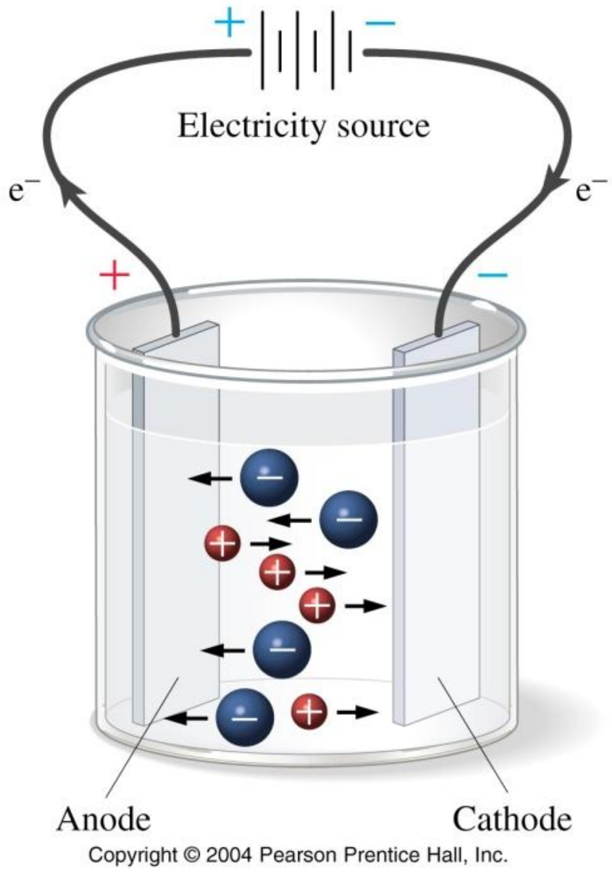
Lecture № 7



Aqueous Solutions of Electrolytes

07.03.2017

LESSON OBJECTIVES:

- Concept of electrolytes
- Define electrolyte, electrolytic solution, ion, cation, anion
- Arrhenius theory of electrolytic dissociation
- Acid and base
- Ostwald's dilution law
- Ionic reactions in electrolyte solutions

Electrolytes

Substances which on dissolution, even at moderate dilution, ionize almost completely

Strong electrolytes

Example:- HCl,HNO_3,NaOH,NaCl,$CaCl_2$ etc

Substances which on dissolution in water, dissociate to a little extent

Weak electrolytes

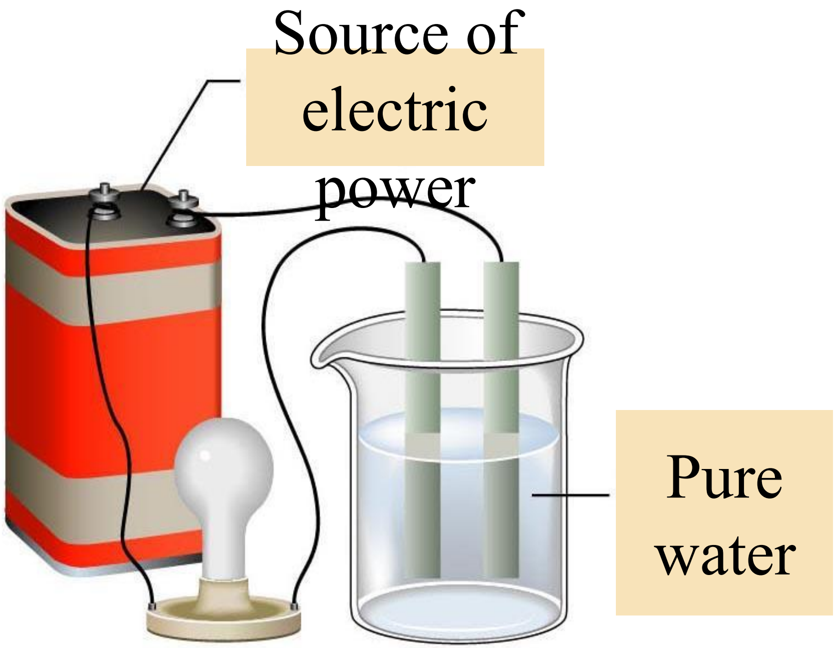
Example:-CH_3COOH, NH_4OH, AgCl etc

In the world of chemistry, **an electrolyte is a substance having the free ions so that the substance is electrical conductor**. We can say that **any substance, which furnishes ions in the solution, is called the electrolyte**.

Due to the presence of free ions some of the solutions can pass electricity through them. As we can say that the pure distilled water is not an electrolyte but if we add some table salt, it becomes an electrolyte and the electric current pass through it.

The electrolyte is an ionic solution but the electrolytes can also be in molten and in the solid state.

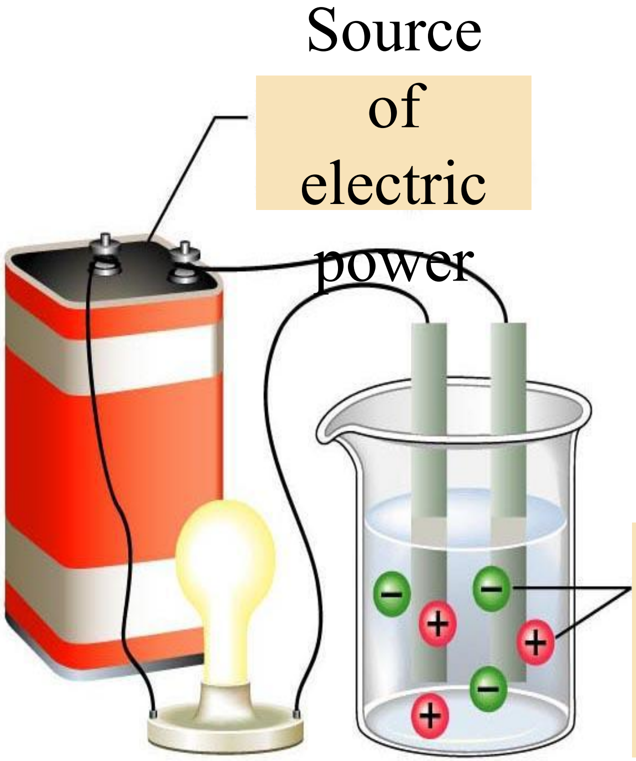
Pure water does not conduct an electric current



