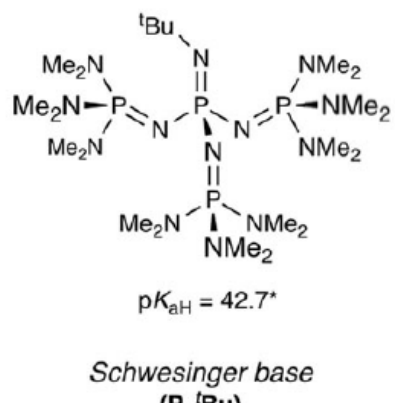
Acc. Chem. Res. 2020, 53, 2235

ACIE, DOI:
10.1002/anie.202111588



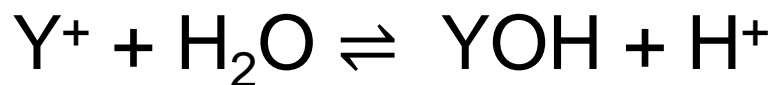
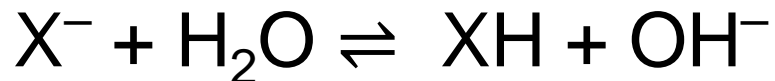
Substrate	pK _a	H ₂ O	(DMSO)
PROTONATED SPECIES			
<chem>Ph[N+](=O)[O-]</chem>	-12.4		
HYDROCARBONS			
(Me) ₃ CH	53		
(Me) ₂ CH ₂	51		
CH ₂ =CH ₂	50		
CH ₄	48		(56)

Evan's pK_a Table



Acid–Base Properties of Salts

- Many ions react with water to create H^+ or OH^- . The reaction with water is often called **hydrolysis**.

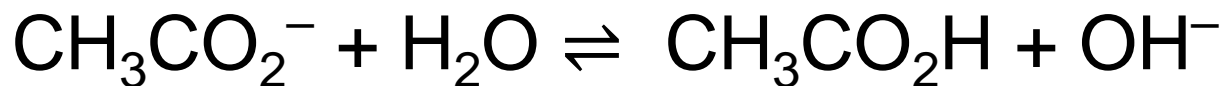


- To determine whether a salt is an acid or a base, you need to look at the cation and anion separately.
- The **cation** can be **acidic or neutral**.
- The **anion** can be **acidic, basic, or neutral**.

Anions

- Anions of **strong acids** are **neutral**. For example, Cl^- will *not* react with water, so OH^- can't be formed.

- Anions of **weak acids** are **conjugate bases**, so they create OH^- and increase pH in water; e.g.,



- Protonated anions from **polyprotic acids** can be **acids or bases**:

- If $K_a > K_b$, the anion will be **acidic**;
- if $K_b > K_a$, the anion will be **basic**.

Cations

- Cations which are the **conjugate acids of strong bases** do not affect pH.
- Polyatomic cations are typically the **conjugate acids of a weak base** and decrease pH; e.g., NH_4^+ .
- **Transition and post-transition metal** cations are **acidic**. (There are no H atoms in these cations!)

