CHEM103
General Chemistry

Chapter 4: Reactions in Aqueous Solution

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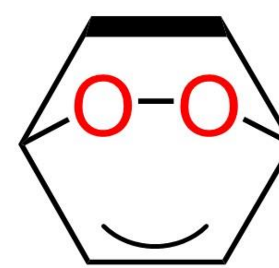


Assignments 2-3 & Mid-term EXAM

Please either **print** the Answer Sheet or **use** your paper; **write down** your answers on your sheet/paper.

Please submit your assignments to any of your TAs or me during the classes. Or you can submit your assignment to the folder **outside room 520**, **research building 1** (anytime you like).

Homework 2

Due date: **17 Sep. (Sat)**

Homework 3

Due date: **21 Sep. (Wed)**

Mid-term EXAM

13 Nov. 10-12 AM (Sun)

Review on Chapter 3

Stoichiometry: Quantity of Substances; Balanced Chemical Formulas and Equations

Chemical Equations: Law of Conservation of Mass; Reactant & Product; States

Reaction Types: Combination, Decomposition & Combustion Reactions

Weights: Formula Weight; Molecular Weight; Percent Composition

Moles: Avogadro's Number; Molar Mass; Moles

Stoichiometric Calculations: Limiting Reactants; Excess Reagent; Theoretical/Actual Yields

Outline of Chapter 4

(Aqueous) Solution, Solvent, Solute

Dissociation: (Strong & Weak) Electrolyte; Conductivity

Precipitation: Solubility; Metathesis (Exchange) Reactions; Molecular and (Net) Ionic Equations

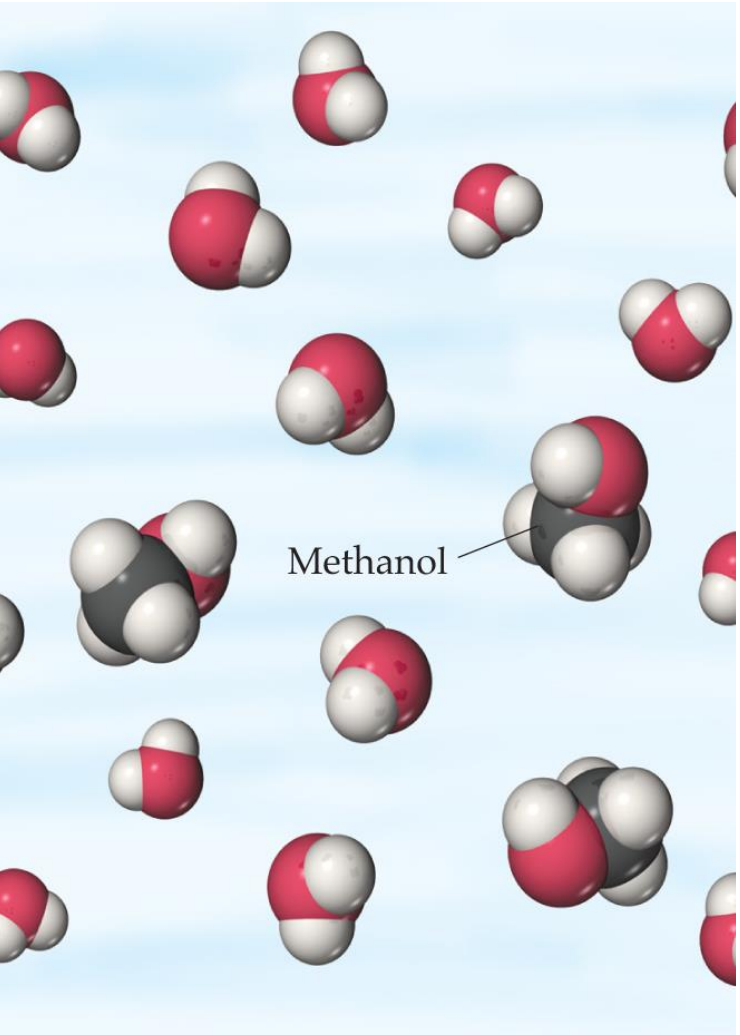
Acid-Base: Arrhenius/Brønsted Acids & Bases; Neutralization; Salt; Gas-forming Reactions

Oxidation-Reduction (Redox) Reaction: Oxidation numbers; Displacement Reactions; Activity Series

Concentration: Molarity; Dilution; Titration

Solutions
(learn more from Chapters 13 & 17)

Solutions (溶液)



(b) Molecular substances like methanol, CH_3OH, dissolve without forming ions

- **Solutions**: **homogeneous mixtures** of **two or more** pure substances (one as **liquid** generally).

- The **solvent** (溶剂) is present in **greatest quantity** & acts as a **dissolving medium**. If **water** is the solvent, → **aqueous** solution.
- The other substances (**smallest amount**) are **solutes** (溶质) & dissolved (溶解) in the solvent.

e.g. a solution of NaCl + Methanol + H_2O (excess).

$$H_2O(l) + CO_2(aq) + CaCO_3(s) \longrightarrow Ca(HCO_3)_2(aq)$$

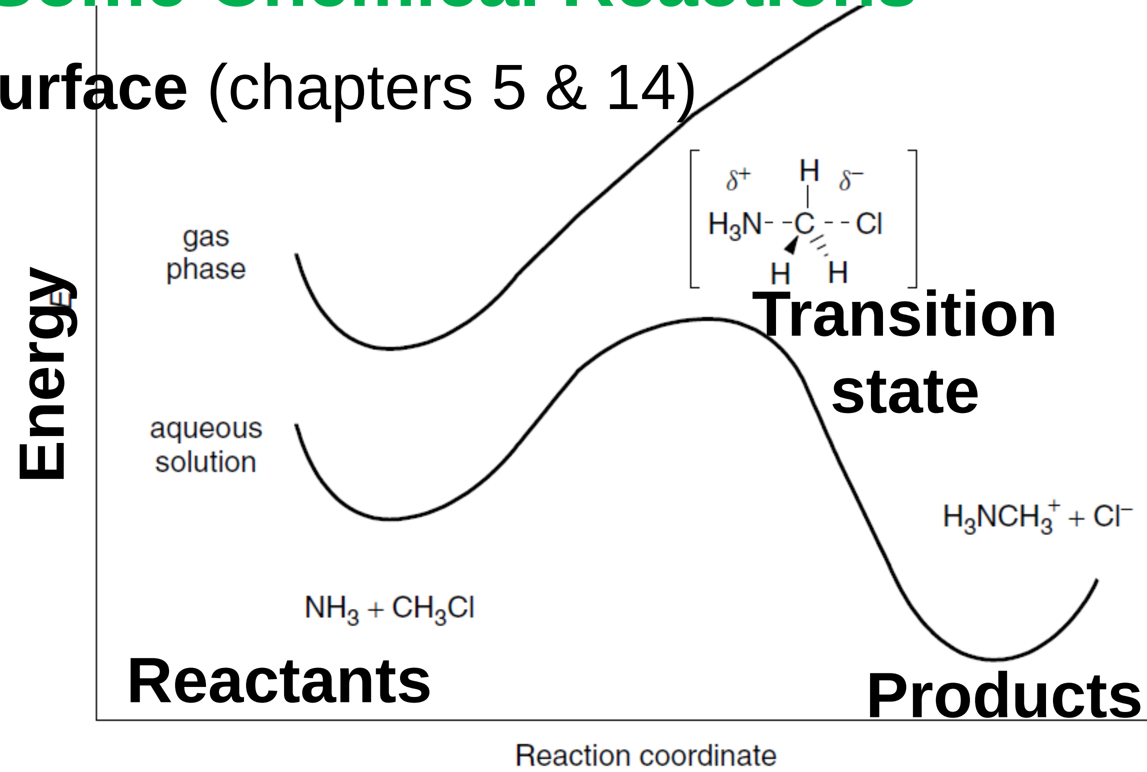
water + carbon dioxide + calcium carbonate → calcium bicarbonate (or calcium hydrogen carbonate)

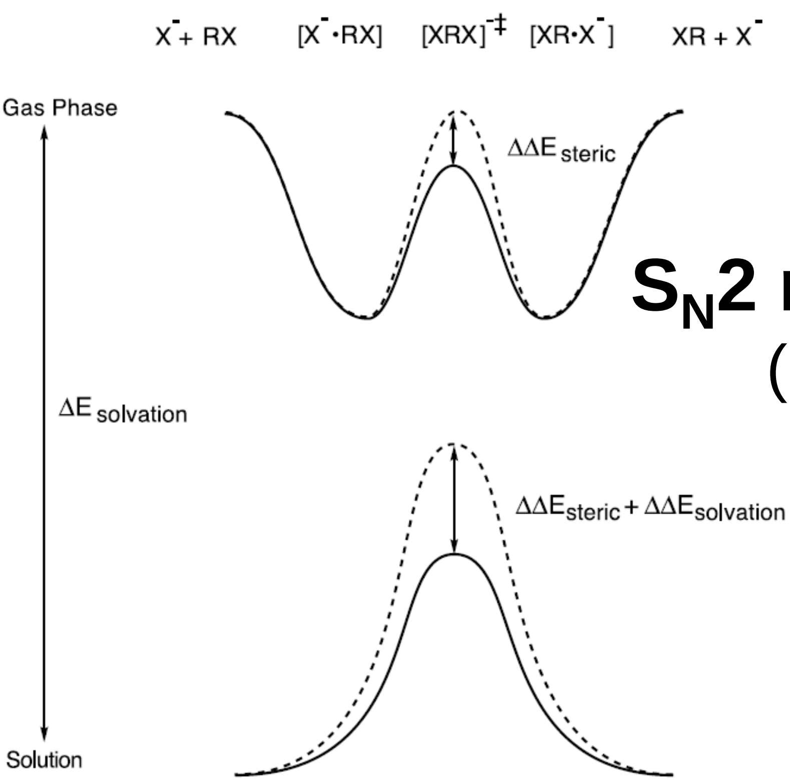
Aqueous Reactions

Effect of Solvent on Some Chemical Reactions (Extra Info.)

Energy surface (chapters 5 & 14)

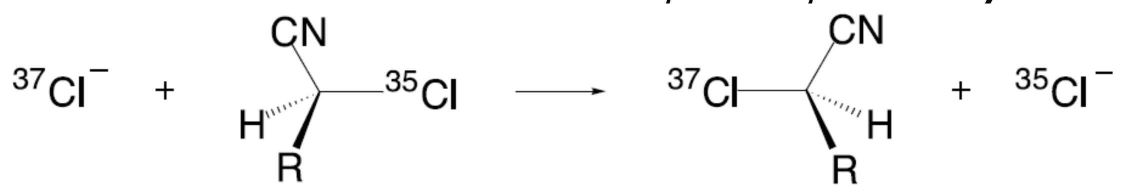
Menschutkin reaction





S_N2 reaction (nucleophilic substitution)

(Brauman *Science* **2002**, *295*, 2245)



$R = CH_3$ **1** $\quad R = C(CH_3)_3$ **2**

Anomalous (异常) or Unusual Properties of Water (Extra Info.)

1. Water has unusually high melting point. [Explanation]
2. Water has unusually high boiling point. [Explanation]
3. Water has unusually high critical point. [Explanation]

1. No aqueous solution is ideal. [Explanation]
2. D_2O and T_2O differ significantly from H_2O in their physical properties. [Explanation]
3. Liquid H_2O and D_2O differ significantly in their phase behavior. [Explanation]
4. H_2O and D_2O ices differ significantly in their quantum behavior. [Explanation]

1. The heat of fusion of water with temperature exhibits a maximum at -17 °C. [Explanation]
2. Water has over twice the specific heat capacity of ice or steam. [Explanation]
3. The specific heat capacity (C_P and C_V) is unusually high. [Explanation]

	COMPOUND	BOILING POINT	FREEZING POINT
H_2Te	Hydrogen Telluride	-4°C	-49°C
H_2Se	Hydrogen Selenide	-42°C	-64°C
H_2S	Hydrogen Sulfide	-62°C	-84°C
H_2O	Water	100°C	0 °C

http://www1.lsbu.ac.uk/water/anmlies.html (some were listed above)
http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Bulk_Properties/Unusual_Properties_of_Water

Is the **density** of **ice** always lower than that of liquid **water**?

H_2O ice in H_2O

1 proton for H

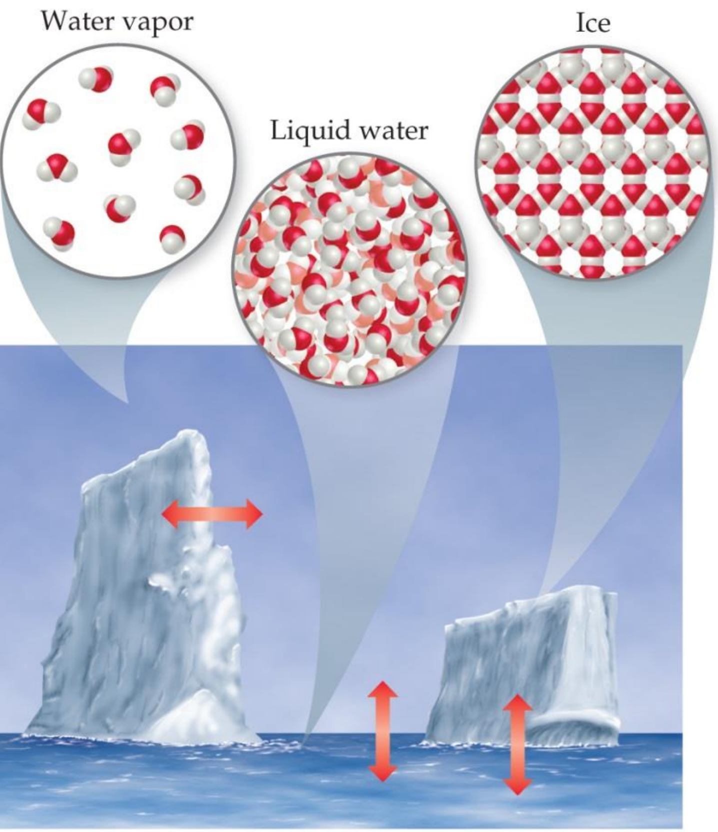
（氢）

D_2O ice in H_2O

1 proton + 1 neutron for deuterium (D,氘）

Aqueous Reactions

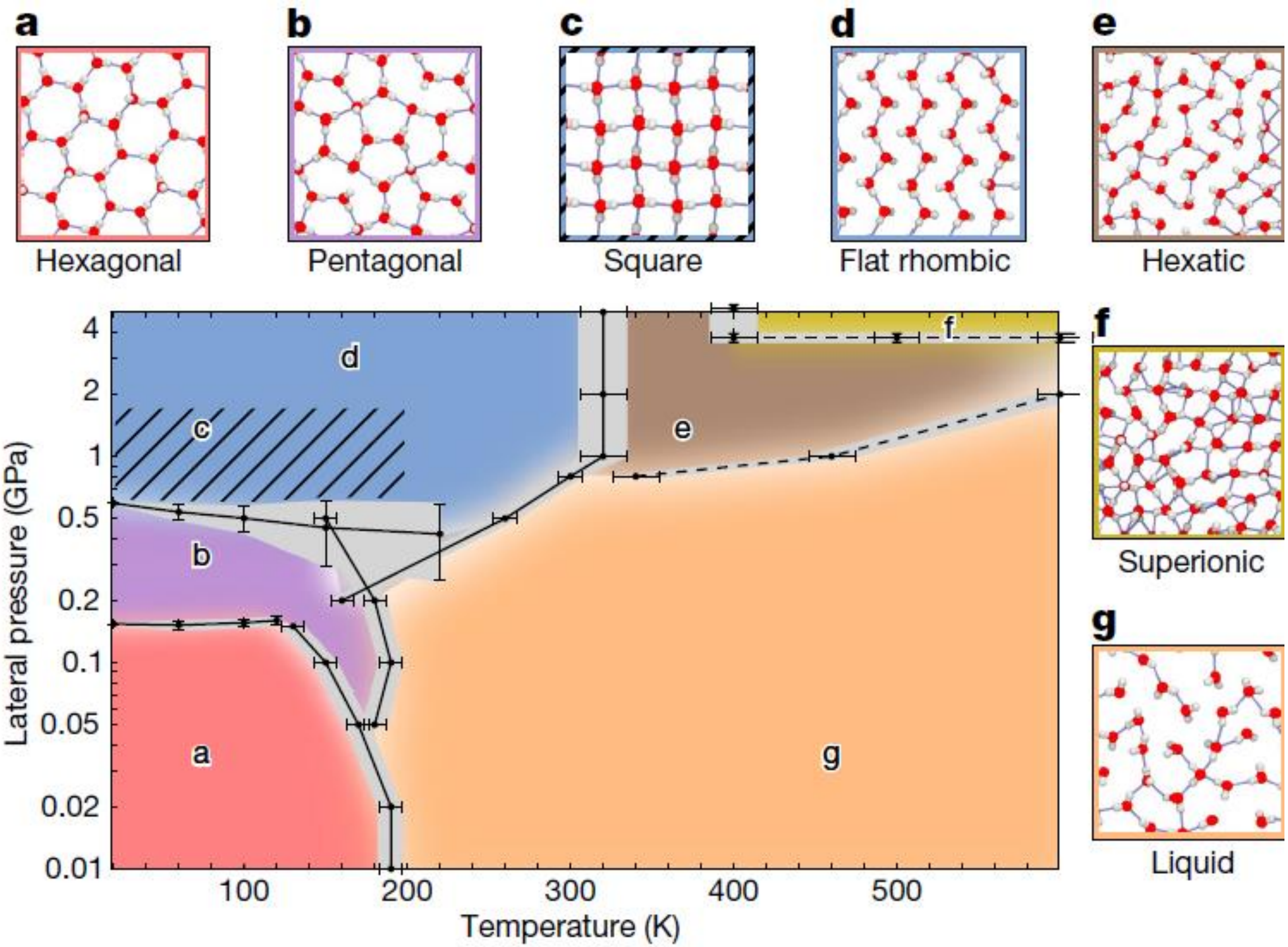
Molecular Dynamics (分子动力学) (Computational Chemistry计算化学): Molecular Scales (Extra Info.)