Source of electric power

Pure water

Ionic Solutions conduct a current

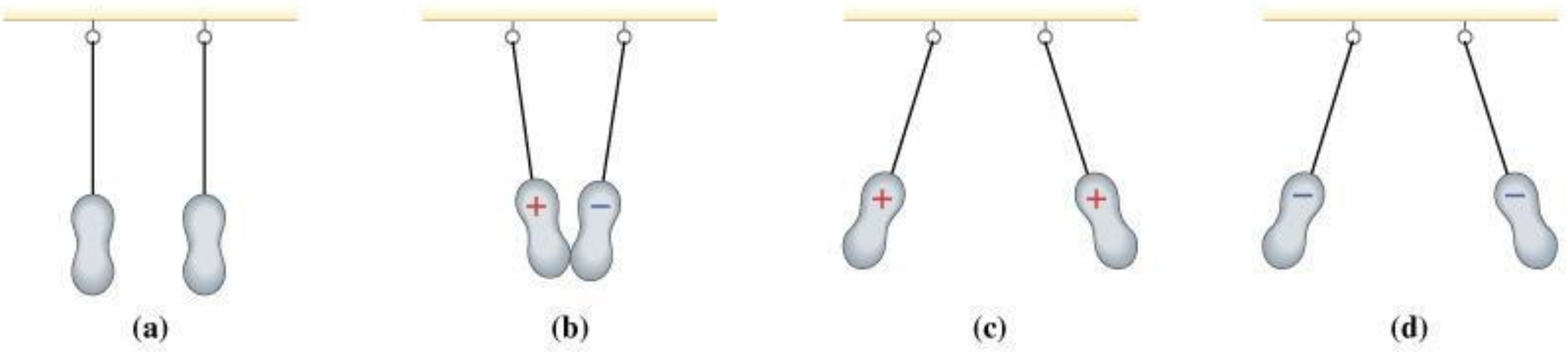


Source of electric power

Free ions present in water

Zumdahl, Zumdahl, DeCoste, World of Chemistry 2002, page 215

Electrostatic Forces



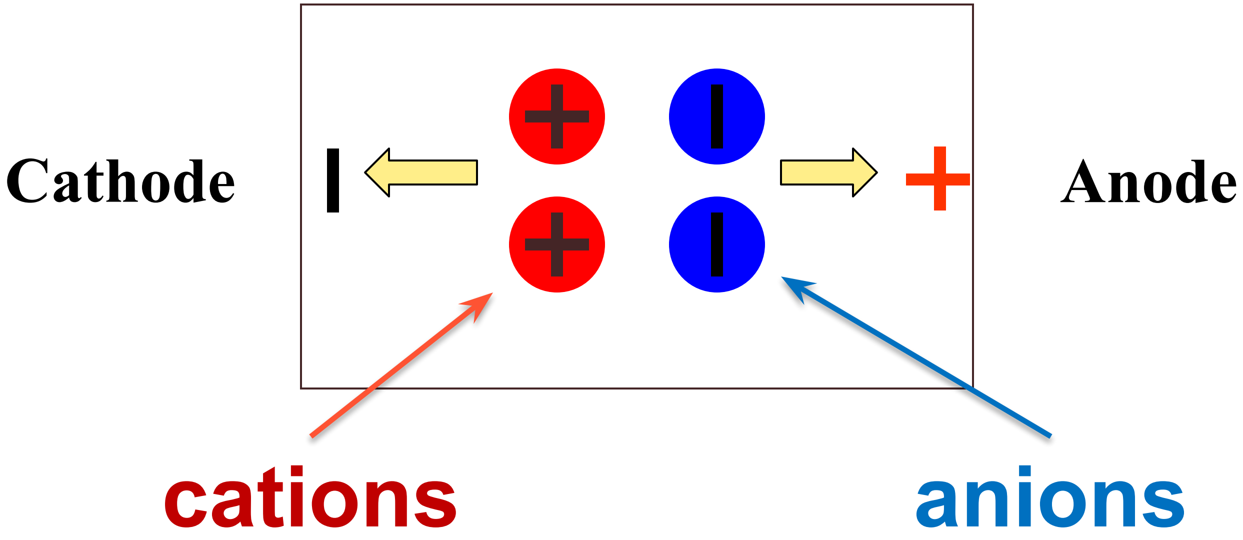
- Unlike charges (+ and –) attract one another.
- Like charges (+ and +, or – and –) repel one another.

Electric current is a movement or flow of electrically charged particles (electrons and ions), typically measured in:

$$Q = I \cdot t$$

Charged particles capable of conducting electrical current are called ***electrical conductors***:

- **Metals are conductors of the first type with an electronic conductivity**
- **Electrolytes are conductors of the second type with an ionic conductivity**

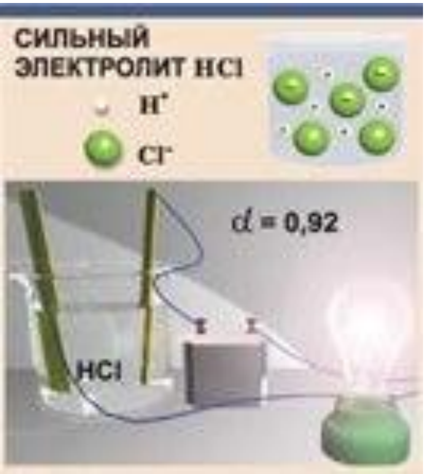


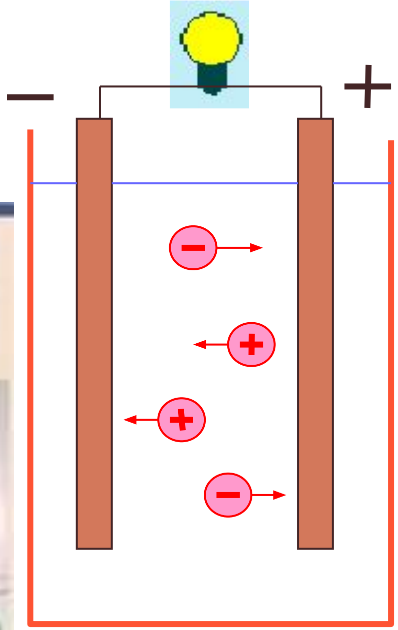
Ions are atoms (or groups of atoms) that carry electrical charge.