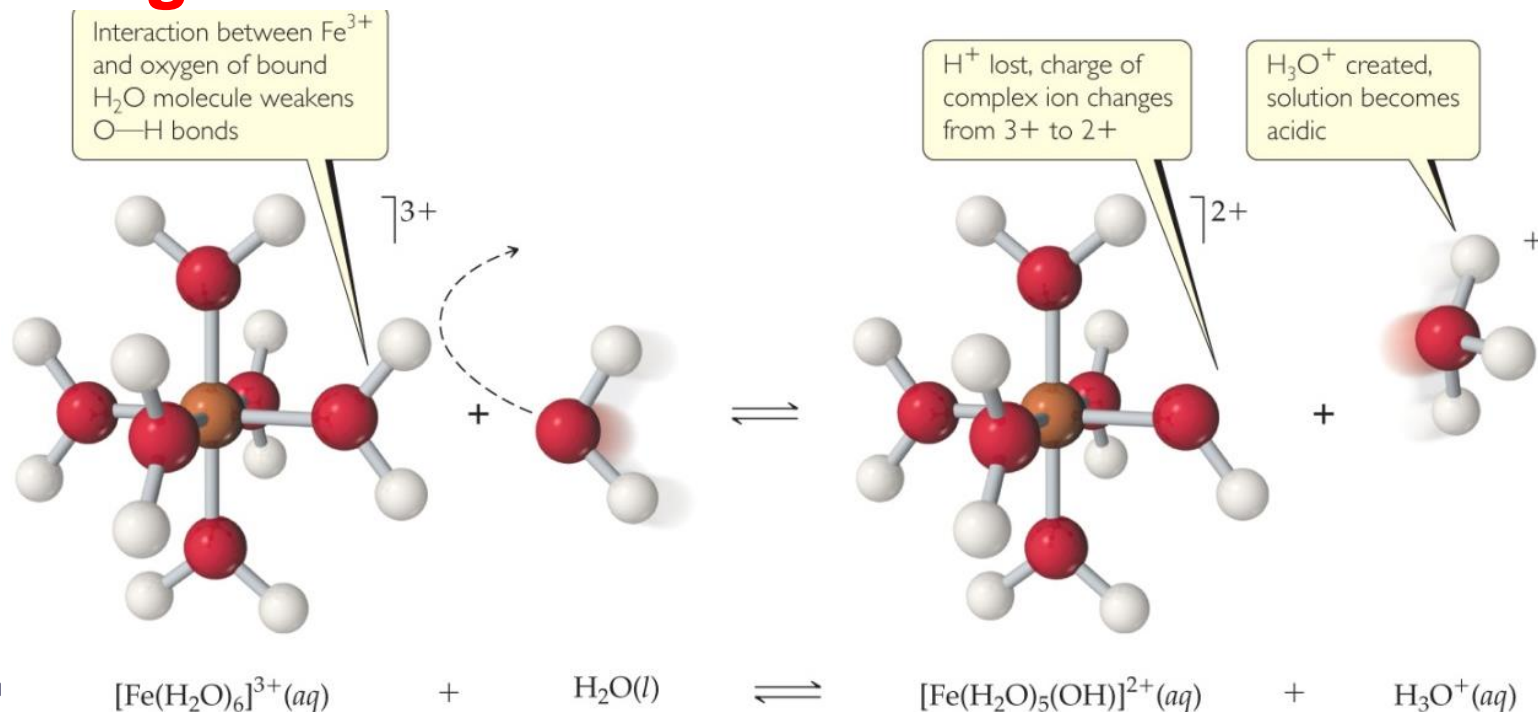


Acids
and
Bases



Hydrated Cations

- Transition & post-transition metals form **hydrated cations**.
- The water attached to the metal is **more polarized** than free water molecules, making these ions **acidic**.
- **Greater charge & smaller size** make a cation **more acidic**.