Freezing and Melting of Water (Iwao Ohmine, a former student of Prof. Martin Karplus 2013 Nobel Winner): *Nature* **2002**, 416, 409; *Nature* **2013**, 498, 350)

The first-principles phase diagram of monolayer nanoconfined water

Venkat Kapil[1]✉, Christoph Schran[1,2,3]✉, Andrea Zen[4,5], Ji Chen[6], Chris J. Pickard[7,8] & Angelos Michaelides[1,2,3]✉

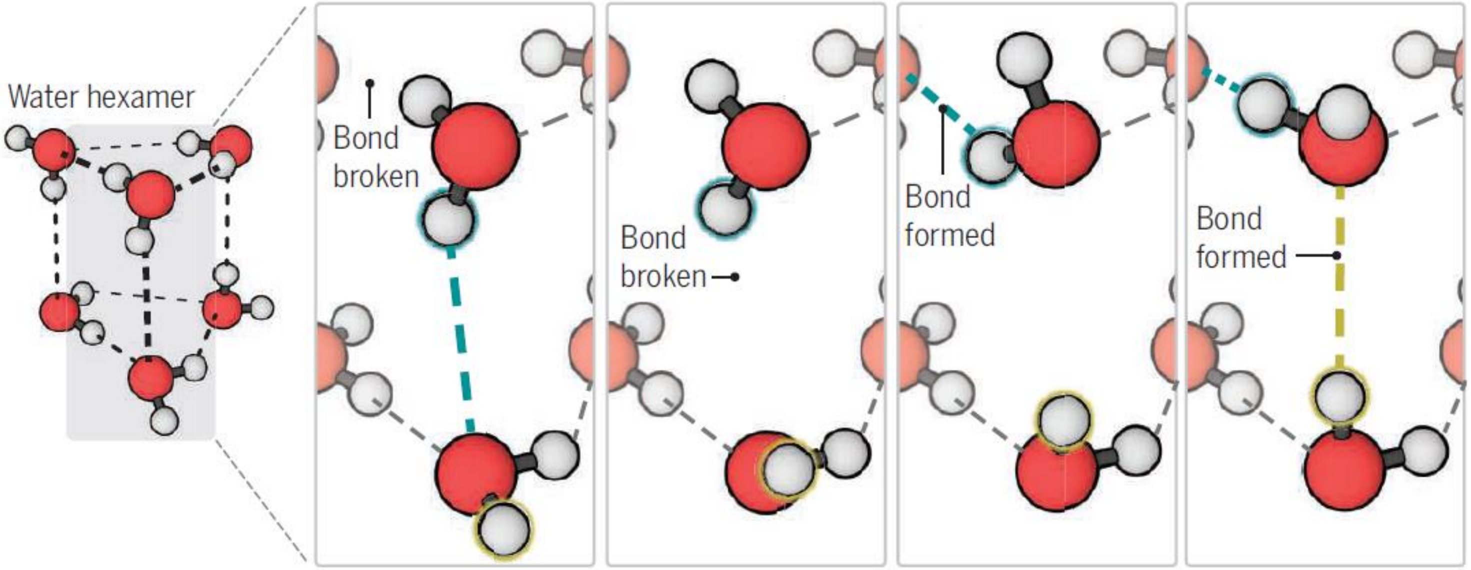


(Extra Info.)

(*Nature* **2022**, *609*, 512)

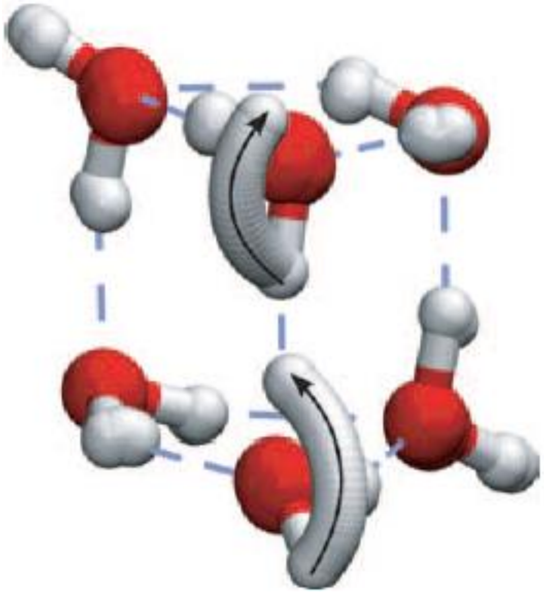
Aqueous Reactions

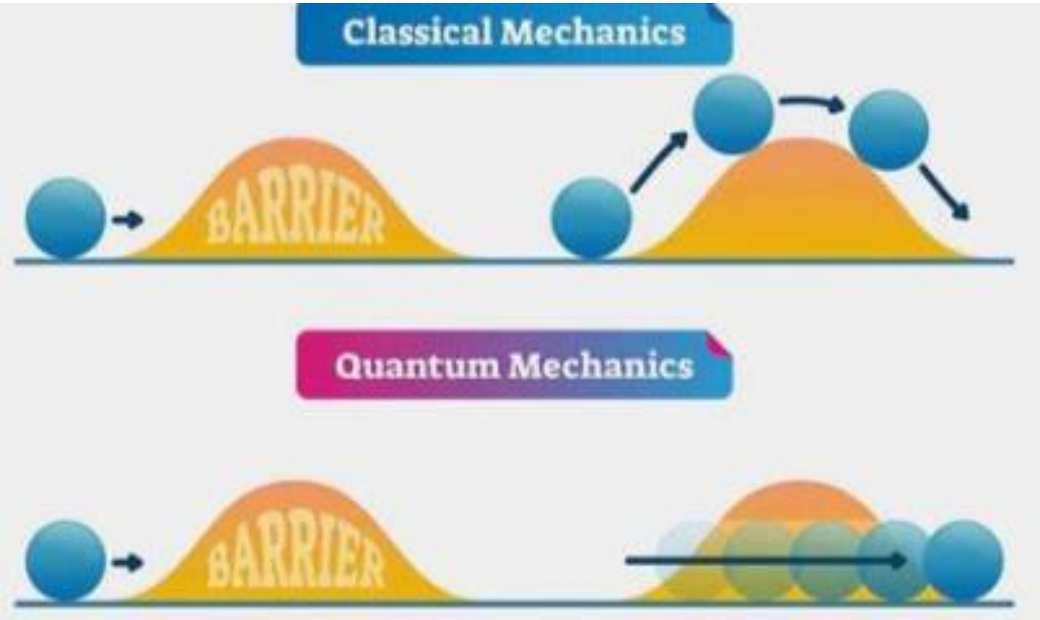
(Extra Info.) Tunneling effect (introduce in Chapter 6)



The smallest water cluster with 3-D H-bond networks.

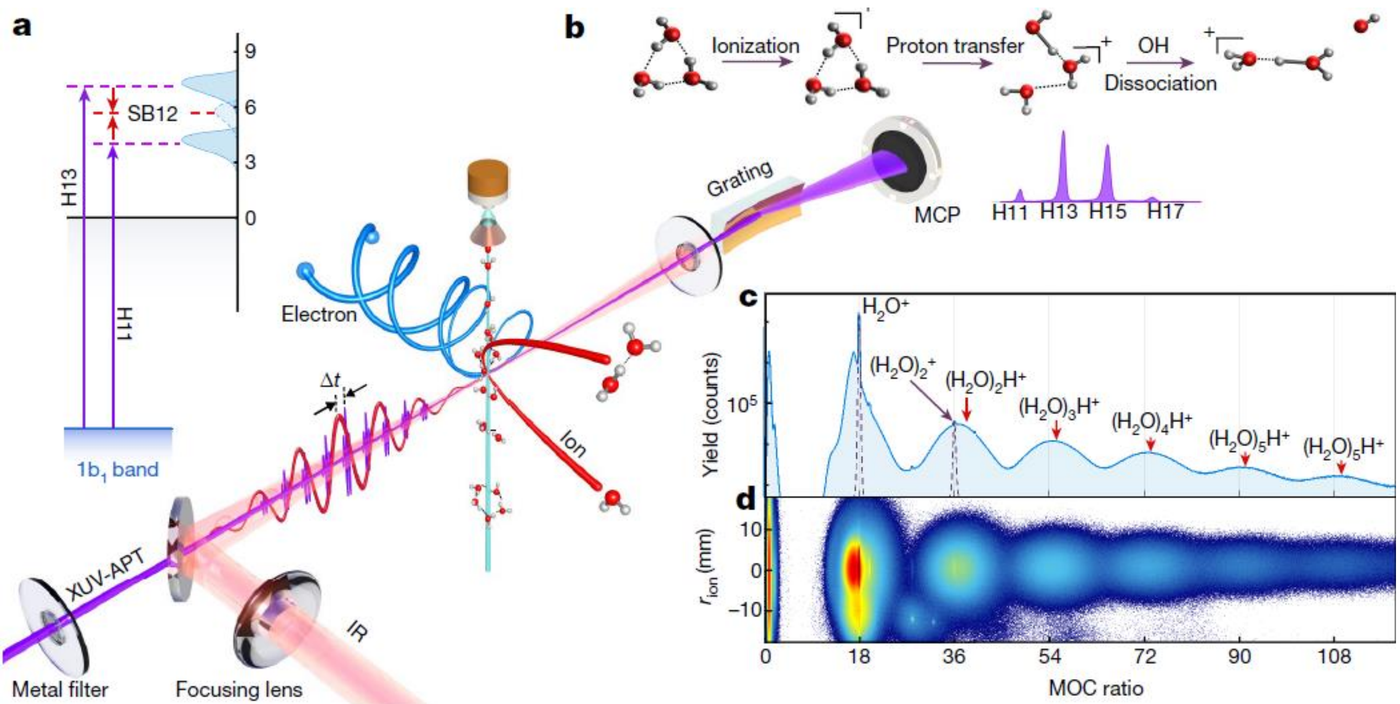
Rotational spectral: Concerted hydrogen-bond breaking by quantum tunneling (*Science* **2016**, *351*, 1310)



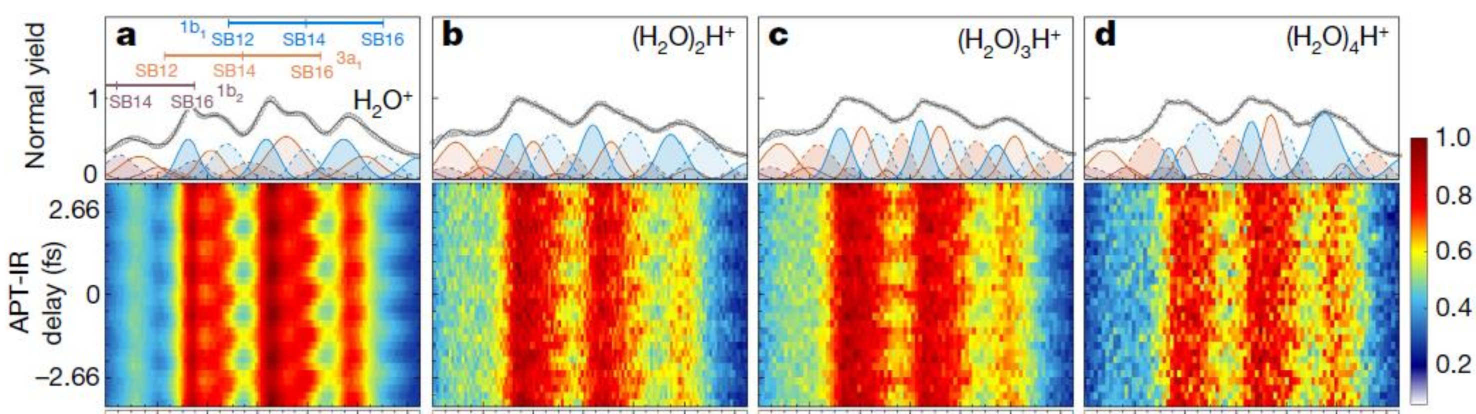


Attosecond spectroscopy of size-resolved water clusters

Xiaochun Gong[1,2,4], Saijoscha Heck[1,4], Denis Jelovina[1], Conaill Perry[1], Kristina Zinchenko[1], Robert Lucchese[3] & Hans Jakob Wörner[1]✉



(Extra Info.)

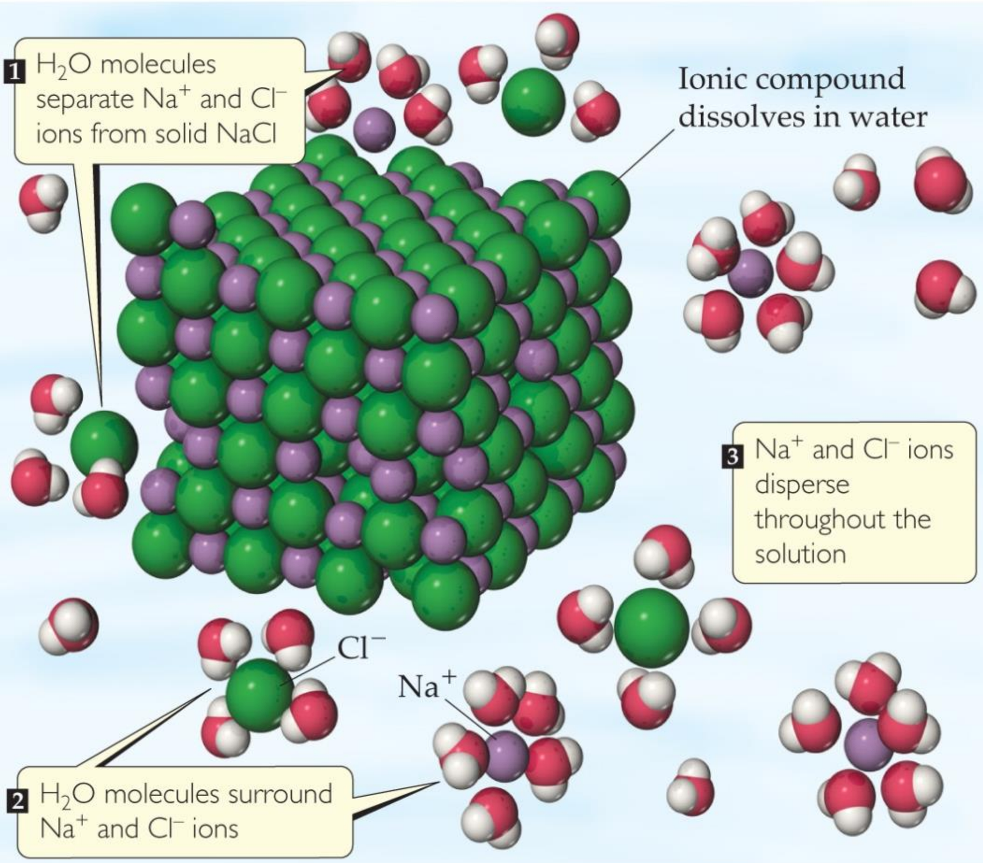


(*Nature* **2022**, *609*, 507)

Aqueous Reactions

Dissociation

Dissociation (解离)

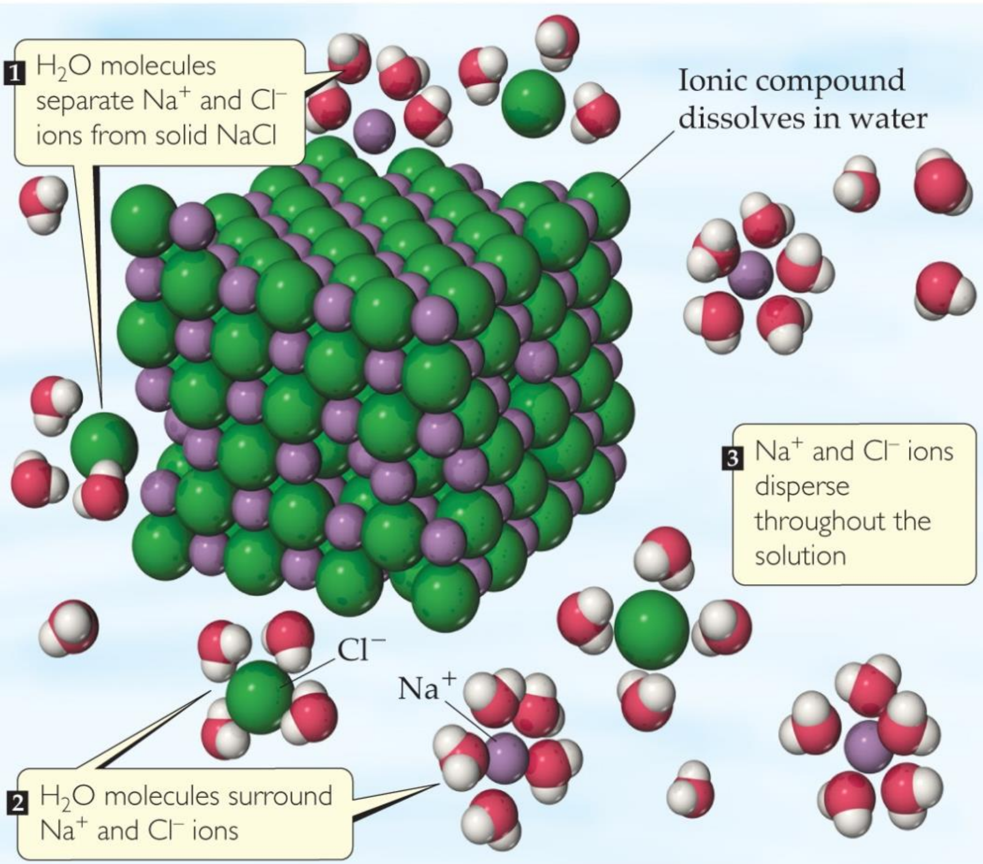


(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve

- When an **ionic** substance (e.g. NaCl, sodium chloride) **dissolves** (溶解) in solvent (e.g. water), the solvent pulls the individual ions from the crystal (晶体); the solvent then **solvates these ions** (**Na^+(*aq*) and Cl^-(*aq*)**).