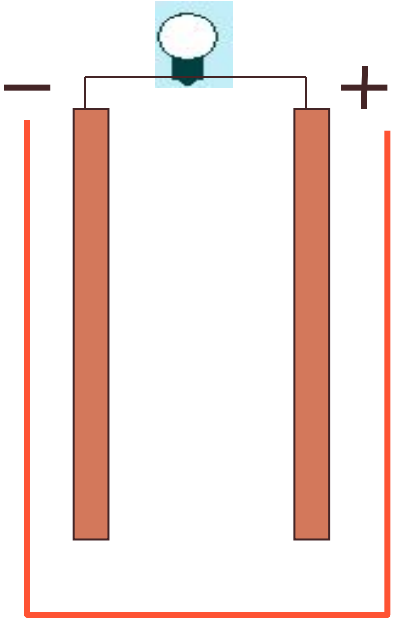
Positively (+) charged ions are called **cations**, whereas negatively (–) charged ions are called **anions**.

- ***Electrolytes*** ***are substances that dissociate into ions when dissolved in water and conduct electricity***

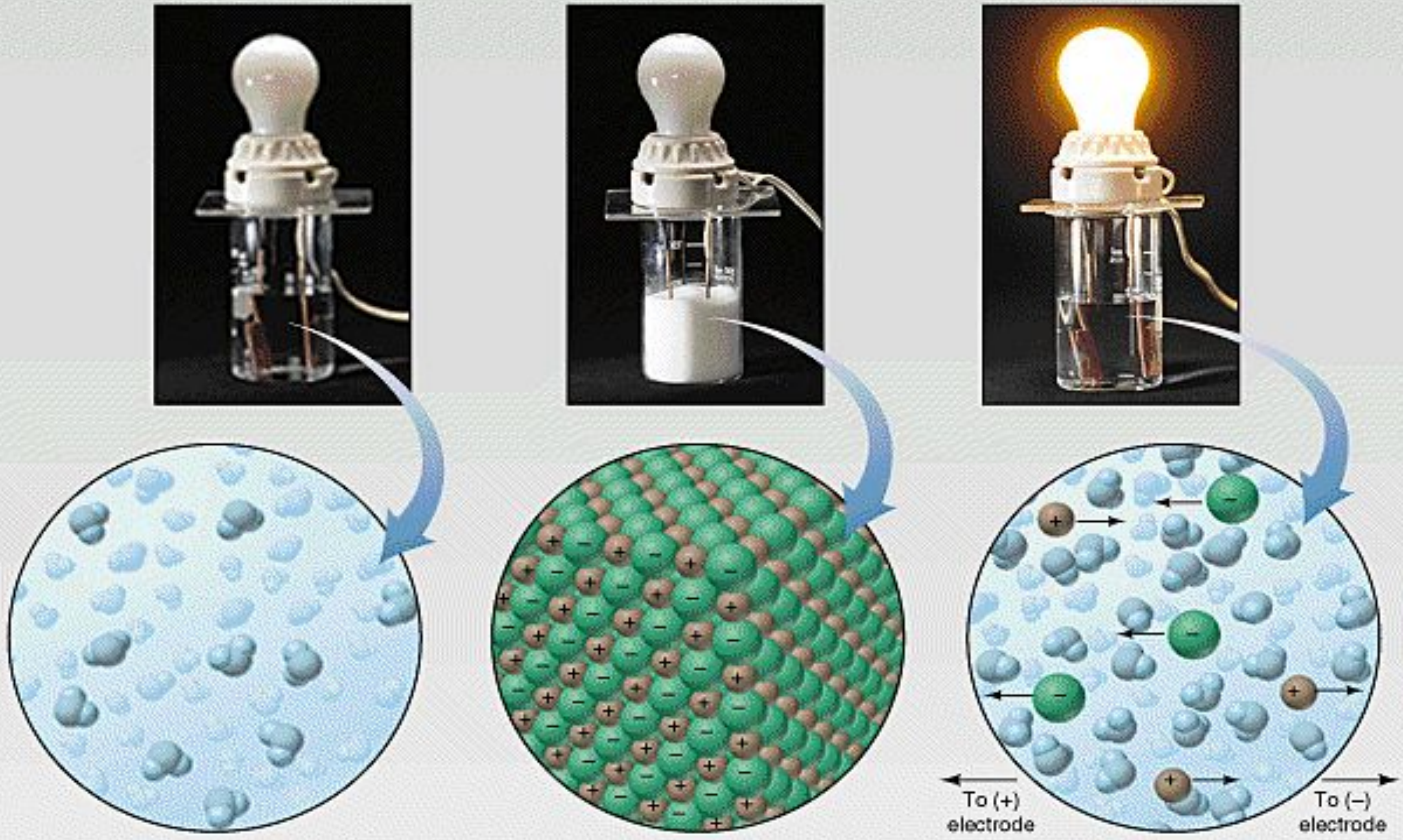
- **Non-electrolytes** ***are substances that do not form ions and do not conduct electricity when placed in water***