Cation	K_a
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}



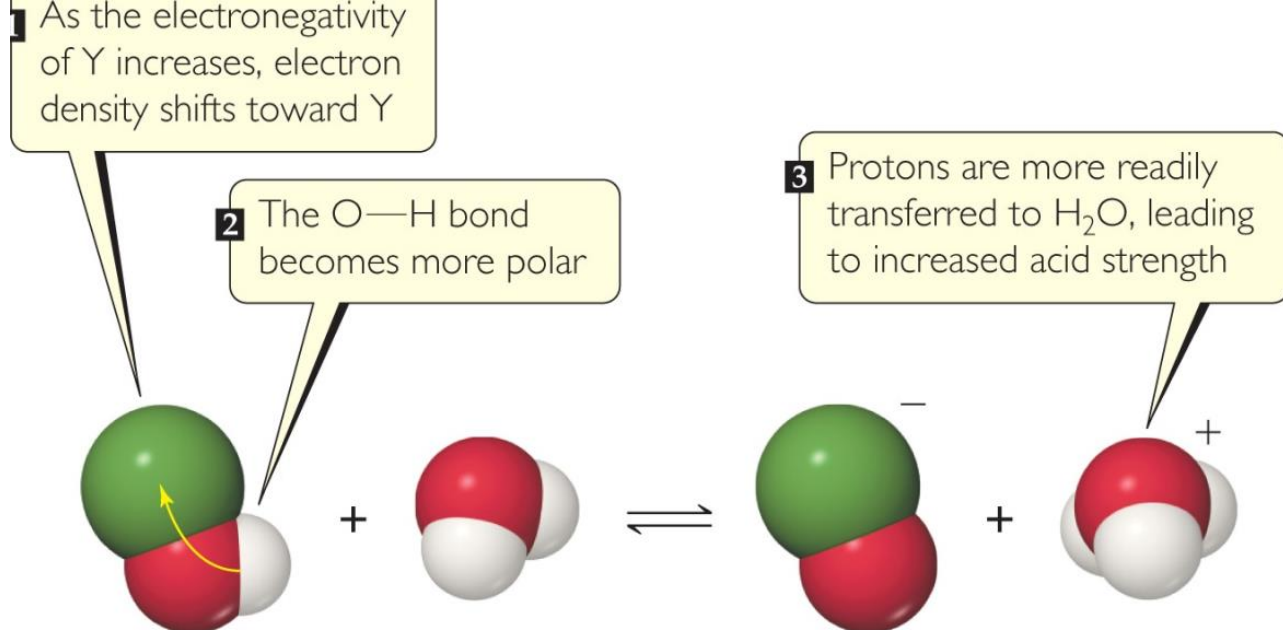
Binary Acids

4A	5A	6A	7A	
CH_4 Neither acid nor base	NH_3 Weak base $K_b = 1.8 \times 10^{-5}$	H_2O	HF Weak acid $K_a = 6.8 \times 10^{-4}$	Increasing acid strength 
SiH_4 Neither acid nor base	PH_3 Very weak base $K_b = 4 \times 10^{-28}$	H_2S Weak acid $K_a = 9.5 \times 10^{-8}$	HCl Strong acid	
		H_2Se Weak acid $K_a = 1.3 \times 10^{-4}$	HBr Strong acid	
Increasing acid strength 				

- Binary acids consist of H and one other element (A).
- Within a **group**, **H-A bond strength** is generally the most important factor.
- Within a **period**, **bond polarity (electronegativity on A)** is the most key factor to determine acid strength.

Acids
and
Bases

Oxyacids



Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

- **Oxyacids** consist of H, O, and one other element (Y), which is a nonmetal.
- Generally, as the **electronegativity** of the **nonmetal** (Y) **increases, the acidity increases** for acids with the same structure.

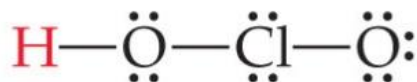
Oxyacids with Same “Other” Element

- If an element can form more than one oxyacid, the oxyacid with **more O atoms is more acidic**; e.g., sulfuric acid versus sulfurous acid.
- Or if the **oxidation number increases, the acidity increases**.