- This process is called **dissociation** (解离): dissolve & dissociate.

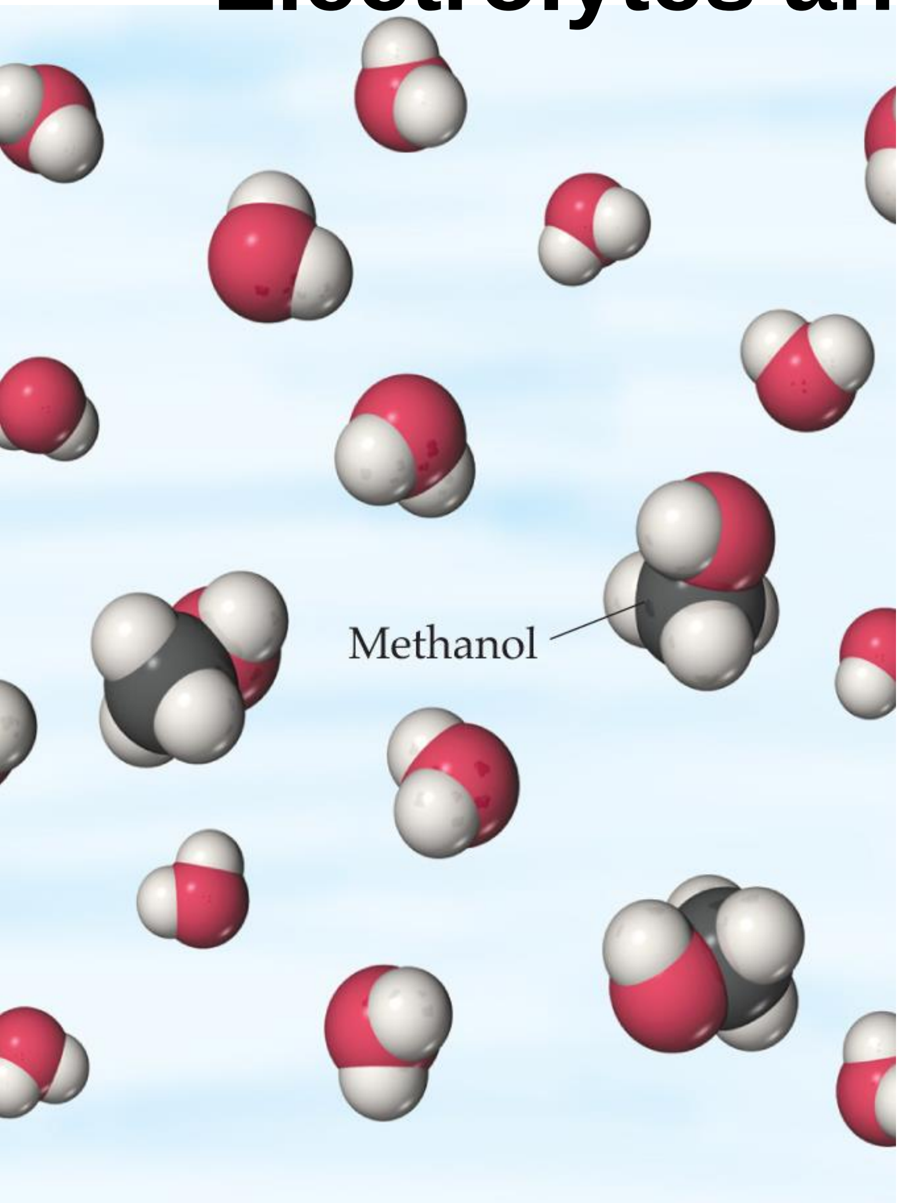
Electrolytes and Nonelectrolytes



(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve

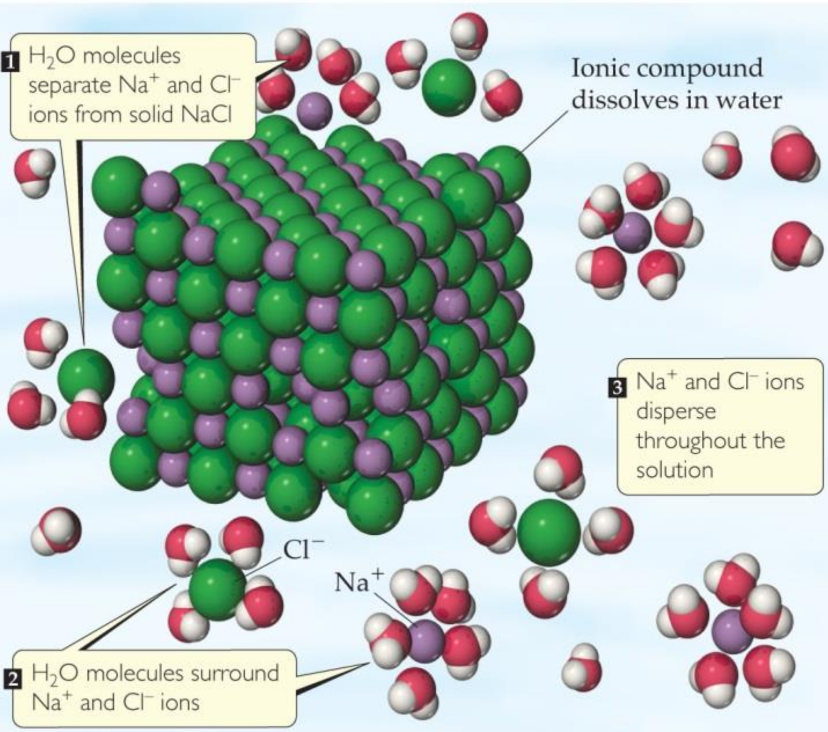
- An **electrolyte**（电解质）is a substance that **dissociates into ions** (e.g. Na^+ and Cl^- for NaCl) when it **dissolves** in water.

Electrolytes and Nonelectrolytes



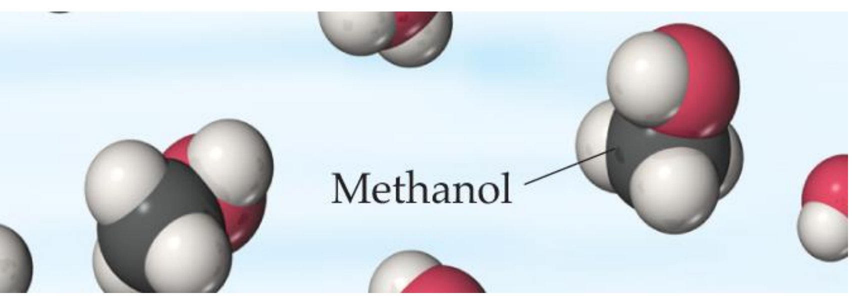
(b) Molecular substances like methanol, CH_3OH, dissolve without forming ions

- A **nonelectrolyte**（非电解质） may **dissolve** in water, but it does **NOT dissociate into ions** (e.g. CH_3OH).



(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve

Soluble （可溶的） **ionic compounds** (metal cations + nonmetal anions) tend to be **electrolytes**.

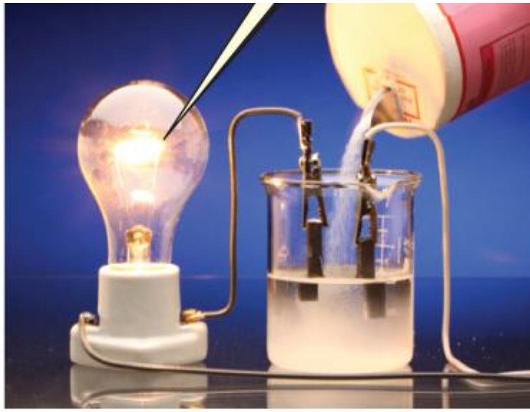


Molecular compounds (mostly **nonmetals**) tend to be **nonelectrolytes**, **except for acids (e.g. HCl) and bases**.

Electrolytes: Conductivity（导电性）

Pure water,
$H_2O(l)$
does not conduct electricity

Sucrose solution,
$C_{12}H_{22}O_{11}(aq)$
Nonelectrolyte
does not conduct electricity



Sodium chloride solution,
$NaCl(aq)$
Electrolyte
conducts electricity

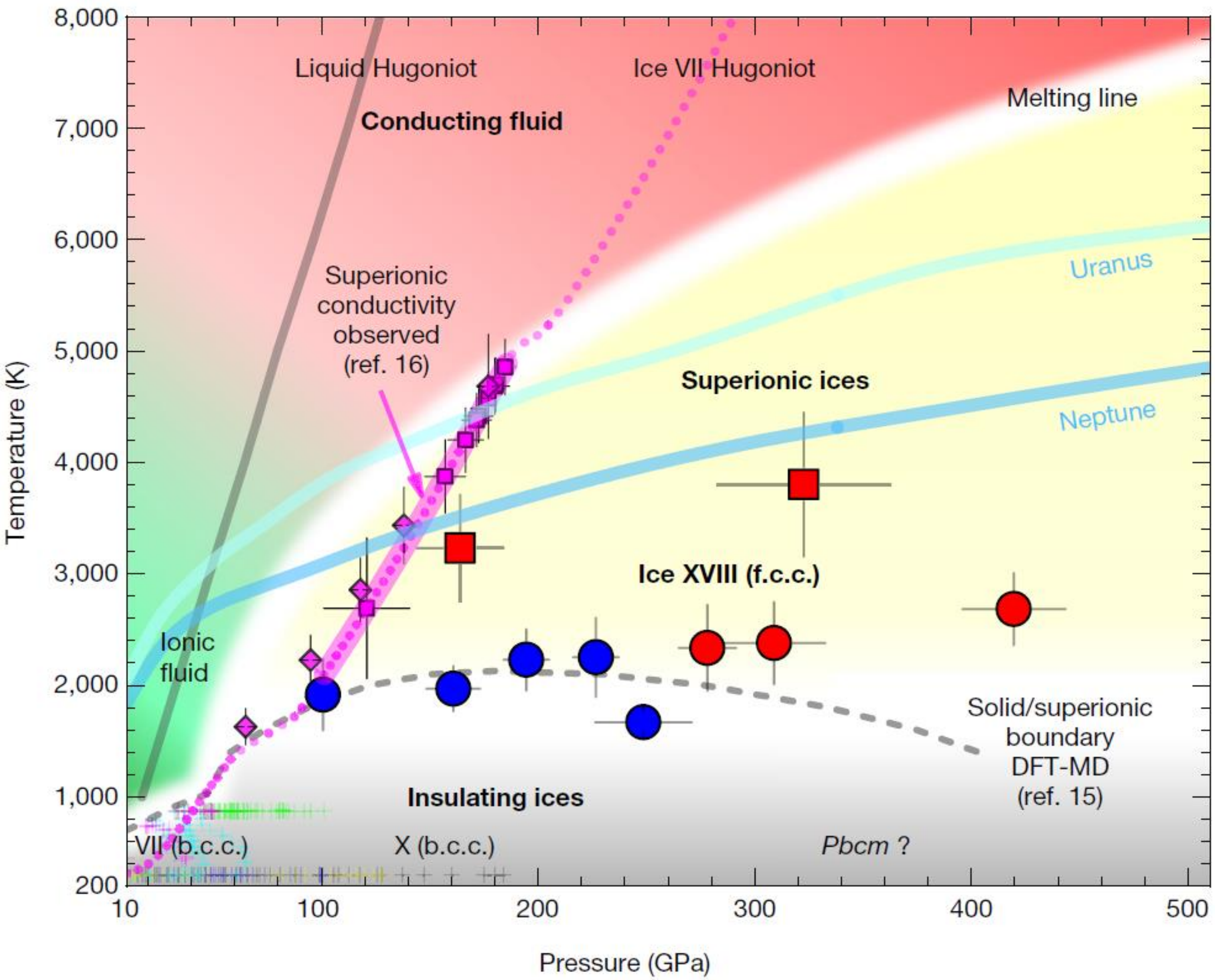
- A **strong electrolyte** dissociates (nearly) **completely** into ions when it dissolves in water → a **good** conductor.

- A **weak electrolyte** only dissociates **partially** when it dissolves in water→ a **poor** conductor.

(Extra Info.)

Nanosecond X-ray diffraction of shock-compressed superionic water ice

Marius Millot[1,3]*, Federica Coppari[1,3]*, J. Ryan Rygg[1,2], Antonio Correa Barrios[1], Sebastien Hamel[1], Damian C. Swift[1] & Jon H. Eggert[1]



Ice XVIII:

Superionic ice phase at 100-400 GPa & 2000-3000 K

Crystalline lattice of oxygen & liquid-like protons

(*Nature* **2019**, *569*, 251)

Aqueous Reactions

Strong Electrolytes

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids, weak bases	All other compounds

- **Soluble ionic salts**
- Strong acids
- Strong bases

Ionic salts are strong electrolytes if the dissolved part completely dissociates in water.

eg. $NaCl(s) \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$

Sodium chloride

Strong Acids & Bases

TABLE 4.2 • Common Strong Acids and Bases

Strong Acids	Strong Bases
Hydrochloric, HCl	Group 1A metal hydroxides [LiOH, NaOH, KOH, RbOH, CsOH]
Hydrobromic, HBr	Heavy group 2A metal hydroxides [$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$]
Hydroiodic, HI	
Chloric, $HClO_3$	
Perchloric, $HClO_4$	
Nitric, HNO_3	
Sulfuric, H_2SO_4	

What dissolved species are present in a solution of

a. KCN,

b. $NaClO_4$?

a.

A. $H_2O(l)$

B. $K^+(aq)$ and $H_2O(l)$

C. $CN^-(aq)$

$\boxed{D.}$ $K^+(aq)$ and $CN^-(aq)$

b.

A. $H_2O(l)$

B. $Na^+(aq)$ and $H_2O(l)$

C. $ClO_4^-(aq)$

$\boxed{D.}$ $Na^+(aq)$ and $ClO_4^-(aq)$

钠离子Na^+ sodium ion

钾离子K^+ potassium ion

高氯酸根离子ClO_4^- perchlorate ion

氰离子CN^- cyanide ion

Which solute will cause the lightbulb in Figure 4.2 to glow most brightly, CH_3OH, NaOH, or CH_3COOH?