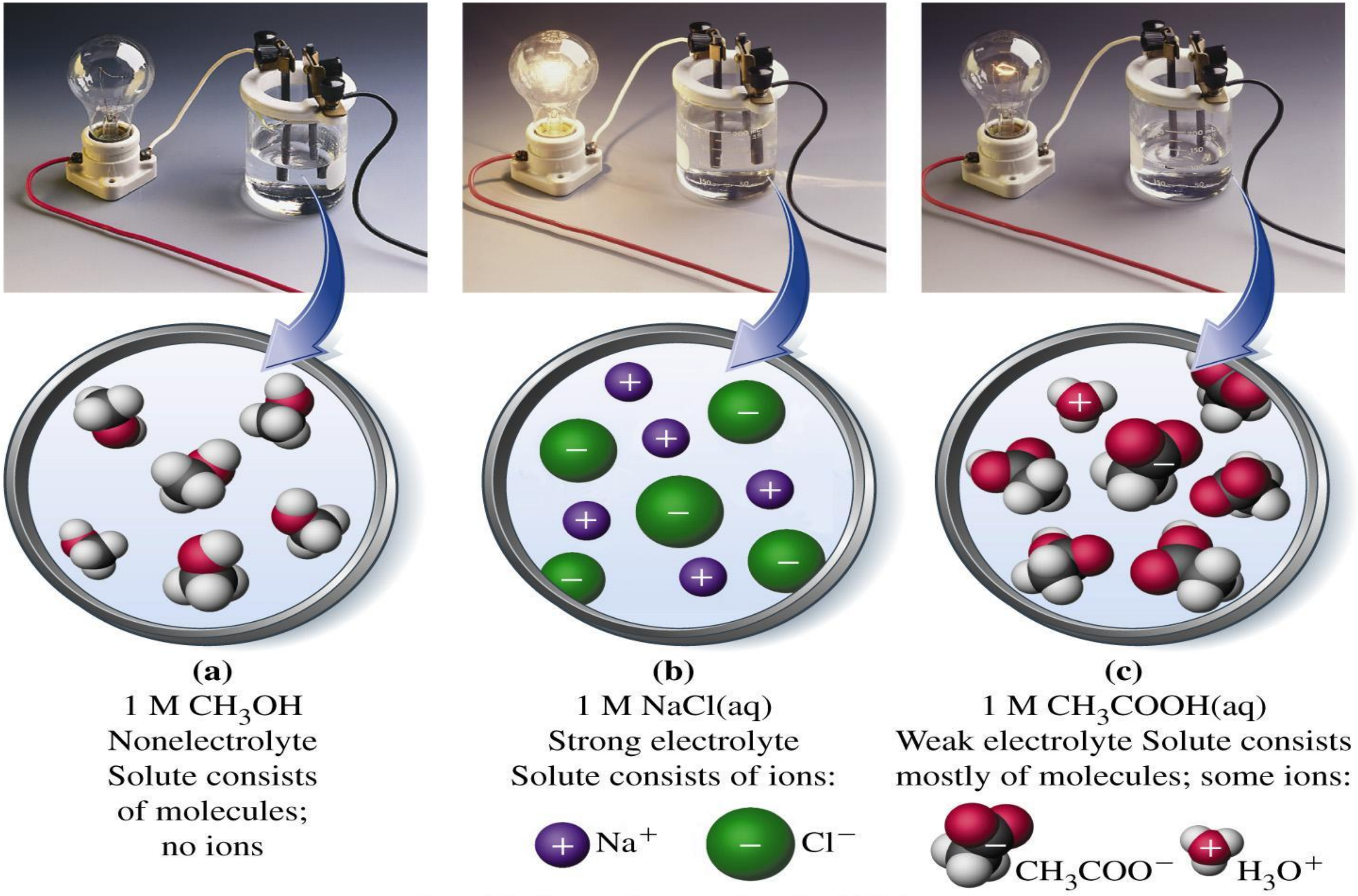
Electrical Conductivity of Ionic Solutions



A Distilled water does not conduct a current

B Positive and negative ions fixed in a solid do not conduct a current

C In solution, positive and negative ions move and conduct a current



(a)
1 M CH_3OH
Nonelectrolyte
Solute consists
of molecules;
no ions

(b)
1 M $NaCl(aq)$
Strong electrolyte
Solute consists of ions:

(c)
1 M $CH_3COOH(aq)$
Weak electrolyte Solute consists
mostly of molecules; some ions:

The more the electrolyte dissociates, the more ions it produces.

TYPES OF ELECTROLYTES

A ***weak electrolyte*** dissociates partially.

- Weak electrolyte solutions are poor conductors.
- Different weak electrolytes dissociate to different extents.

Weak electrolytes include:

- Weak acids and weak bases (NH_4OH)
- A few insoluble ionic compounds
- A water H_2O

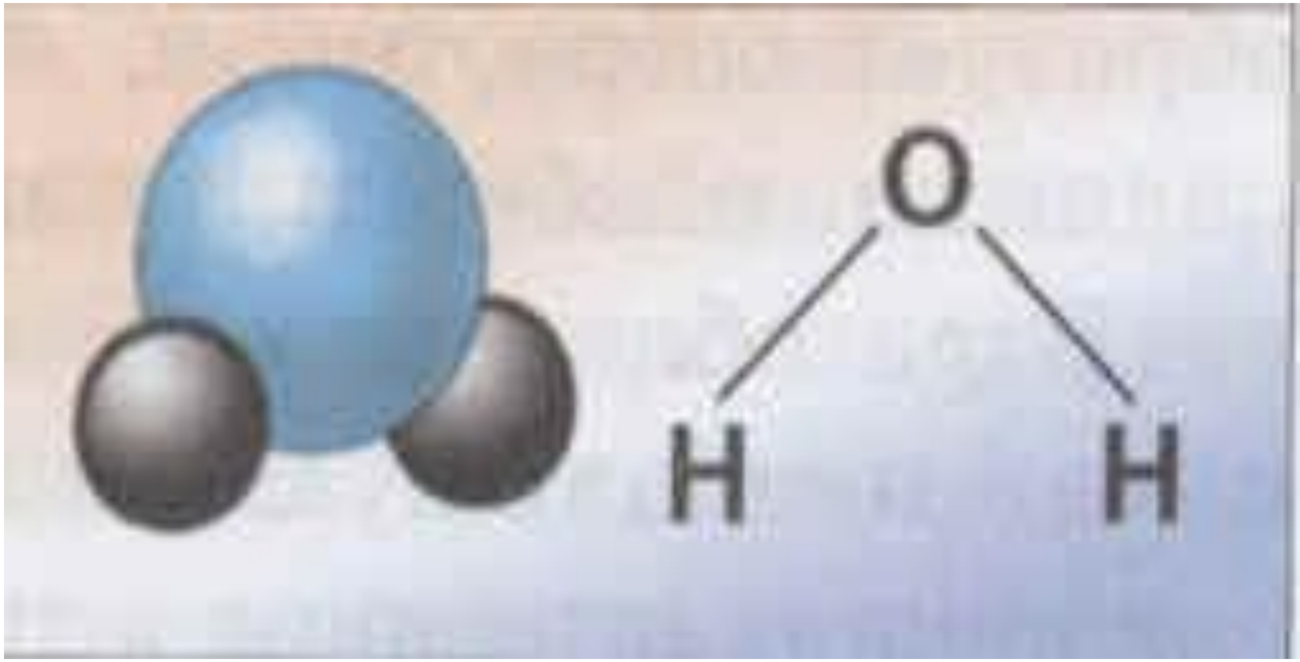
A ***strong electrolyte*** dissociates completely.