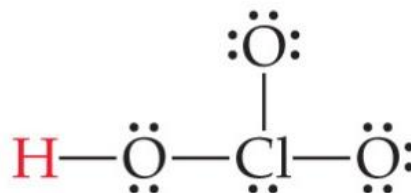
Hypochlorous



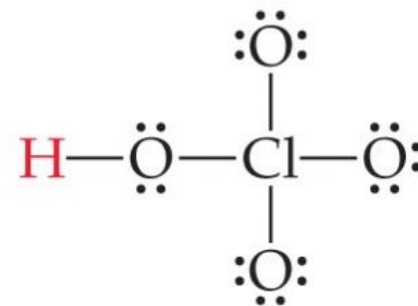
Chlorous



Chloric



Perchloric



$$K_a = 3.0 \times 10^{-8}$$

$$K_a = 1.1 \times 10^{-2}$$

Strong acid

Strong acid

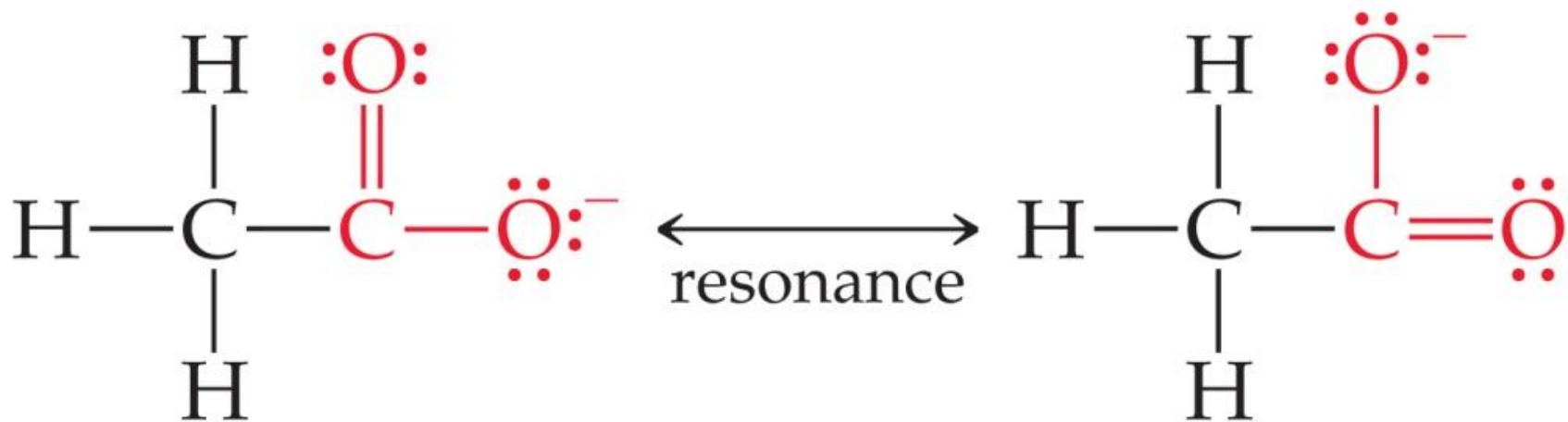


Increasing acid strength

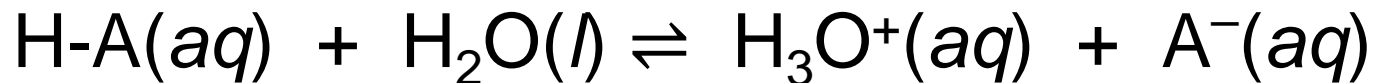
and
Bases

Carboxylic Acids

- Organic acids containing the -COOH group.
- Factors contributing to their acidic behavior:
 - Other O attached to C draws electron density from O-H bond, increasing polarity.
 - Its conjugate base (carboxylate anion) has resonance forms to stabilize the anion.



Factors that Affect Acid Strength



1) H-A bond must be **polarized** with δ^+ on the H atom and δ^- on the A atom.

2) **Bond strength**: Weaker bonds can be broken more easily, making the acid stronger.

3) **Stability of A^-** : More stable anion means stronger acid.

Acid: H—F
pK_a: 3.2

H—Cl
-7

H—Br
-9

H—I
-10

Acids
and
Bases

Effect of electronegativity

For the same row: **more electronegativity** → **more acidic**

Consider series of C, N, O, F acids

Acid:	CH₄	NH₃	H₂O	H—F
pK _a :	48	38	15.7	3.2

1. C-H bond is the least polarized; H-F bond is the **most polarized**.

2. Anions of these conjugate bases is more stabilized by the **higher-electronegative** atom.

Effect of hybridization

More 's' character in the orbital → more stable anion

Consider Alkynes, Alkenes, Alkanes

Acid:	$\text{HC}\equiv\text{CH}$	$\text{H}_2\text{C}=\text{CH}_2$	$\text{H}_3\text{C}-\text{CH}_3$
pK_a:	25	44	50
Hybrid.	sp	sp²	sp³
% s:	50	33	25

Effect of Inductive Effects

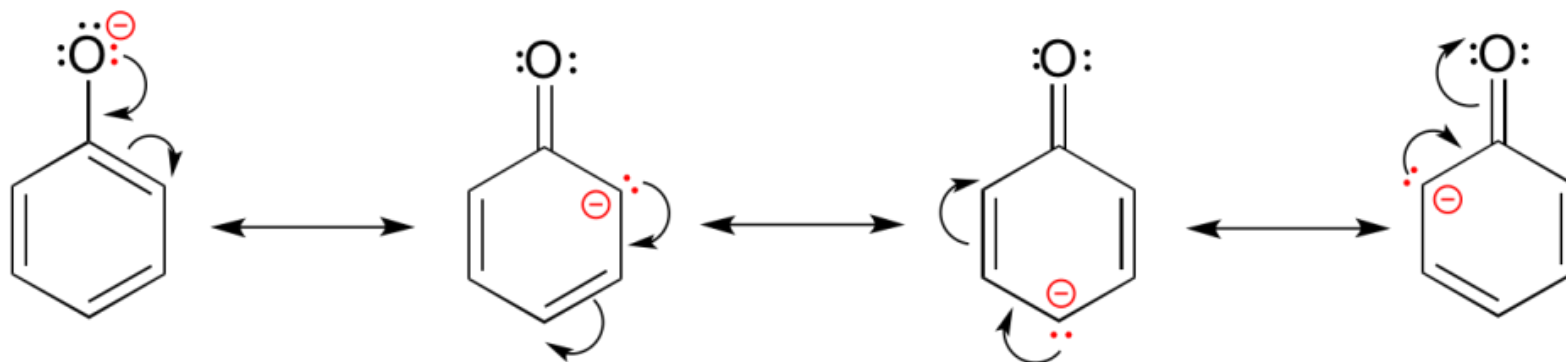
Polarized bonds affect neighboring atoms (high-electronegative atoms), also so-called electron-withdrawing effect.