A. $CH_3OH(aq)$
B. NaOH(aq)
C. $CH_3COOH(aq)$
D. Cannot determine from Figure 4.2

醋酸-acetic acid

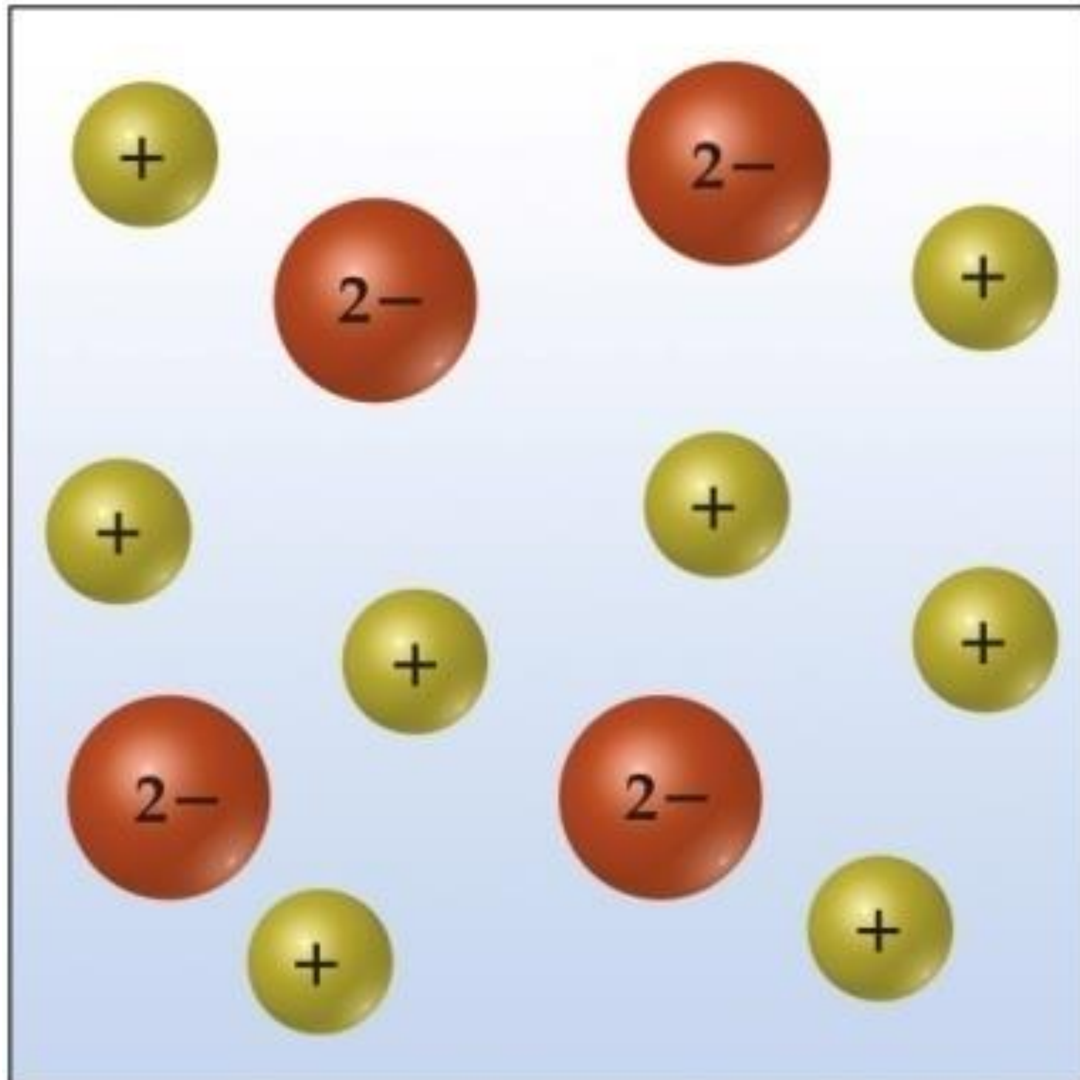
$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

A strong electrolyte completely dissociates into ions.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

A weak electrolyte partially dissociates: **equilibrium**.

The below diagram represents an aqueous solution of either $MgCl_2$, KCl, or K_2SO_4. Which solution does the drawing best represent?



ANS: K_2SO_4

Classify these dissolved substances as a strong, weak, or nonelectrolyte: $CaCl_2$, HNO_3, C_2H_5OH (ethanol), HCOOH (formic acid), KOH.

Check ionic compound or molecular compound?

1. **Ionic** compounds: $CaCl_2$ and KOH → strong electrolytes

2. **Molecular** compounds: HNO_3, HCOOH and C_2H_5OH

2a. HNO_3 and HCOOH are acids.

HNO_3 is a **strong acid** → a strong electrolyte

HCOOH is a **weak acid** → a weak electrolyte

2b. C_2H_5OH, is neither an acid nor a base → a nonelectrolyte.

HCOOH formic acid (甲酸, 蚁酸)

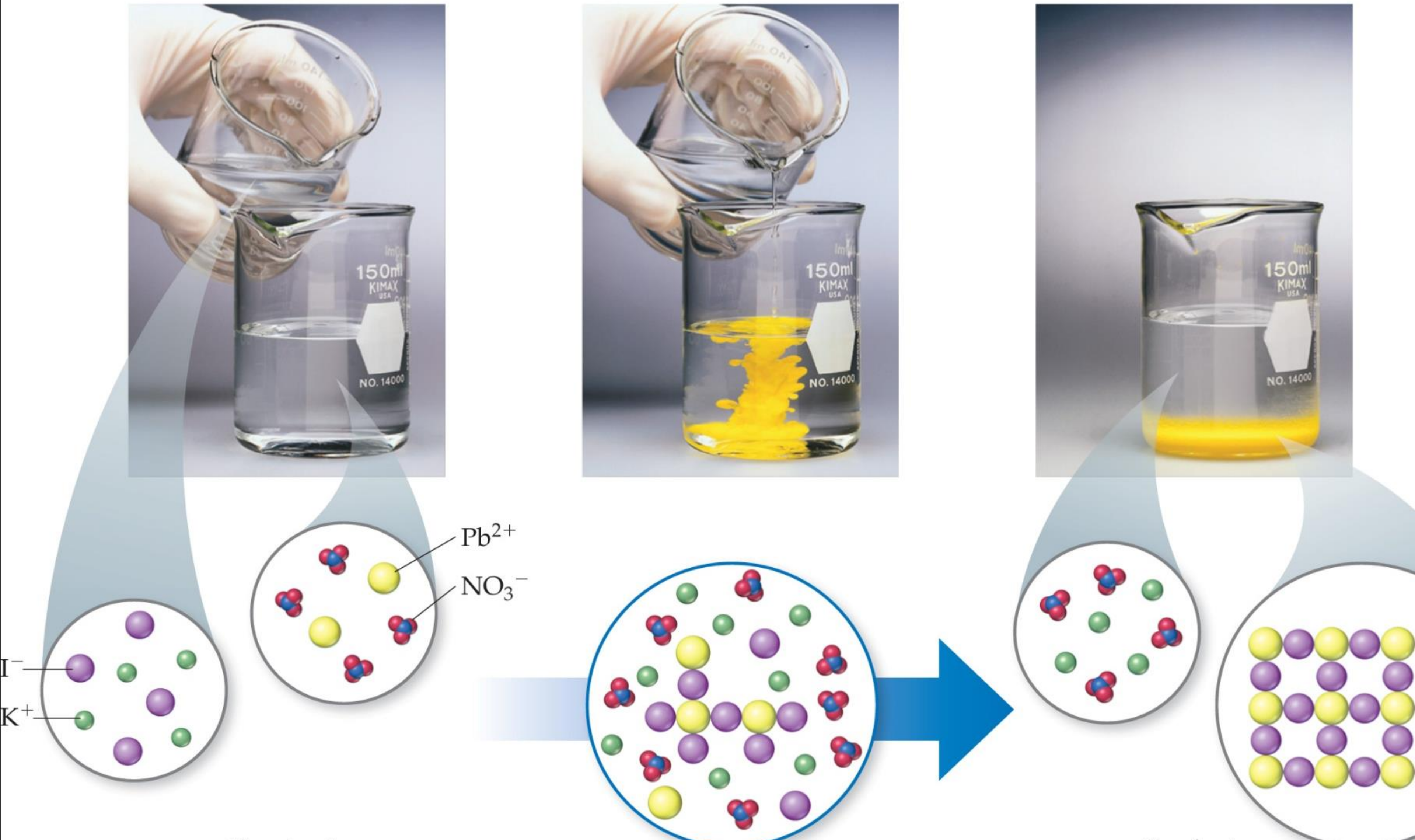
Precipitation

Precipitation（沉淀反应） Reactions

When one mixes ions that **form** **insoluble** (不可溶的) **compounds** (could be predicted by the solubility guidelines), a **precipitate** (沉淀物) in a **solid** form is formed.

Interactions between the cations and anions are **too strong** to be separated (dissolved).

Which ions remain in solution after PbI_2 precipitation is complete?



Reactants
$2\ KI(aq) + Pb(NO_3)_2(aq)$

$\longrightarrow$
$Pb^{2+}(aq)$ and $I^-(aq)$ combine to form precipitate

Products
$\boxed{PbI_2(s)} + 2\ KI(aq)$
$+\ KNO_3$

Solubility guidelines (Nitrate, acetate, chloride, bromide, iodide, sulfate, sulfide, carbonate, phosphate, hydroxide)

TABLE 4.1 • Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		**Important Exceptions**
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}

Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

I^- 碘离子 iodide ion; I 碘 iodine;
Br^- 溴离子 bromide ion; Br 溴 bromine
Cl^- 氯离子 chloride ion; Cl 氯 chlorine
F^- 氟离子 fluoride ion; F 氟 fluorine

Aqueous Reactions

Metathesis (Exchange) Reactions

复分解(交换)反应

- Metathesis: from a Greek word that means “to transpose (调换).”

$$AX + BY \rightarrow AY + BX$$

$AgNO_3(aq) + KCl(aq) \longrightarrow$

Metathesis (Exchange) Reactions
复分解(交换)反应

- Metathesis: from a Greek word that means "to transpose (调换)."

- Appears as though the ions in the reactant compounds **exchange** or transpose **ions**:

$$\mathbf{Ag}NO_3(aq) + K\mathbf{Cl}(aq) \longrightarrow \mathbf{AgCl}(s) + KNO_3(aq)$$

Solution Chemistry

- It is helpful to pay attention to *exactly* what species are present in a reaction mixture (i.e., solid, liquid, gas, aqueous solution).

$$BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\ KCl(aq)$$

- If we like to understand **reactivity**, we must be **aware** of just **what** is **changing** during the course of a reaction.

Molecular Equation

The **molecular equation** lists the reactants and products in their **molecular form**:

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

Ionic Equation

- In the **ionic equation,** **all strong electrolytes** (strong acids, strong bases, and soluble ionic salts) are **dissociated into their ions** (e.g. $Na^+(aq)$ and $Cl^-(aq)$).

- This **more accurately reflects the species** that are found in the reaction mixture:

$$\mathbf{Ag^+}(aq) + NO_3^-(aq) + K^+(aq) + \mathbf{Cl^-}(aq) \longrightarrow$$
$$\mathbf{AgCl}(s) + K^+(aq) + NO_3^-(aq)$$

- Ions which do not involve the reaction are called **spectator ions** (they were **deleted** from the **net ionic equation**). e.g. $NO_3^-(aq)$ & $K^+(aq)$.

Net Ionic Equation (净离子方程式)

- To form the **net** ionic equation, **delete anything (spectator ions)** that does **not change** from both the left and right sides of the equation:

$$\mathbf{Ag^+}(aq) + \cancel{NO_3^-}(aq) + \cancel{K^+}(aq) + \mathbf{Cl^-}(aq) \longrightarrow \mathbf{AgCl}(s) + \cancel{K^+}(aq) + \cancel{NO_3^-}(aq)$$

- The only things left in the equation are ions that change (i.e., react) during the course of the reaction:

$$\mathbf{Ag^+}(aq) + \mathbf{Cl^-}(aq) \longrightarrow \mathbf{AgCl}(s)$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(aq)$$

Classify these ionic compounds as soluble or insoluble in water: (a) sodium carbonate, Na_2CO_3, (b) lead sulfate, $PbSO_4$.

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

(a) Most carbonates are insoluble, carbonates of the alkali metal cations (such as Na^+) are an exception: **soluble**.

(b) Although most sulfates are water soluble, $PbSO_4$ is exceptionally **insoluble**.

When $Fe(NO_3)_2$ dissolves in water, the particles in solution are

a. Fe^{+} and $(NO_3)_2^{-}$.
b. Fe^{2+} and 2 NO_3^{-}.
c. Fe and 2 NO_3.
d. Fe and N_2 and 3 O_2.

Which compound below is NOT soluble in water?

a. NaBr
b. KNO_3
c. $MgSO_4$
d. ZnS

Which ions, if any, are spectator ions in the reaction?

$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2NaNO_3(aq)$

A. $Ba^{2+}(aq)$ and $NO_3^-(aq)$
B. $NO_3^-(aq)$ and $SO_4^{2-}(aq)$
C. $Na^+(aq)$ and $NO_3^-(aq)$
D. No spectator ions are involved

Writing Net Ionic Equations

1. Write a balanced molecular equation.

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

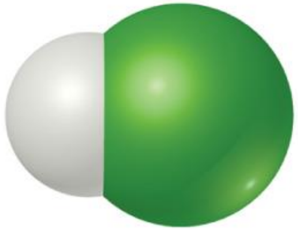
2. Express dissociation of all strong electrolytes into **ions** (e.g. $K^+(aq)$, $Cl^-(aq)$).

$$Ag^+(aq) + NO_3^-(aq) + K^+(aq) + Cl^-(aq) \longrightarrow$$
$$AgCl(s) + K^+(aq) + NO_3^-(aq)$$

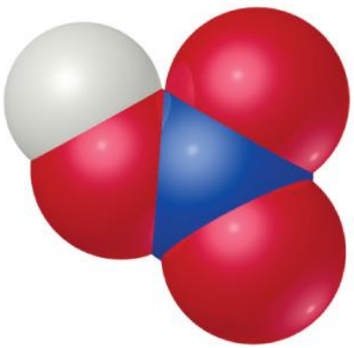
3. Delete spectator ions from **both the sides** of the equation.

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

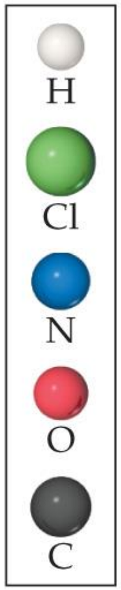
Acids & Bases
(learn more from Chapters 16-17)

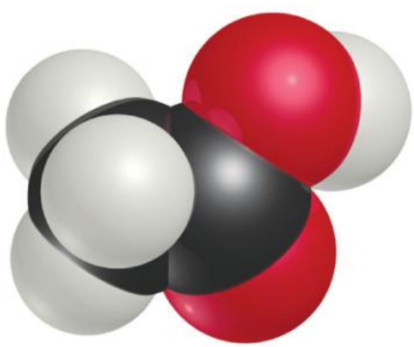


Hydrochloric acid, HCl



Nitric acid, HNO_3





Acetic acid, CH_3COOH

Acids

- **Arrhenius** defined acids as substances that **increase the concentration of H$^+$(*aq*)** when it **dissolves** in water (**Arrhenius acid-base** theory 阿伦尼乌斯酸碱理论).

- Both **Brønsted** and Lowry defined them as **proton donors** (质子供体) (**Brønsted**-Lowry acid-base theory 布朗斯特–劳里酸碱理论).

H$^+$: proton ion; **H**: hydrogen atom
H$^-$: hydride ion

Extra Info.: more general definition by Lewis acid-base theory (in terms of "electron", Chapter 17).

Seven **strong acids** (**complete ionization** to give $H^+(aq)$, strong electrolyte):

Hydrochloric Acid (HCl)
Hydrobromic Acid (HBr)
Hydroiodic Acid (HI)
Nitric Acid (HNO_3)
Sulfuric Acid (H_2SO_4)
Chloric Acid ($HClO_3$)（氯酸）
Perchloric Acid ($HClO_4$)（高氯酸）

$$HA(aq) \longrightarrow H^+(aq) + A^-(aq)$$

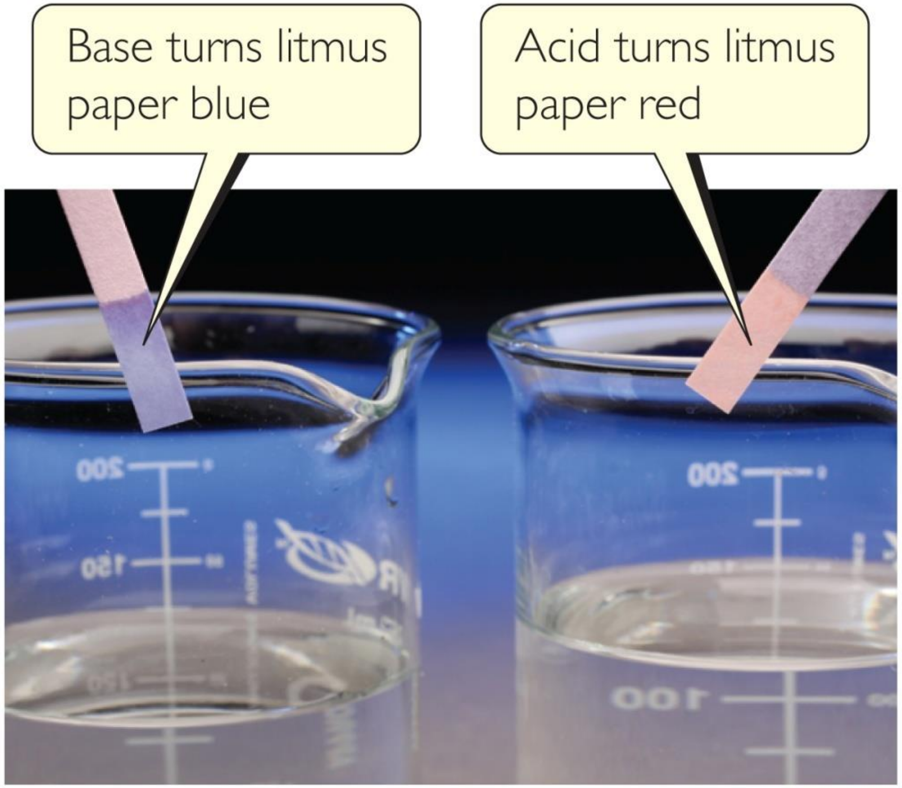
Weak acids (**partial ionization** to give $H^+(aq)$): e.g. Acetic acid (CH_3CO_2H).