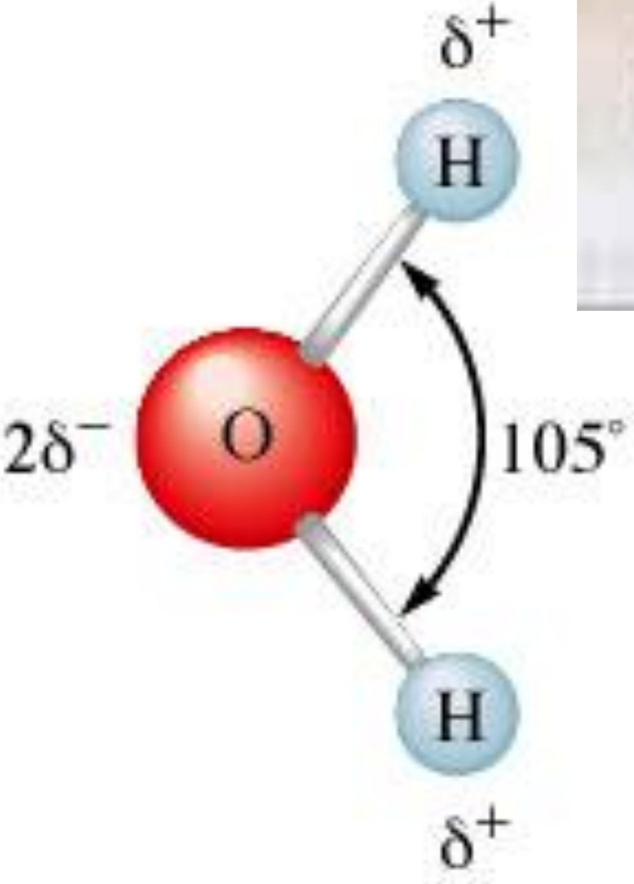
- A strong electrolyte is present in solution almost exclusively as ***ions***.
- Strong electrolyte solutions are good conductors.

Strong electrolytes include:

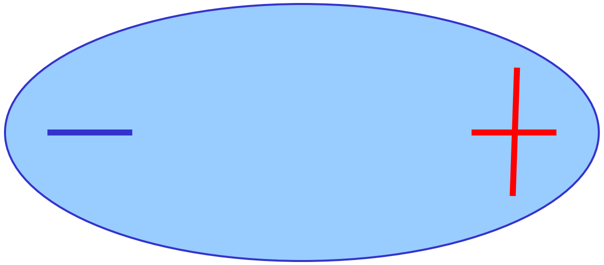
- Strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$)
- Strong bases (IA and IIA metals hydroxides)
- Most water-soluble ionic compounds (salts)