The further away from F, the less the inductive effect

Acid	Formula	$K_a(25^\circ\text{C})$
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	CH_2ClCOOH	1.4×10^{-3}
Dichloroacetic	CHCl_2COOH	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

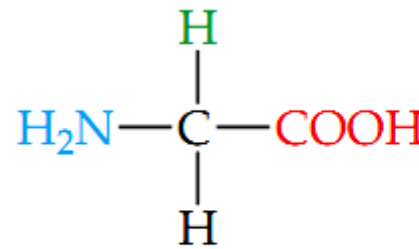
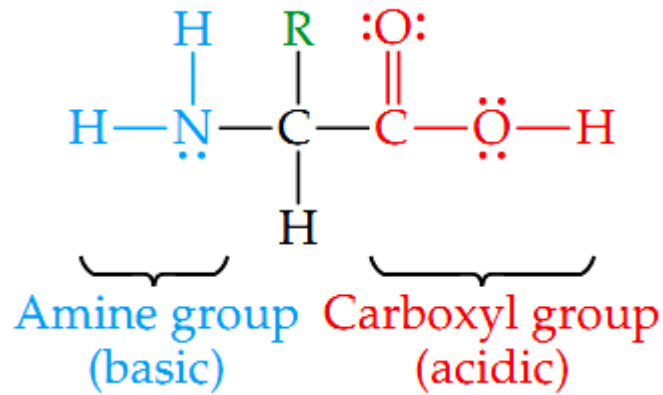
Effect of Resonance Effect



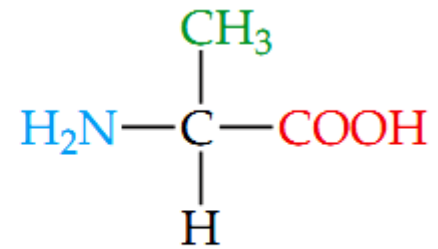
$$K_a \text{ of PhO-H} = 1.3 \times 10^{-10}$$

Anion of these conjugate bases can become more stabilized by the resonance structures.