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Monoprotic acid (HA) & Diprotic acid (H_2A)

Bases

- **Arrhenius** defined bases as substances that **increase the concentration of $OH^-(aq)$** when it dissolves in water.
- **Brønsted** and Lowry defined them as **proton acceptors** （质子受体）.



Litmus paper (石蕊试纸)

The **strong bases** are the ***soluble*** **metal hydroxide (MOH)** with **complete ionization (dissociation)**:

Metals (M):

Alkali metals（碱金属）

Calcium（钙）

Strontium（锶）

Barium（钡）

$$MOH(aq) \longrightarrow M^+(aq) + OH^-(aq)$$

$$H^+(aq) + B^-(aq) \longrightarrow HB(aq)$$

(e.g. B^- is OH^-)

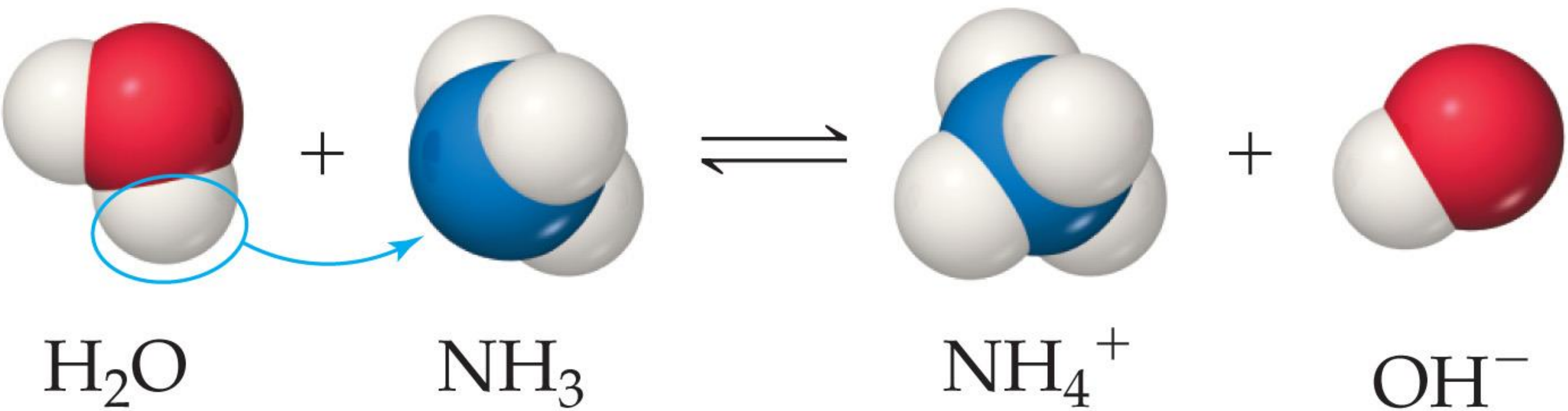
Weak bases:

e.g. NH_3

$$H^+(aq) + B^-(aq) \rightleftharpoons HB(aq)$$

Acid-Base Reactions

In an acid-base reaction, the acid donates a proton (H^+) to the base.



partial ionization **~1 %**

Neutralization Reactions (中和反应)

Generally, when solutions of an acid and a base are combined, the products are a **salt** and **water**:

$$CH_3CO_2H(aq) + NaOH(aq) \longrightarrow CH_3CO_2Na(aq) + H_2O(l)$$

When a strong acid reacts with a strong base, the net ionic equation is

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

$$H^+(aq) + \cancel{Cl^-}(aq) + \cancel{Na^+}(aq) + OH^-(aq) \longrightarrow \cancel{Na^+}(aq) + \cancel{Cl^-}(aq) + H_2O(l)$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Gas-Forming Reactions

1. When a **carbonate** (CO_3^{2-}) **or hydrogen carbonate** (**bicarbonate**, HCO_3^-) reacts with an acid, the products are a salt, **gaseous carbon dioxide**, and water.

$$NaHCO_3(aq) + HBr(aq) \longrightarrow NaBr(aq) + \mathbf{H_2CO_3(aq)}$$

$$\mathbf{H_2CO_3(aq)} \longrightarrow NaBr(aq) + \mathbf{CO_2(g)} + H_2O(l)$$

$$CaCO_3(s) + HCl(aq) \longrightarrow CaCl_2(aq) + \mathbf{CO_2(g)} + H_2O(l)$$

Calcium Carbonate 碳酸钙

Sodium hydrogen carbonate 碳酸氢钠

Aqueous Reactions

2. When a **sulfite** (SO_3^{2-}) reacts with an acid, the products are a salt, **gaseous sulfur dioxide**, and water:

$$SrSO_3(s) + 2HI(aq) \longrightarrow SrI_2(aq) + \mathbf{SO_2(g)} + H_2O(l)$$

Strontium sulfite 亚硫酸锶

3. When a **sulfide** (S^{2-}) reacts with an acid, the products are a salt and **bad-smell** gas (**H_2S**):

$$Na_2S(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + \mathbf{H_2S(g)}$$

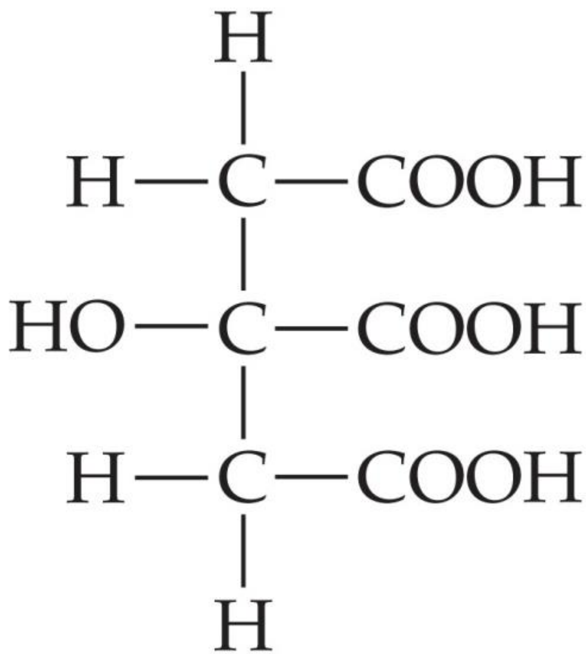
Sulfuric acid 硫酸

Hydrogen sulfide 硫化氢

Antacids（抗酸剂）

Commercial Name	Acid-Neutralizing Agents
Alka-Seltzer®	$NaHCO_3$
Amphojel®	$Al(OH)_3$
Di-Gel®	$Mg(OH)_2$ and $CaCO_3$
Milk of Magnesia	$Mg(OH)_2$
Maalox®	$Mg(OH)_2$ and $Al(OH)_3$
Mylanta®	$Mg(OH)_2$ and $Al(OH)_3$
Rolaids®	$NaAl(OH)_2CO_3$
Tums®	$CaCO_3$

The structural formula of citric acid, a main component of citrus fruits, is



柠檬酸

How many $H^+(aq)$ can be generated by each citric acid molecule dissolved in water?

A. 4

B. 1

C. 2

D. 3

Aqueous Reactions

Why isn't $Al(OH)_3$ classified as a strong base?

A. $Al(OH)_3$ is not basic in water.
B. $Al(OH)_3$ is insoluble in water.
C. $Al(OH)_3$ is a strong acid in water, not basic.
D. $Al(OH)_3$ is a weak acid in water, not basic.

Aluminium hydroxide (氢氧化铝)

When an acid reacts with a base, the result is

a. cancellation.
b. elimination.
c. neutralization.
d. adduct formation.

Which compound below is NOT a strong acid?

a. CH_3CO_2H
b. H_2SO_4
c. HNO_3
d. HBr

By analogy to examples given in the text, predict what gas forms when $Na_2SO_3(s)$ reacts with $HCl(aq)$.

A. $SO_2(g)$
B. $H_2(g)$
C. $CO_2(g)$
D. $H_2S(g)$

sodium sulfite 亚硫酸钠
Sodium sulfide 硫化钠
Sodium sulfate 硫酸钠
Sulfur dioxide 二氧化硫
Sulfite ion 亚硫酸根离子
Bisulfite 亚硫酸氢根离子
Sulfate ion 硫酸根

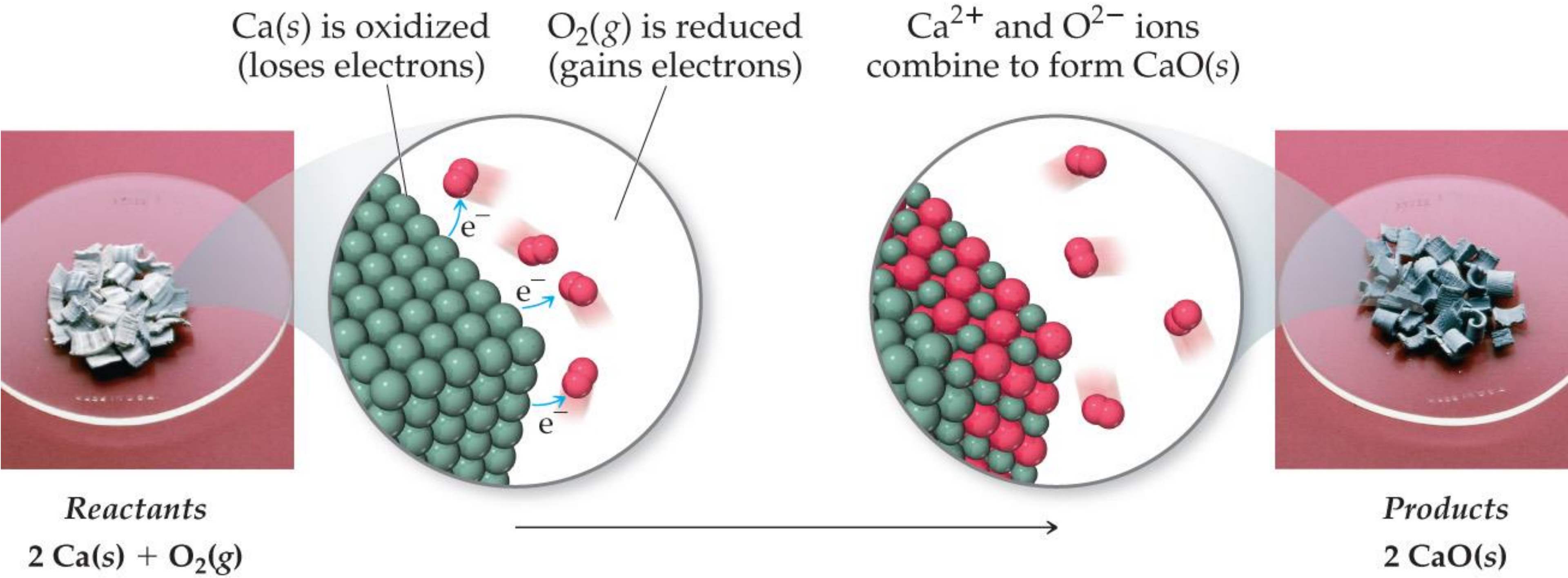
$$Na_2SO_3(aq) + 2HCl(aq) \longrightarrow SO_2(g) + NaCl(aq) + H_2O$$

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow SO_2(g) + H_2O$$

Oxidation-Reduction Reactions (learn more from Chapter 20)

Oxidation-Reduction (Redox) Reactions

(氧化–还原反应)



- An **oxidation** occurs when an atom, molecule or ion (e.g. metals) ***loses*** electron(s).
- A **reduction** occurs when an atom, molecule or ion (the right side of periodic table) ***gains*** electron(s).
- One **CANNOT occur without the other**.

Oxidation Numbers（氧化数）

For an oxidation-reduction reaction, we assign an **oxidation number** (oxidation state) to **each** **element** in a neutral compound or charged species.

- Atoms (i.e. neutral) in their **elemental form** have an oxidation number of **0**.
e.g. He, Li, H_2, O_2, N_2, P_4

- The oxidation number of a **monatomic ion** is the **same** as its **charge**. e.g.

+1: Li^+, Na^+; **+**2: Mg^{2+}, Ca^{2+}; **+**3: Al^{3+}
-1: F^-, Cl^-; -2: O^{2-}, S^{2-}

- **Nonmetals**(非金属) tend to have **negative** oxidation numbers, although **some are positive** in certain compounds or ions. e.g.

Oxygen usually has an oxidation number of **−2** (e.g. H_2O) except peroxide (过氧化物) compounds: **−1 (H_2O_2)** and unusually **+2** for OF_2 (oxygen difluoride, 剧毒气体,火箭工程液体助燃剂).

Hydrogen:

−1 when bonded to a **metal** (e.g. NaH, sodium hydride).

+1 when bonded to a **nonmetal** (e.g. H_2O, H_2S).

Fluorine（氟） **always** has an oxidation number of **−1** (e.g. HF) in all compounds: the **highest electronegativity**.

The other halogens（卤素） have an oxidation number of **−1** in most binary compounds, but they can have positive oxidation numbers in oxyanions: e.g.

Cl:

+7: ClO_4^- (perchlorate): $x + 4*(-2) = -1 \rightarrow x =$ **+7**

+5: ClO_3^- (chlorate): $x + 3*(-2) = -1 \rightarrow x =$ **+5**

+3: ClO_2^- (chlorite): $x + 2*(-2) = -1 \rightarrow x =$ **+3**

+1: ClO^- (hypochlorite): $x + -2 = -1 \rightarrow x =$ **+1**

-1: HCl : $1 + x = 0 \rightarrow x =$ **-1**

- The **sum** of the oxidation numbers of all atoms in a **neutral** **compound** is **0**. e.g.

H_2Se: $2*(+1) + x = \mathbf{0} \Rightarrow x = -2$

- The **sum** of the oxidation numbers of all atoms in a polyatomic **ion** is the **charge** on the ion.