The Water Molecule is Polar

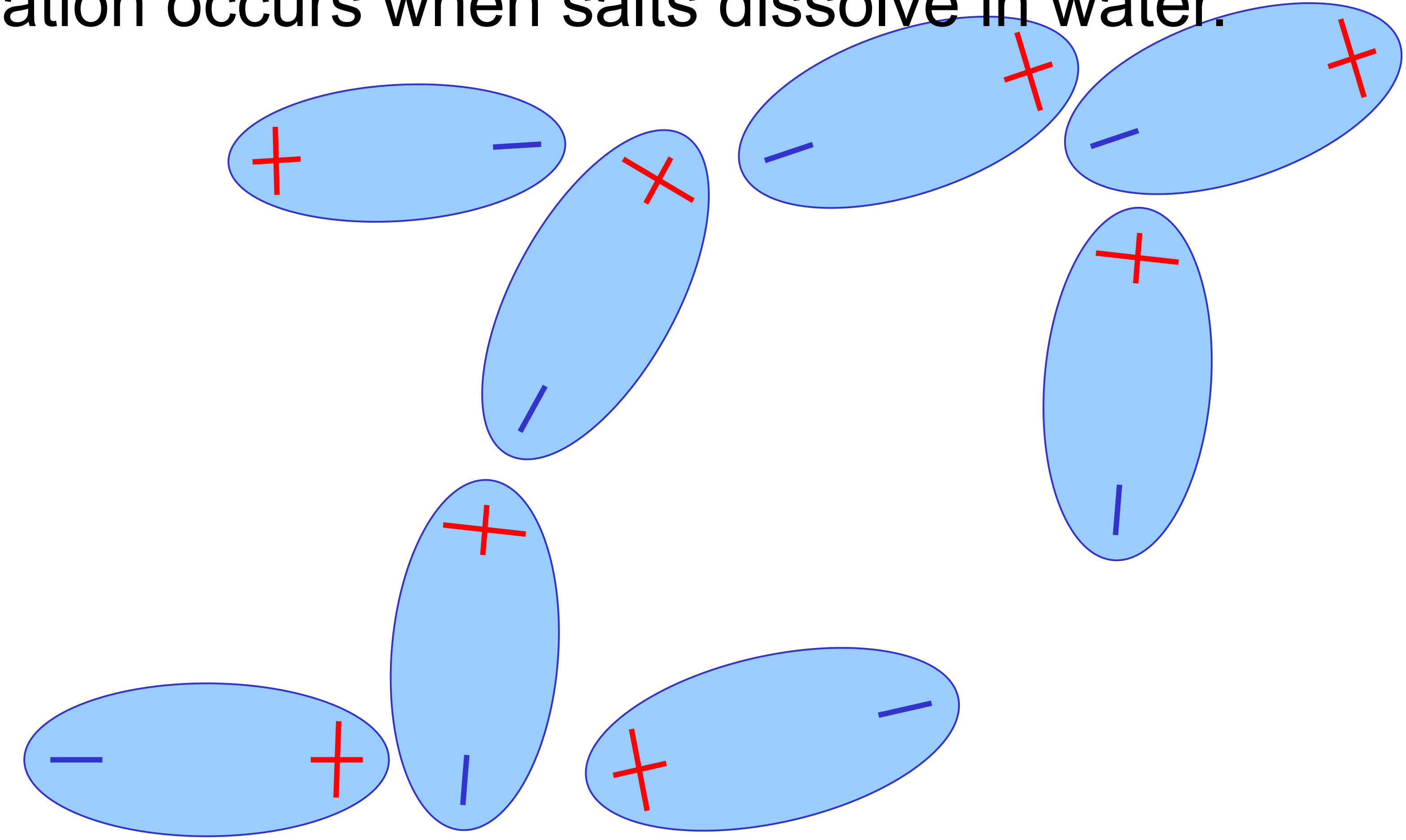




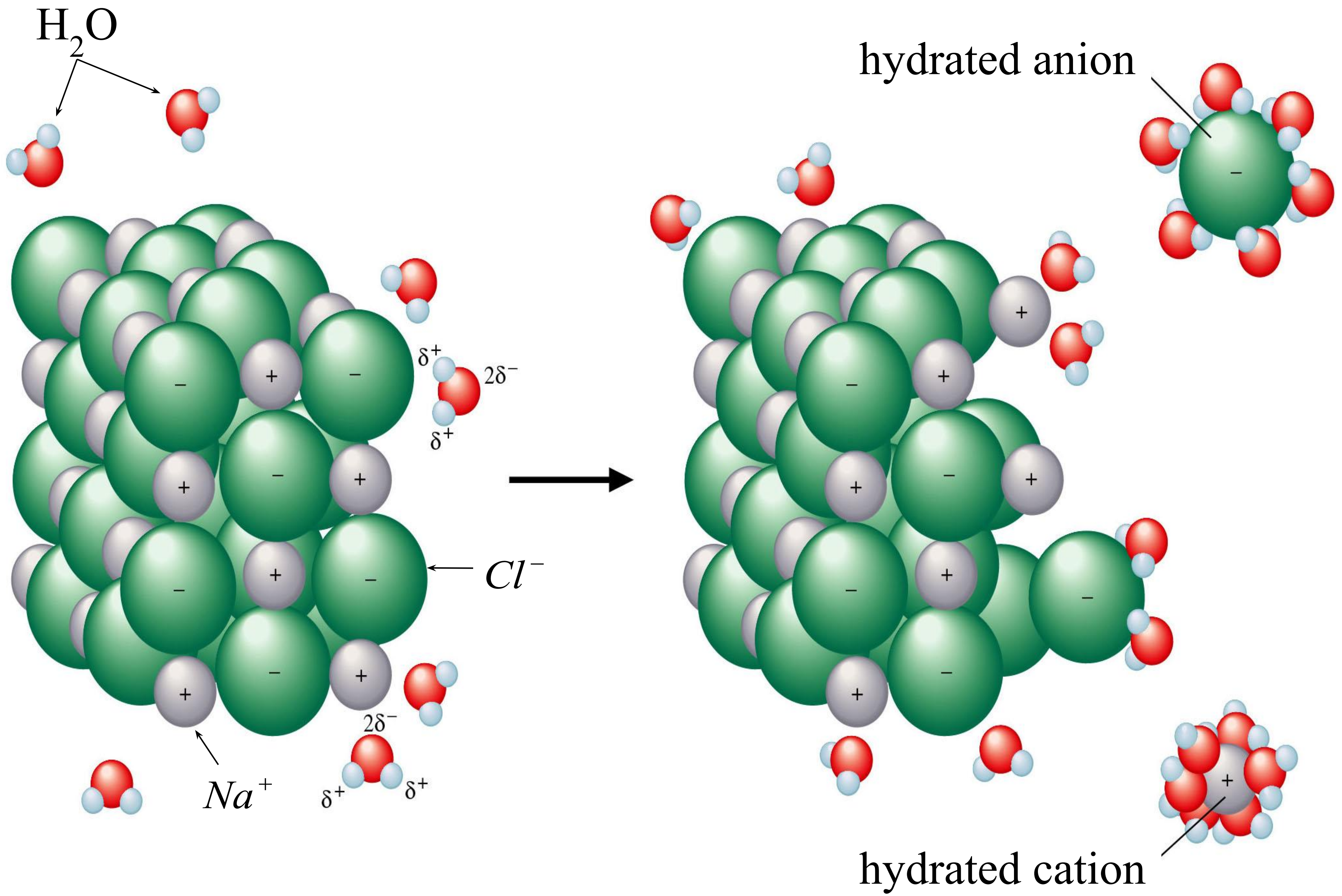
dipol

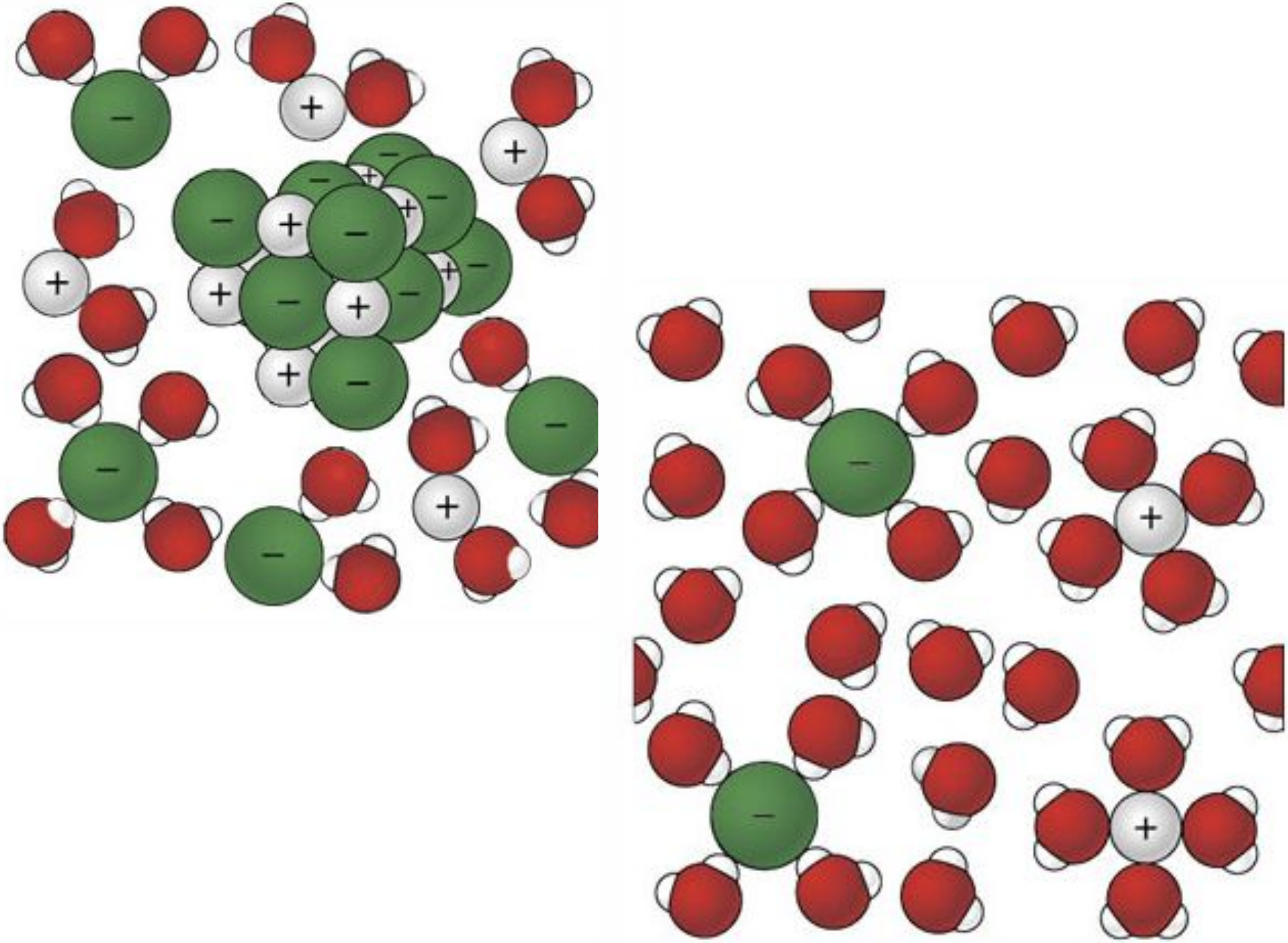


- Water is “bent” or V-shaped.
- The **O – H** bonds are covalent.
- Water is a polar molecule.
- Hydration occurs when salts dissolve in water.

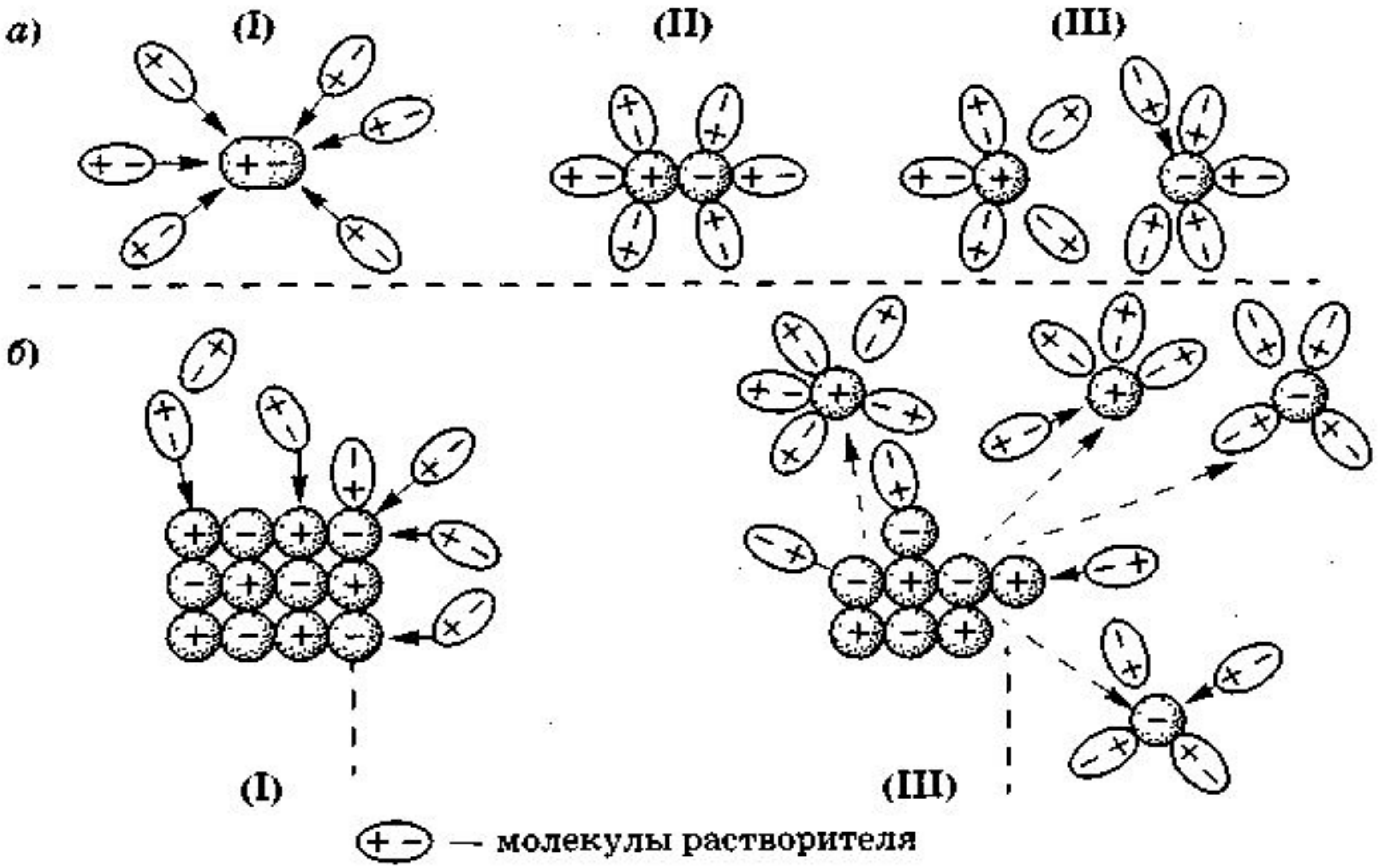


How Water Dissolves an Ionic Substance





Теория электролитической диссоциации



Этапы электролитической диссоциации полярных молекул (*а*) и ионных кристаллов (*б*): I – сольватация; II – ионизация; III – диссоциация.

ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of electrolytic dissociation or ionic theory.