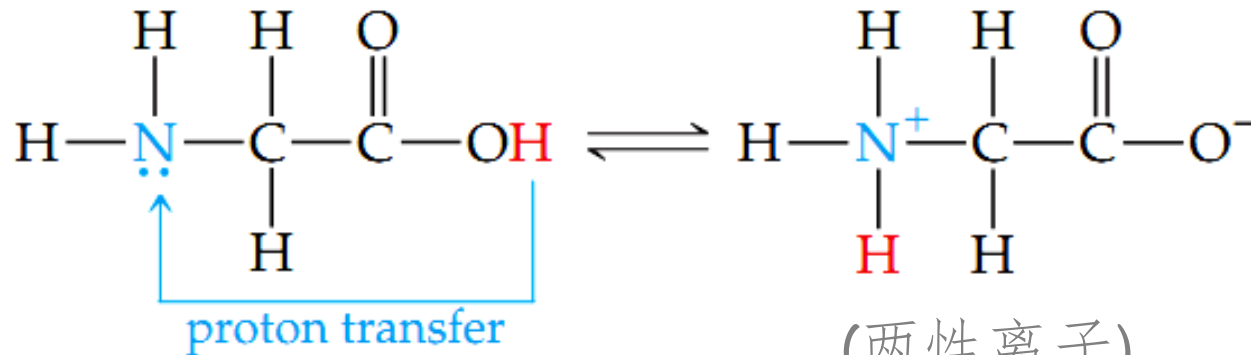
Amphiprotic Behavior of Amino Acids



Glycine



Alanine



Neutral molecule

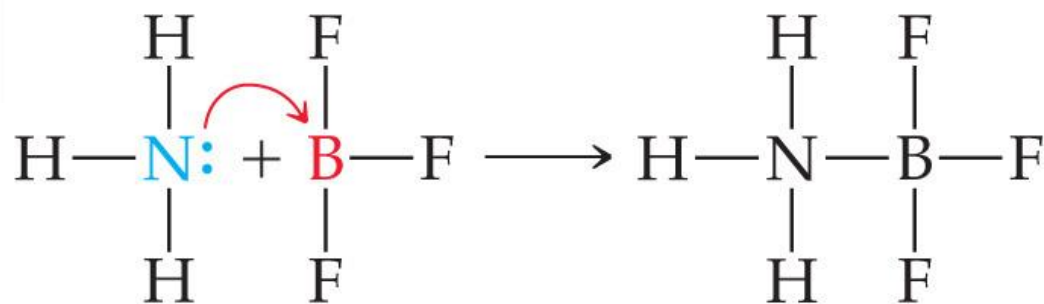
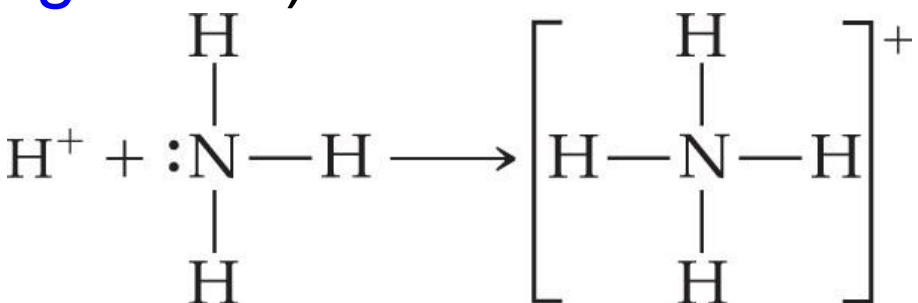
(两性离子)

Zwitterion

- Crystalline amino acids have **relatively high melting points**, which is characteristic of **ionic solids**.
- Amino acids are far **more soluble in water** than in nonpolar solvents.

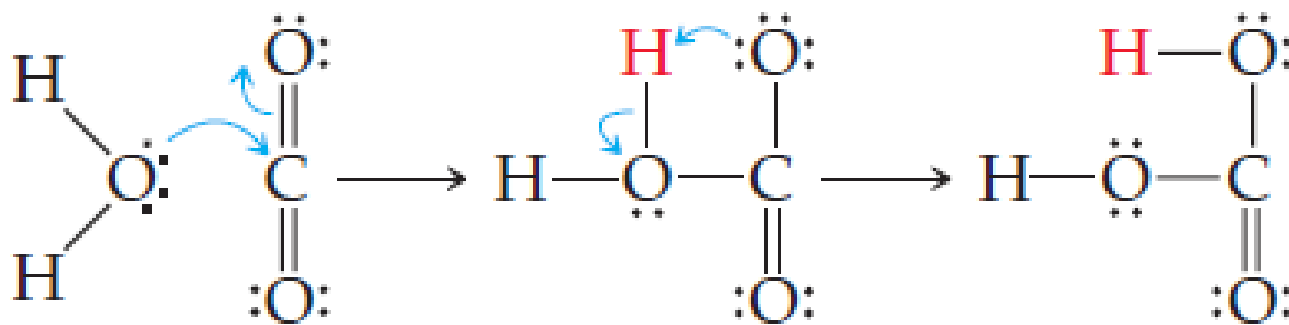
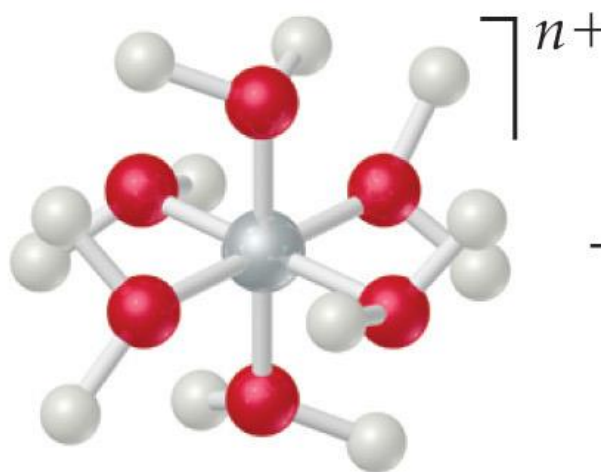
Lewis Acid/Base Chemistry

- Lewis **acids**: **electron pair acceptors**.
- Lewis **bases**: **electron pair donors**.
- All Brønsted–Lowry acids and bases are also called Lewis acids and bases.
- There are compounds which do *not* meet the Brønsted–Lowry definition which meet the (**more general**) Lewis definition.



Lewis
base

Lewis
acid



A Brønsted-Lowry acid is

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

A Brønsted-Lowry base is

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

A Lewis acid is

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

A Lewis base is

- a. a proton donor.
- b. a proton acceptor.
- c. an electron-pair donor.
- d. an electron-pair acceptor.

Which of the following is the conjugate base of HPO_4^{2-} ?

- a. H_3PO_4
- b. $\text{H}_2\text{PO}_4^{1-}$
- c. PO_4^{3-}
- d. HPO_3^{2-}

Which of the following is the conjugate acid of SO_4^{2-} ?