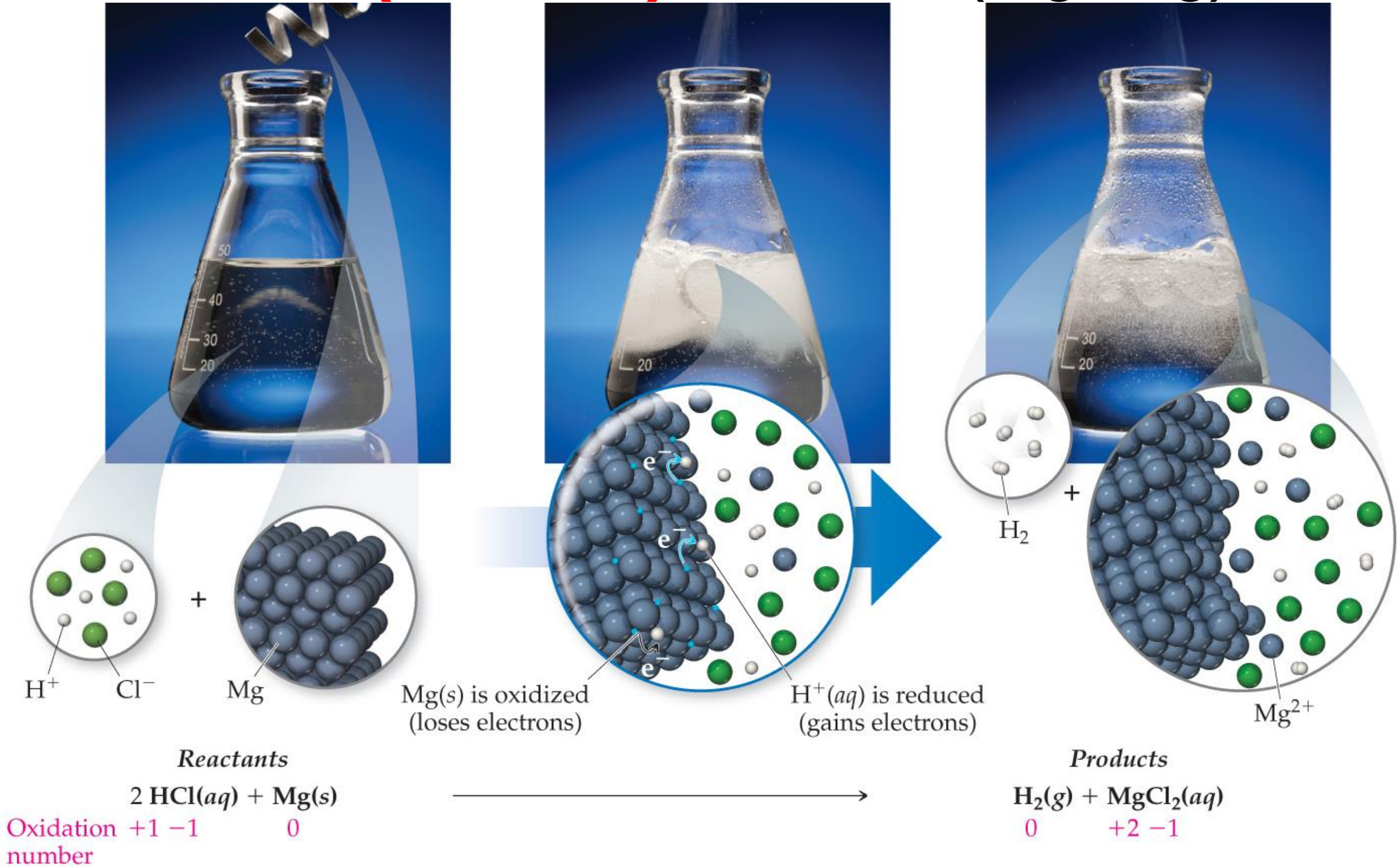
SO_4^{2-} Sulfate ion: $x + 4*(-2) = \mathbf{-2} \Rightarrow x = +6$
NO_3^{-} Nitrate ion: $x + 3*(-2) = \mathbf{-1} \Rightarrow x = +5$
CO_3^{2-} Carbonate ion: $x + 3*(-2) = \mathbf{-2} \Rightarrow x = +4$

Displacement Reactions (置换反应)

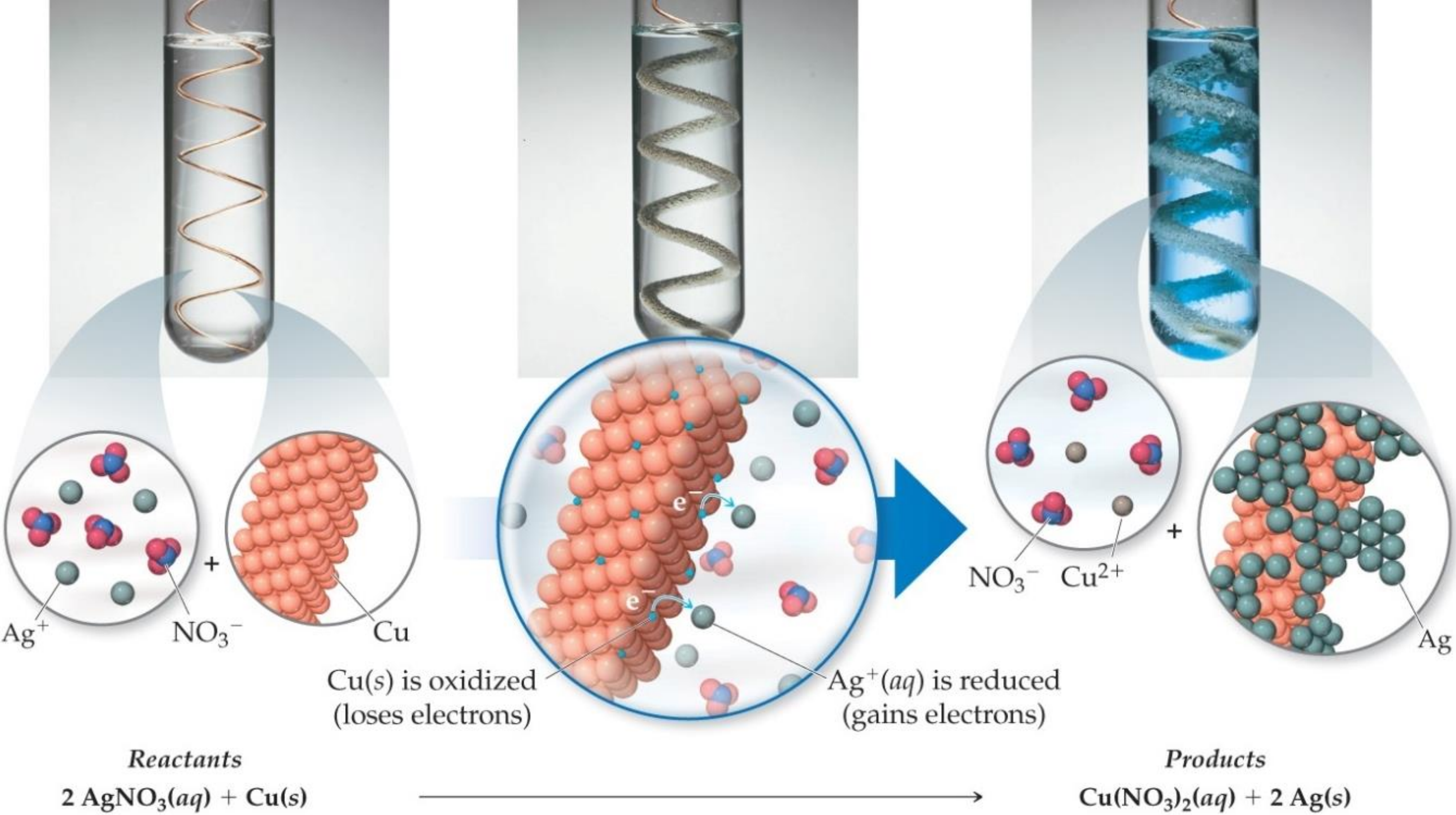
A + BX → AX + B

Mg(s) + 2HCl(aq) → $MgCl_2$(aq) + H_2(g)

The **cation** (e.g. H^+) in solution is replaced by **oxidation of an (reactive) element** (e.g. Mg).



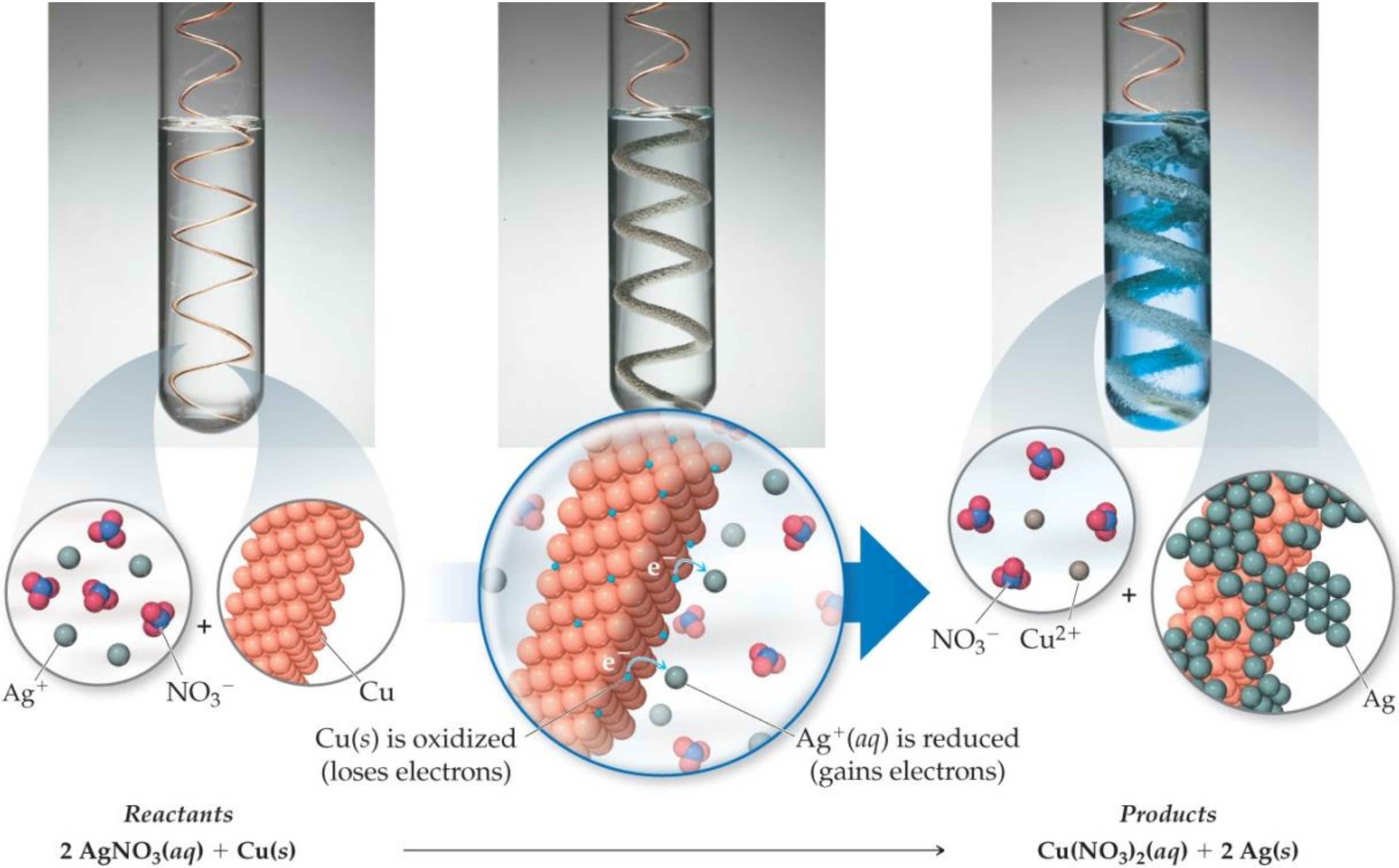
Aqueous Reactions



Redox reactions **(1)** between **metals** and **acids** as well as those **(2)** between **metals** and **salts**.

e.g. silver ions oxidize copper metal:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$



The **reverse**（逆）reaction does **NOT** occur:

$$Cu^{2+}(aq) + 2Ag(s) \not\rightarrow Cu(s) + 2Ag^{+}(aq)$$

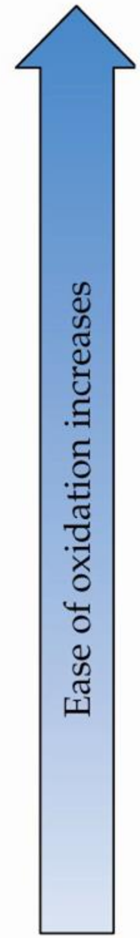
Activity Series (活性顺序)

$nA + mB^{n+} \rightarrow nA^{m+} + mB$

Active metals

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^{+}(aq) + e^{-}$
Potassium	$K(s) \longrightarrow K^{+}(aq) + e^{-}$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^{-}$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$
Sodium	$Na(s) \longrightarrow Na^{+}(aq) + e^{-}$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^{-}$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-}$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$
Hydrogen	$H_2(g) \longrightarrow 2\,H^{+}(aq) + 2e^{-}$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$
Silver	$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^{-}$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^{-}$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$

Noble metals



Any active **metal A** can be oxidized by the **ions of elements B** below the **metal A** in this list.

Aqueous Reactions

? Essay : New energy application

Extra Info./References:

The **reactivity series**: list of metals (sometimes with H & C added as baseline) **arranged by the ability to reduce** other chemicals in nonspecific way.

Reactivity series:

K, *Na, *Ca, Mg, Al, Zn, Fe, Sn, Pb, Cu, Hg, Ag, Au

← **increase in reactivity**

*: the position of Ca & Na are **different** in **electro-chemical series**, Ca is more electropositive than Na, but not for the reactivity series.

This is **in contract with** **the electrochemical series**:
List of reducing agents arranged by the way of negative potential in an electrochemical cell.

Extra Info./References:

- Na being above Ca in the Reactivity Series;
  Ca being above Na in the Electrochemical Series.
- Metals with lower valencies tend to be higher in the Reactivity Series because they only need to lose one electron to form a stable noble gas structure with a full outer electron shell.
- The reason for this being that metals with higher valencies tend to be higher in the Electrochemical Series, because more electrons are needed to produce each atom.

http://chemwiki.ucdavis.edu/Reference/Reference_Tables/Electrochemistry_Tables/P3%3A_Activity_Series_of_Metals

http://en.wikipedia.org/wiki/Reactivity_series

$$Cu(s) + AgNO_3(aq) \longrightarrow Ag(s) + Cu(NO_3)_2(aq)$$

Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$

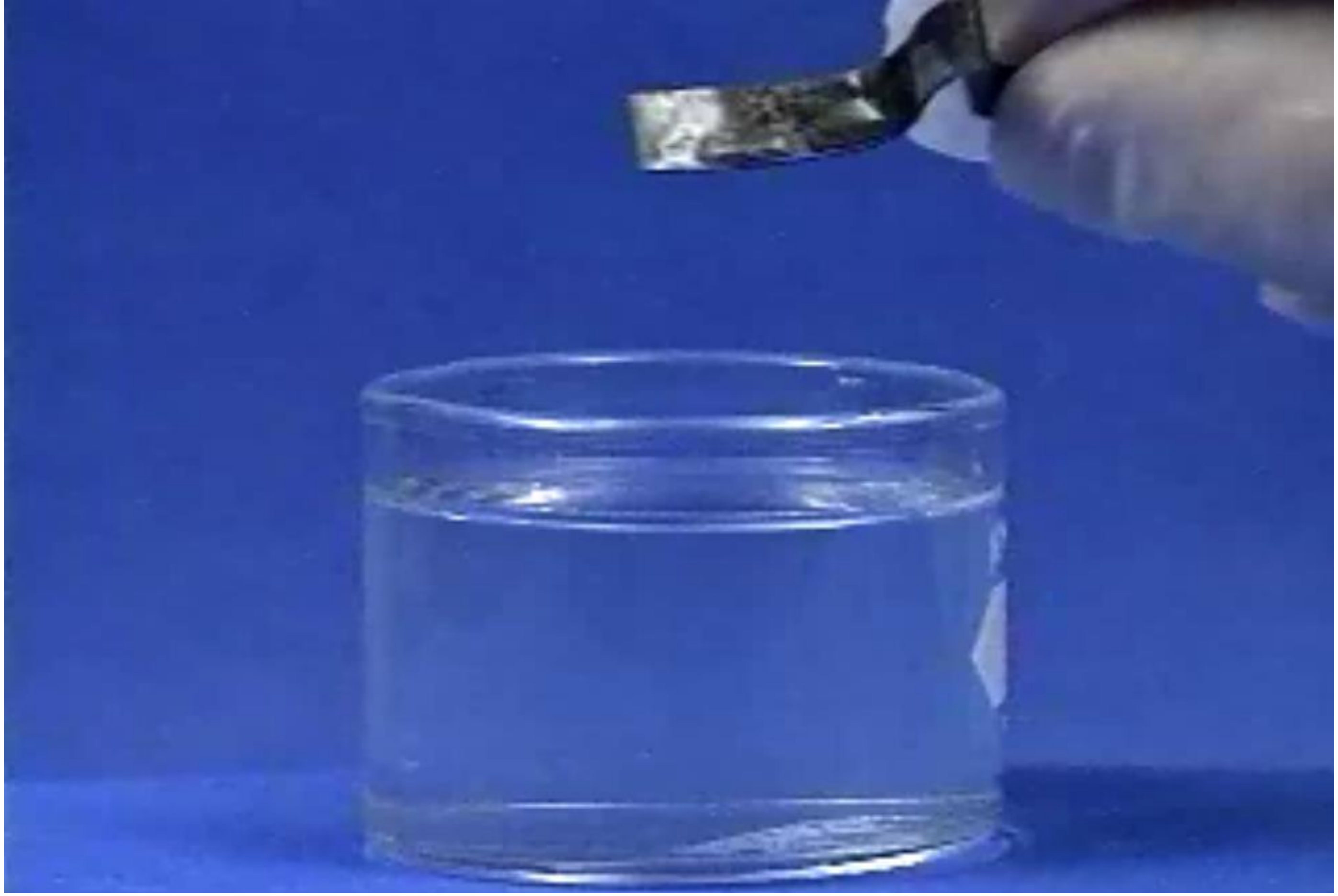
$$Zn(s) + AgNO_3(aq) \longrightarrow Ag(s) + Zn(NO_3)_2(aq)$$

Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$

$$Zn(s) + Pb(NO_3)_2(aq) \longrightarrow Pb(s) + Zn(NO_3)_2(aq)$$

Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

Lead（铅）

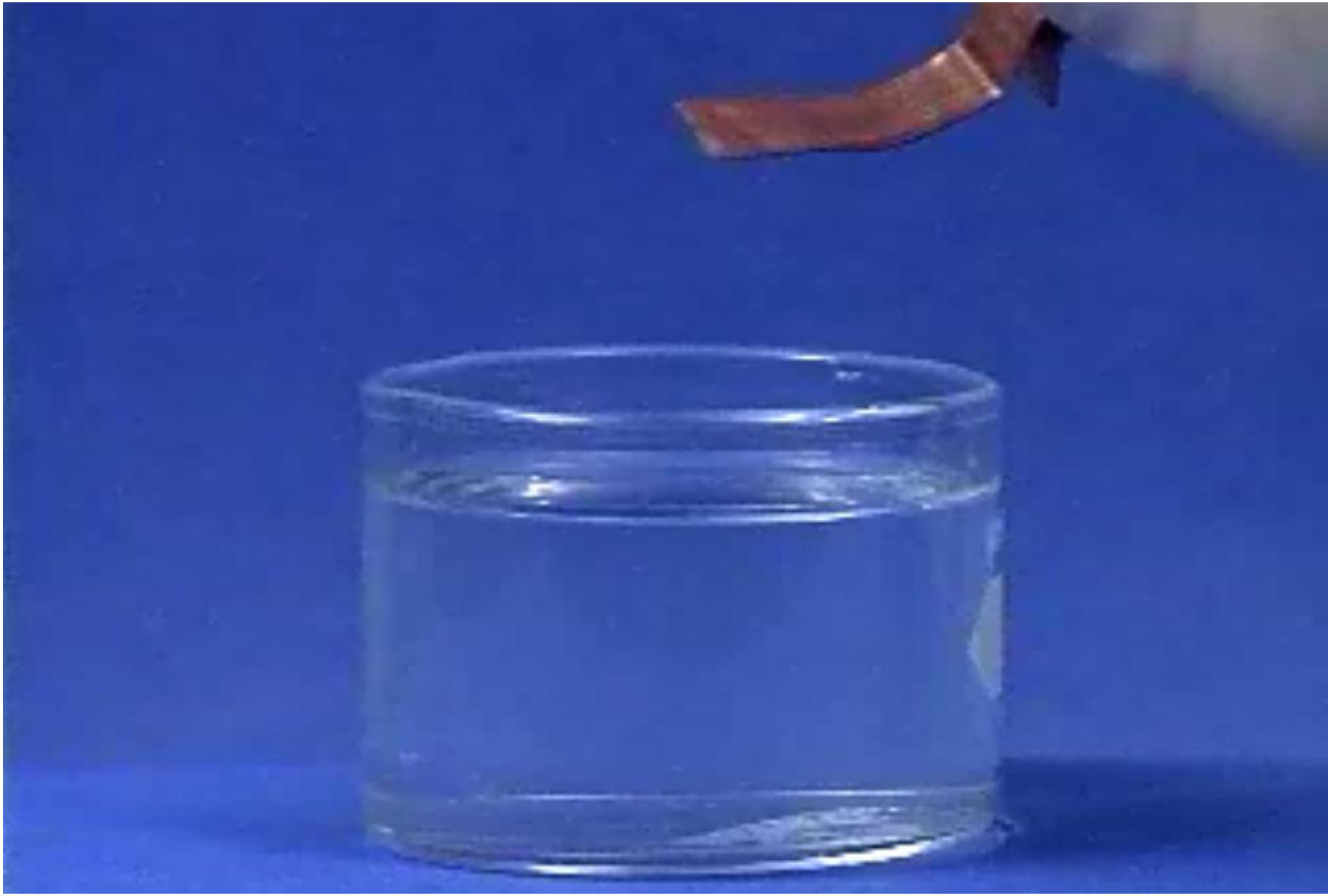


$$Zn(s) + 2HCl(aq) \longrightarrow H_2(g) + ZnCl_2(aq)$$

Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2\,H^+(aq) + 2e^-$

Hydrochloric acid

(盐 酸)



$$Cu_{(s)} + 2HCl_{(aq)} \not\longrightarrow H_{2(g)} + CuCl_{2(aq)}$$

Hydrogen	$H_2(g) \longrightarrow 2\,H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Aqueous Reactions

When an atom undergoes oxidation, it _______ electrons.

a. gains
b. loses
c. retains
d. balances

When an atom undergoes reduction, it _______ electrons.

a. gains
b. loses
c. retains
d. balances

What is the oxidation number of nitrogen (a) in aluminum nitride, AlN, and (b) in nitric acid, HNO_3?

氮化铝

a.

A. +1

B. -1

C. -2

$\boxed{\text{D.}}$ -3

b.

A. +6

$\boxed{\text{B.}}$ +5

C. +4

D. -1

Determine the oxidation number of sulfur in **(a)** H_2S, **(b)** S_8, **(c)** SCl_2, **(d)** Na_2SO_3, **(e)** SO_4^{2-}.

(a) When bonded to a nonmetal (S), H has an oxidation number of +1 ➔ $2*(+1) + x = 0$; $x =$ **-2**

(b) S_8 is an elemental form ➔ **0**

(c) Chlorine to have an oxidation number of –1 ➔ $x + 2*(-1) = 0$; $x =$ **+2**

(d) Sodium (**metal**) has an oxidation number of +1. Oxygen has a common oxidation state of –2 ➔ $2(+1) + x + 3(-2) = 0$; $x =$ **+4**.

(e) The oxidation state of O is –2 ➔ $x + 4(-2) = -2$; $x =$ **+6**.

hydrogen sulfide, sulphur, sulfur chloride, sodium sulfite, sulfate ion

The oxidation number of boron for the below compound?

A. +1
B. -1
C. 0
D. +3

$Al + H^+ \rightarrow Al^{3+} + H_2$

When the oxidation-reduction reaction above is correctly balanced, the coefficients are

a. 1, 2 → 1, 1.
b. 1, 3 → 1, 2.
c. 2, 3 → 2, 3.
d. 2, 6 → 2, 3.

Aqueous Reactions

Does a reaction occur (a) when an aqueous solution of $NiCl_2(aq)$ is added to a test tube containing strips of metallic zinc, and (b) when $NiCl_2(aq)$ is added to a test tube containing $Zn(NO_3)_2(aq)$?

a.

$\boxed{\text{A.}}$ Yes

B. No

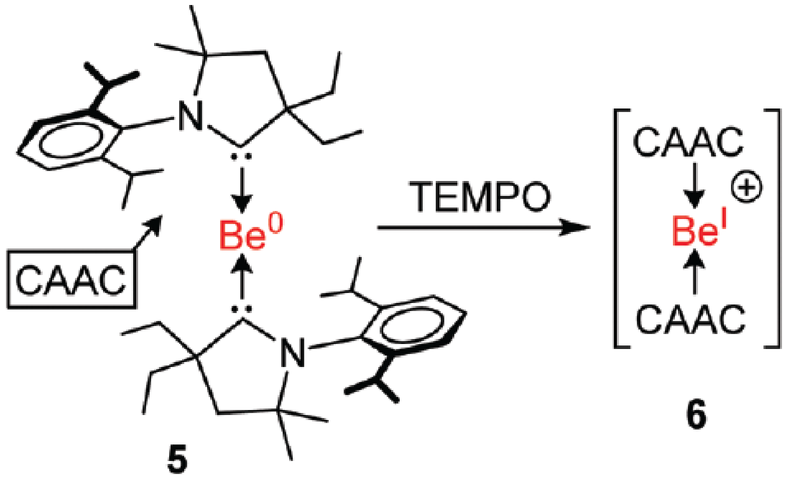
b.

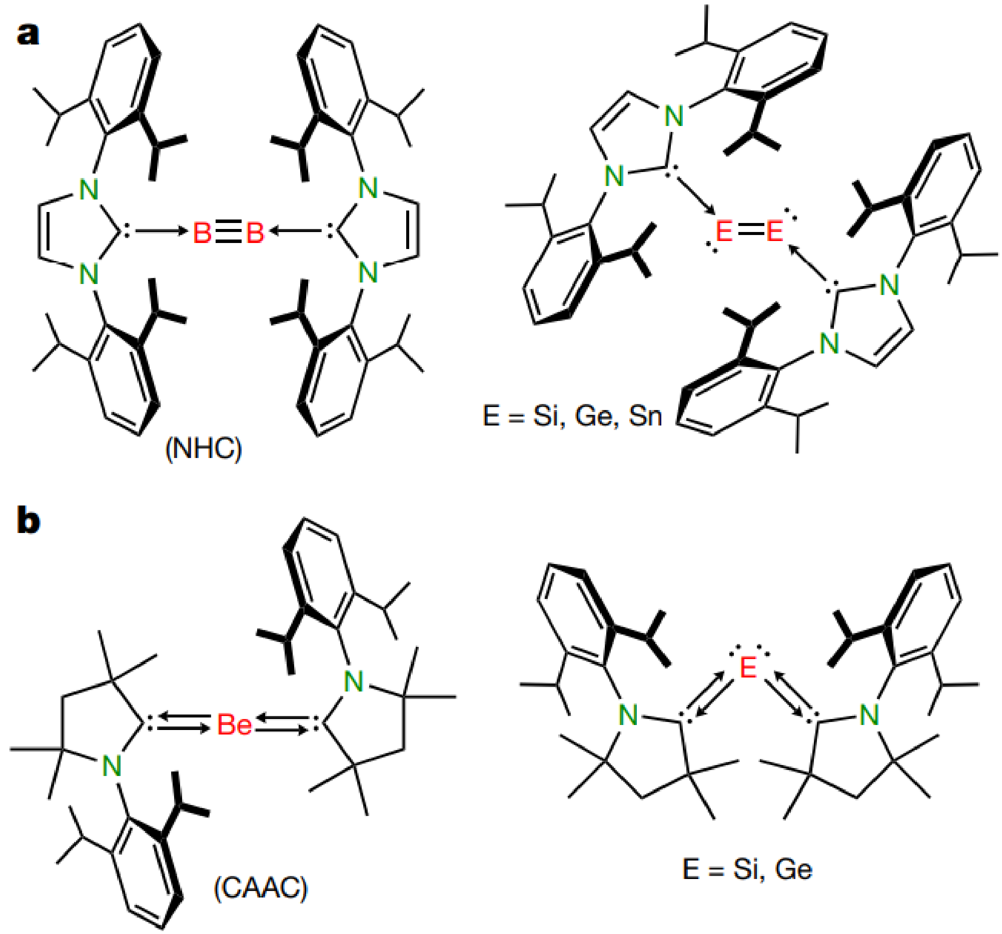
A. Yes

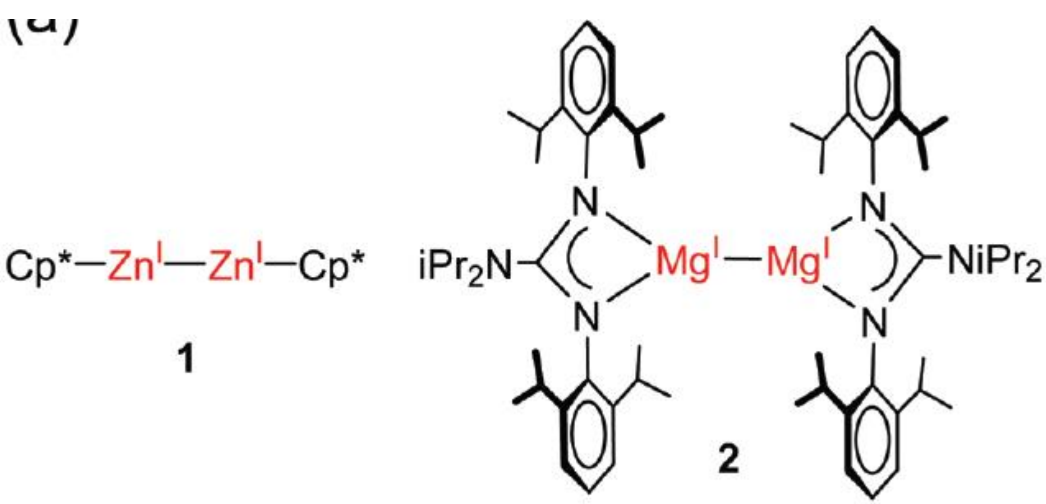
$\boxed{\text{B.}}$ No

Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$

Low-valent Metals (Extra Info.)







Chem. Commun **2021**, 9354.

Nature **2021**, *592*, 717.

Aqueous Reactions

Low-valent Metals (Extra Info.) *Nature* **2021**, *592*, 717.

Strongly reducing magnesium(0) complexes

https://doi.org/10.1038/s41586-021-03401-w

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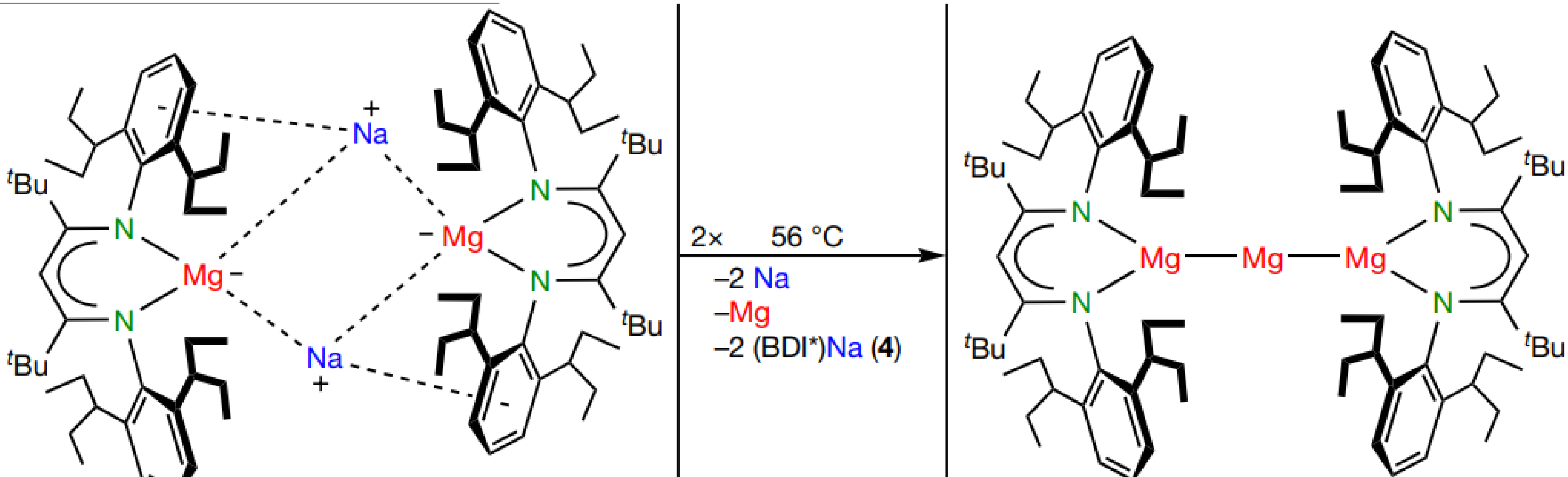
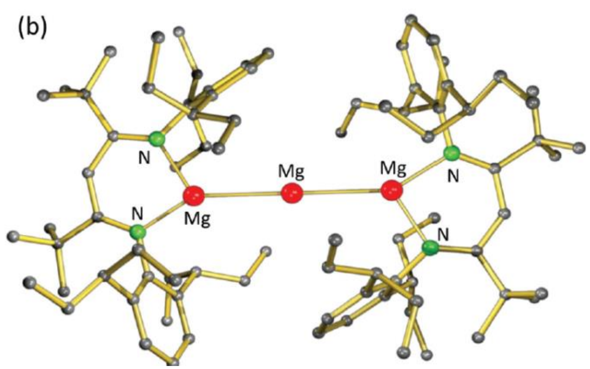
A complex of a metal in its zero oxidation state can be considered a stabilized, but



1 **5**



Aqueous Reactions

Concentration

Molarity (摩尔浓度)

- Two solutions can contain the same compounds, but different amounts/proportions of the compounds.
- **Molarity** is one way to measure the **concentration** of a **solution** (1 **M** = 1 **mol/L**):

$$\text{Molarity } (M) = \frac{\textbf{moles} \text{ of } \textbf{solute}}{\text{volume of } \textbf{solution} \text{ in } \textbf{liters}}$$

$$\text{Mole} = \frac{\text{Mass}}{\text{Molecular/Formula Weight}}$$

$$K_2SO_4(aq) \longrightarrow SO_4^{2-}(aq) + \mathbf{2}\, K^+(aq)$$

$$1\text{ M } K_2SO_4(aq) = 1\text{ M } SO_4^{2-}(aq) + \mathbf{2M}\, K^+(aq)$$

Mixing a Solution

To prepare a solution of a known molarity:

1. one weights out a known mass of the solute ➔ number of moles;