- a. H_2SO_4
- b. HSO_4^{1-}
- c. SO_3^{2-}
- d. H_3SO_4^+

The stronger the acid, the (X) its conjugate base.
Acids and bases react to form their (Y) conjugates.

- a. X = stronger, Y = stronger
- b. X = stronger, Y = weaker
- c. X = weaker, Y = stronger
- d. X = weaker, Y = weaker

For a conjugate acid-base pair, $K_w = K_a \text{ ______ } K_b$.

- a. +
- b. -
- c. ×
- d. /

What is the pH of a 0.0200 M aqueous solution of HBr?

- a. 1.00
- b. 1.70
- c. 2.30
- d. 12.30

What is the pH of a 0.0400 M aqueous solution of KOH?

- a. 12.60
- b. 10.30
- c. 4.00
- d. 1.40

Which solution has the higher pH, a 0.001 *M* solution of NaOH or a 0.001 *M* solution of Ba(OH)₂?

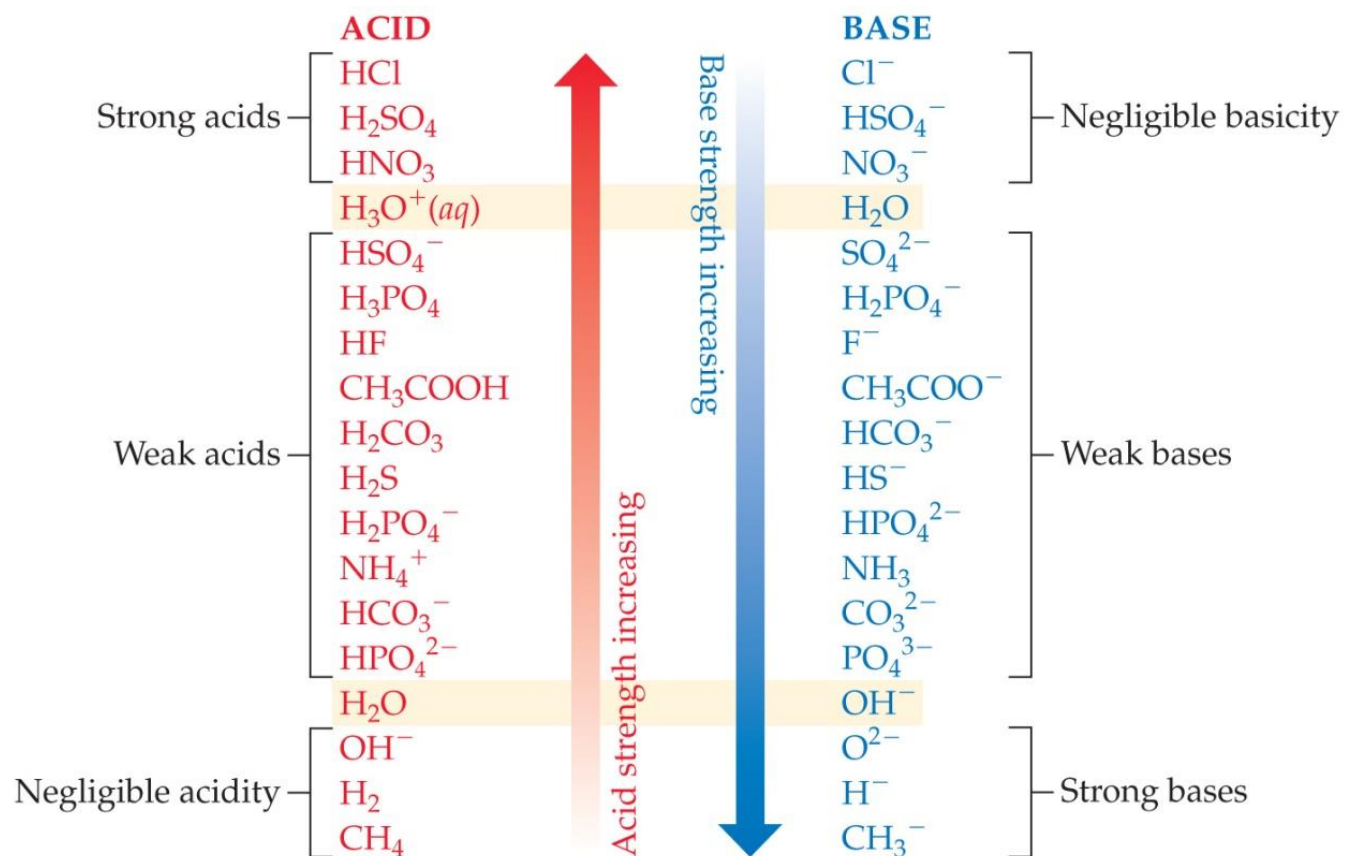
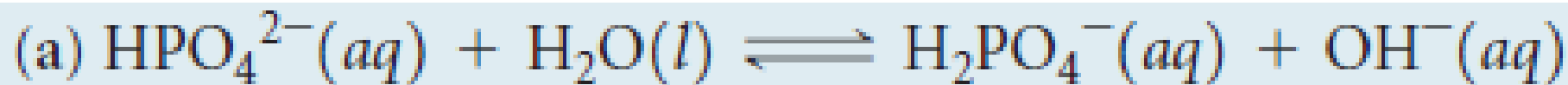
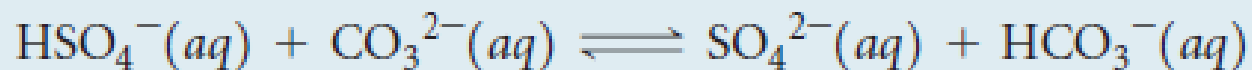
- A. 0.001 *M* solution of Ba(OH)₂ has the higher pH.
- B. 0.001 *M* solution of NaOH has the higher pH.
- C. Both solutions have the same pH as both have the same concentration.