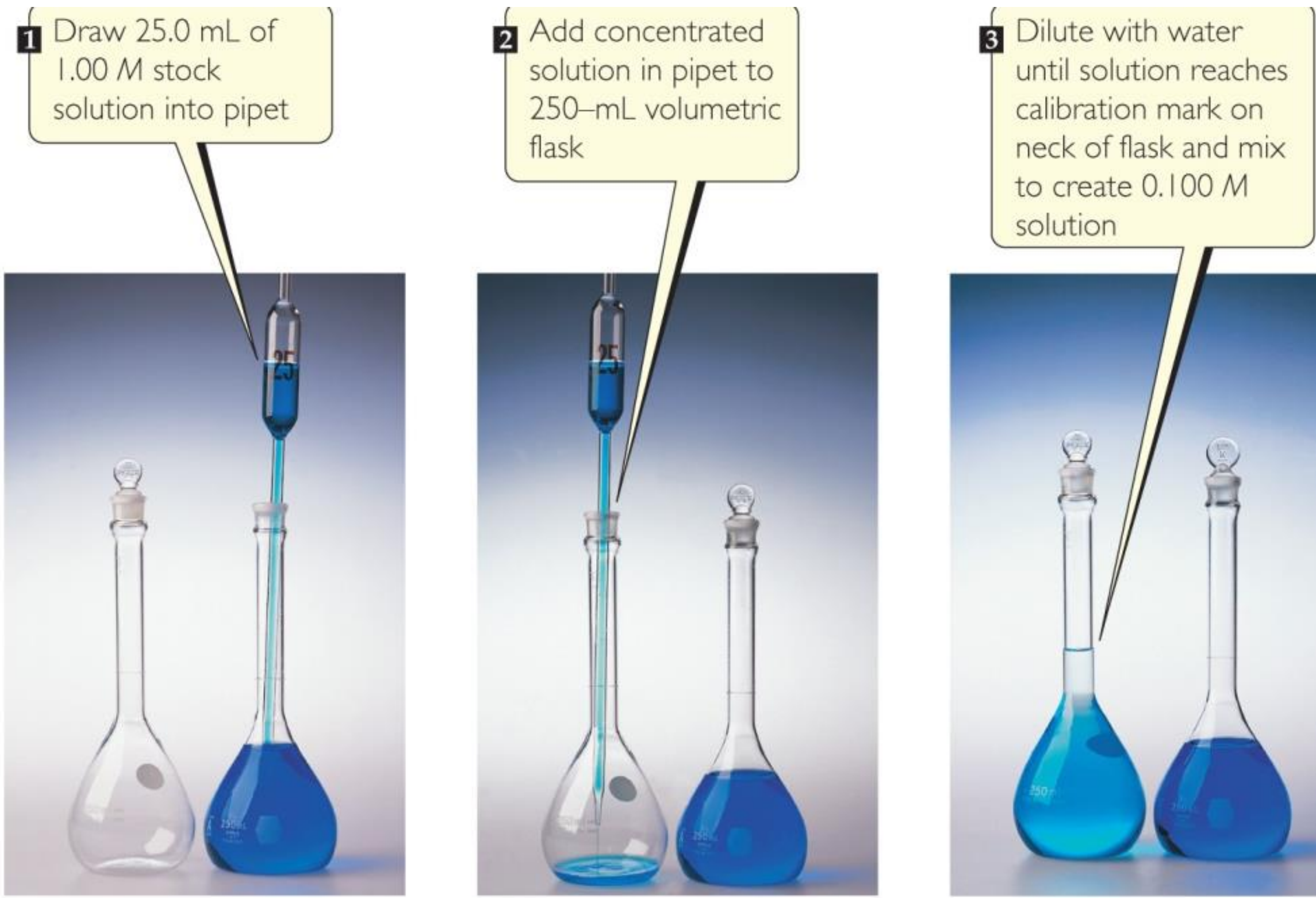
2. the solute is added to a volumetric flask (容量瓶);

3. solvent is added until reaching the line on the neck of the flask.

Dilution (稀释)

- Dilute a more **concentrated** solution by

1. using a pipet（移液管）to deliver a volume of the solution to a new volumetric flask;
2. adding solvent until reaching the line on the neck of the new flask.



The molarity of the new solution by dilution can be determined as follows (**the same amount of the solute (= $M*V$) before and after the dilution**):

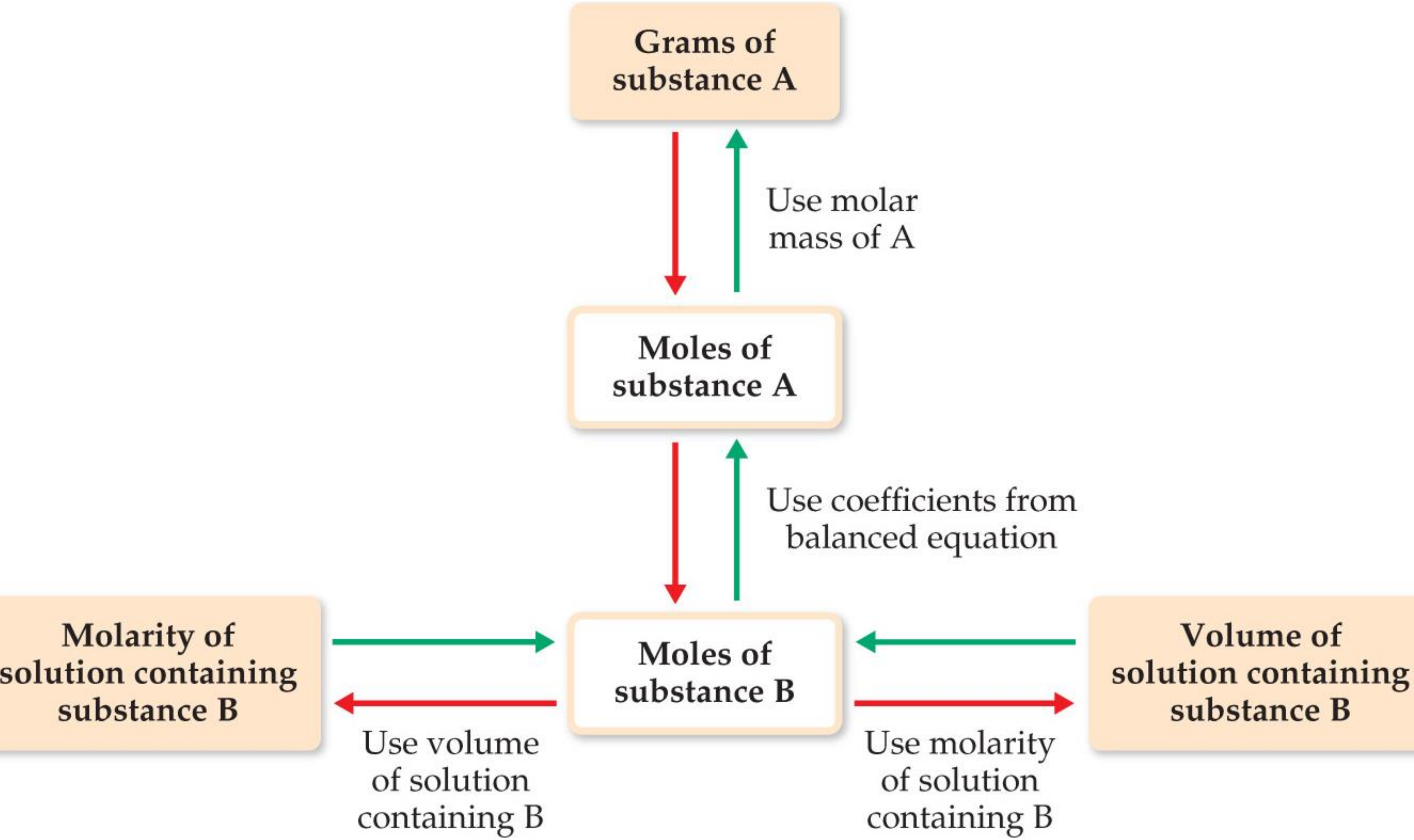
$$M_c \times V_c = M_d \times V_d,$$

where M_c & M_d are the **molarity** (M) of the **concentrated** (**before**) & **dilute** (**after**) solutions, respectively; V_c & V_d are the **volume** (V) of the two solutions.

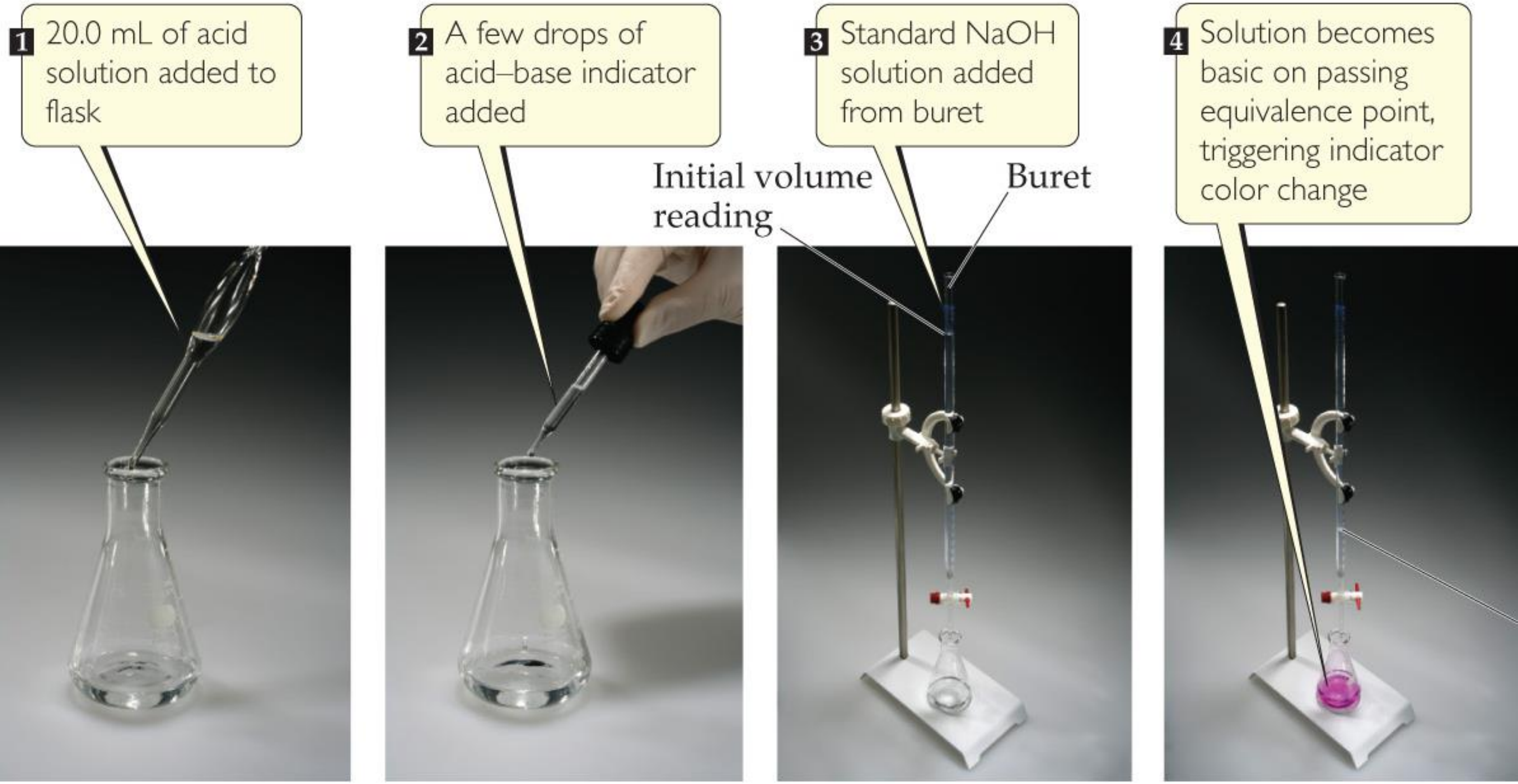
(When **NOT calculating molarity**, the above conversion does not require to use “M” & “L” units only, but the same units for M and V on the both sides are feasible):

$$mM*L = mM*L; \quad M*mL = M*mL$$

Molarities in Stoichiometric Calculations

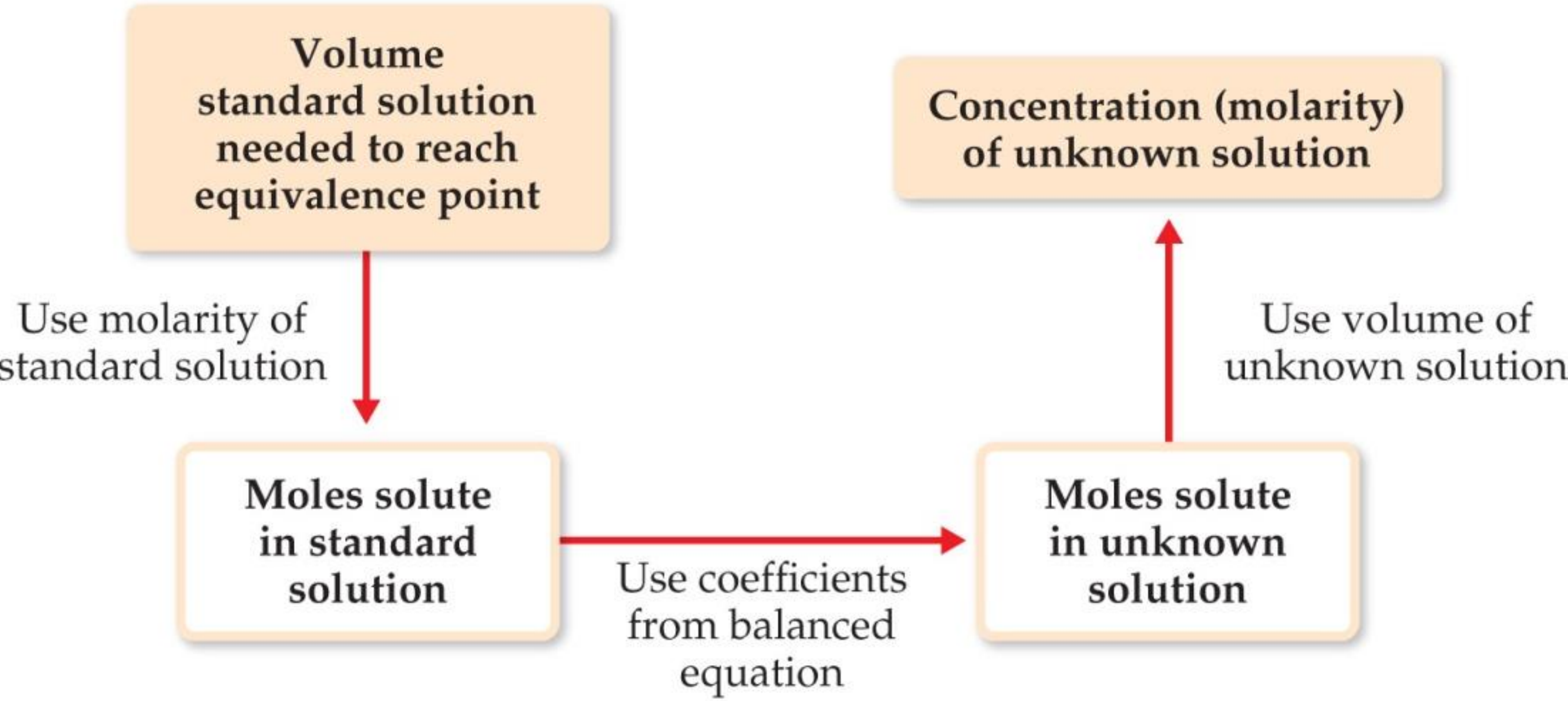


Titration（滴定）



Titration: an analytical technique to determine the concentration of a solute in a solution. (equivalence point 当量点)

Aqueous Reactions


Volume standard solution needed to reach equivalence point
Use molarity of standard solution
Moles solute in standard solution
Use coefficients from balanced equation
Moles solute in unknown solution
Use volume of unknown solution
Concentration (molarity) of unknown solution

250.0 mL of 0.100 M $AgNO_3$ solution contains ______ grams of silver nitrate.

a. 4.25

b. 8.50

c. 17.0

d. 34.0

Mole of $AgNO_3$: 0.100 M *0.2500 L = 0.0250 mol

➔

Mass of $AgNO_3$: 0.0250 mol *169.87 g/mol = 4.25 g

To make 250.0 mL of 0.500 M KI solution, ______ mL of 6.00 M KI must be used.

a. 20.8
b. 41.7
c. 500.0
d. 3000.0

250.0 mL * 0.500 M = *x**6.00 M

➔

x = 250.00*0.500/6.00 ml

$HX + NaOH \rightarrow NaX + H_2O$

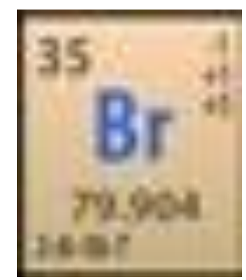
232 mg of HX was titrated using 29.70 mL of 0.0965 M NaOH. What is element X?

a. F
b. Cl
c. Br
d. I

mole of X: 0.02970*0.0965 = 0.00287

➔

Mass of X = 0.232/0.00287 – 1.008 = 79.9



Key Summary

(Aqueous) Solution, Solvent, Solute

Dissociation: (Strong & Weak) Electrolyte; Conductivity

Precipitation: Solubility; Metathesis (Exchange) Reactions; Molecular and (Net) Ionic Equations

Acid-Base: Arrhenius/Brønsted Acids & Bases; Neutralization; Salt; Gas-forming Reactions

Oxidation-Reduction (Redox) Reaction: Oxidation numbers; Displacement Reactions; Activity Series

Concentration: Molarity; Dilution; Titration

Thank You for Your Attention!
Any Questions?