Is it possible for a solution to have a negative pH? If so, would that pH signify a basic or acidic solution?

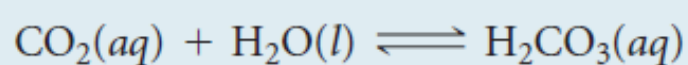
- A. No, the pH range is 1-14.
- B. No, the definition of pH does not permit it to have a negative value.
- C. Yes, for any solution with a concentration of base greater than 1 *M*.
- D. Yes, for any solution with a concentration of acid greater than 1 *M*.



For the following proton-transfer reaction use Figure 16.3 to predict whether the equilibrium lies to the left ($K_c < 1$) or to the right ($K_c > 1$):



The solubility of CO_2 in water at 25°C and 0.1 atm is 0.0037 M . The common practice is to assume that all the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced in the reaction



K_{a1}	K_{a2}
4.3×10^{-7}	5.6×10^{-11}

What is the pH of a 0.0037 M solution of H_2CO_3 ?

Calculate the percentage of HF molecules ionized in (a) a 0.10 M HF solution, (b) a 0.010 M HF solution.

$$K_a = 6.8 \times 10^{-4}.$$

(a) The equilibrium reaction and equilibrium concentrations are as follows:

	$\text{HF}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{F}^-(aq)$
Initial	0.10 M		0		0
Change	$-x M$		$+x M$		$+x M$
Equilibrium	$(0.10 - x) M$		$x M$		$x M$

The equilibrium-constant expression is

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4}$$

What is the pH of a 0.100 M aqueous solution of NH_3 ?
The K_b of NH_3 is 1.8×10^{-5} .

- a. 1.00
- b. 4.74
- c. 9.36
- d. 11.13

The CH_3^- ion is the conjugate base of CH_4 , and CH_4 shows no evidence of being an acid in water. What happens when CH_3^- is added to water?

- A. Nothing happens when CH_3^- is added to water.
- B. CH_3^- loses a proton to form CH_2^{2-} when added to water.
- C. CH_3^- reacts with water to form CH_3OH and H^+ .
- D. CH_3^- removes a proton from water to form CH_4 and OH^- .



Which acid has the larger acid-dissociation constant, HIO_2 or HBrO_3 ?

- A. HIO_2
- B. HBrO_3

Which of the following correctly lists the acids in order of decreasing strength?

- a. $\text{HClO}_2 > \text{HClO} > \text{HBrO} > \text{HIO}$
- b. $\text{HClO} > \text{HBrO} > \text{HIO} > \text{HClO}_2$
- c. $\text{HIO} > \text{HBrO} > \text{HClO} > \text{HClO}_2$
- d. $\text{HClO}_2 > \text{HIO} > \text{HBrO} > \text{HClO}$

Summary of Chapter 16

Arrhenius/Brønsted/Lewis acids & bases

Conjugate acids and bases

Amphiprotic, autoionization, ion product constant (K_w)

Acid and base strength (pH), acid dissociation constant (K_a or pK_a), base dissociation constant (K_b or pK_b), percent ionization

Polyprotic acids, binary acids, oxyacids, zwitterion

**Thank You for Your
Attention!
Any Questions?**