Svante Arrhenius,
Swedish chemist
and
Nobel laureate,
1859-1927.

THE MAIN POINTS OF THE THEORY ARE:

- ***An electrolyte, when dissolved in water, breaks up into two types of charged particles***. These charged particles are called ions.
- ***When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs***.
- ***The process of splitting of the electrolytes molecules into ions under the influence of polar molecules of solvent is called ionization (dissociation):***

$$K_xA_y \leftrightarrow \underset{\textbf{cation}}{xK^{+m}} + \underset{\textbf{anion}}{yA^{-n}}$$

- ***The properties of electrolytes in solution are the properties of ions present in solution***. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^- ions and OH^- ions respectively.
- *The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure*.
- *The conductively of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions*.

An <u>acid</u> is a substance that increase H^+ when dissolved in water:

$$HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO^-_{3(aq)}$$

Some acids have more than one ionizable hydrogen atom. They ionize in "steps":

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

hydrogen sulfate ion

$$HSO_4^- \rightarrow H^+ + SO_4^{2-}$$

sulfate ion

Reactions of Acid: Strong and Weak Acids

- ***Strong acids*** are strong electrolytes; completely ionized in water:

In water: $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

No HCl in solution, only H^+ and Cl^- ions.

- **Weak acids** are weak electrolytes. ***Some*** of the dissolved molecules ionize; the rest remain as molecules.

In water: $CH_3COOH(l) \square H^+(aq) + CH_3COO^-(aq)$

Just a little H^+ forms.

A <u>base</u> is a substance that increase *OH^-* when dissolved in water:

$$NaOH_{(aq)} \rightarrow Na^+{}_{(aq)} + OH^-_{(aq)}$$

An ampholyte is a substance dissolving in water to *OH^-* and *H^+* ions:

$$H_2O \rightarrow H^+ + OH^-$$

$$Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^-$$

$$H_2ZnO_2 \rightarrow 2H^+ + ZnO_2^{2-}$$

Strong and Weak Bases

- ***Strong bases***: Most are ionic hydroxides (Group IA and IIA, though some IIA hydroxides aren't very soluble).
- ***Weak bases*****:** Like weak acids, they ionize partially. Ionization process is *different*.
- Weak bases *form* OH^- by accepting H^+ from water …

$$NH_3 + H_2O \;\square\; NH_4^+ + OH^-$$

$$CH_3NH_2 + H_2O \;\square\; CH_3NH_3^+ + OH^-$$

methylamine methylammonium ion

Most of the weak base remains in the molecular form.

Just a little OH^- forms.

Common Strong Acids and Strong Bases

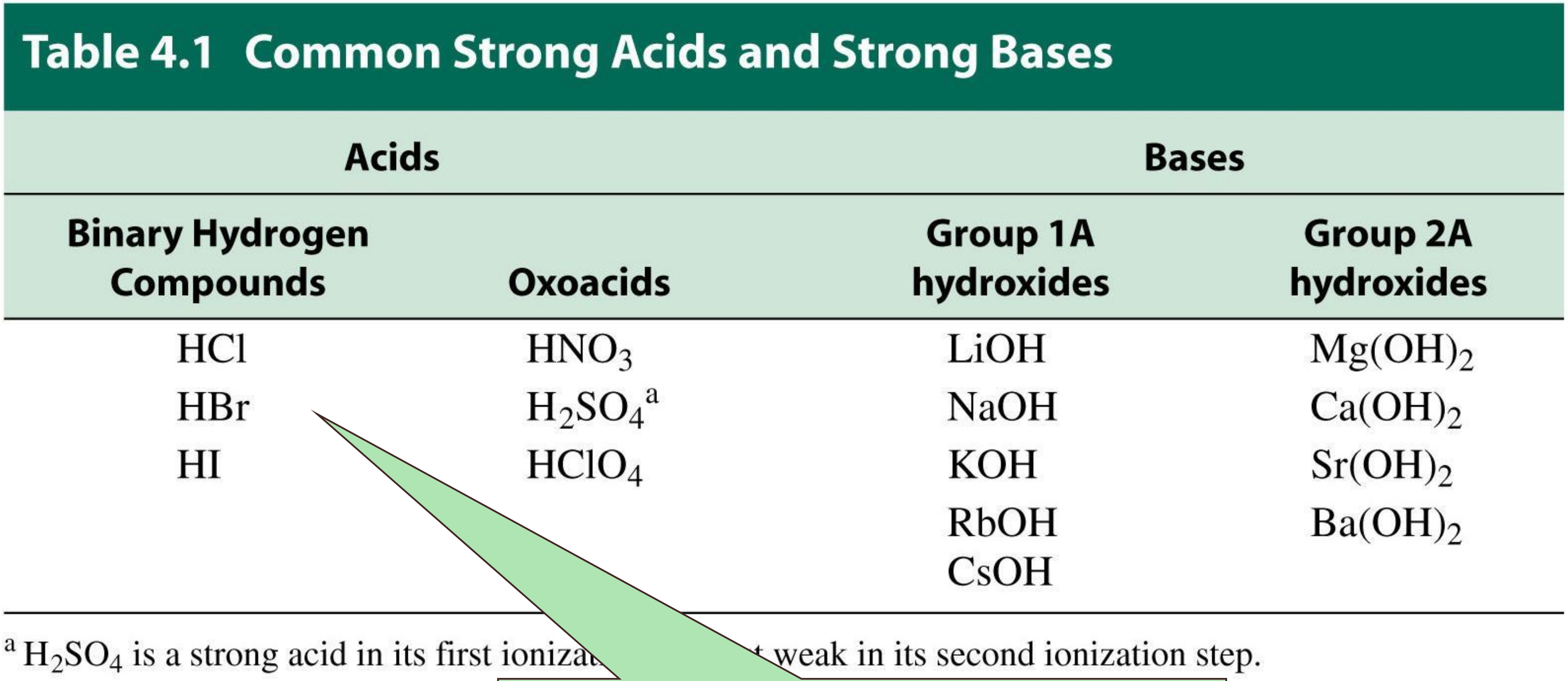


Table 4.1 Common Strong Acids and Strong Bases

Acids		Bases	
Binary Hydrogen Compounds	**Oxoacids**	**Group 1A hydroxides**	**Group 2A hydroxides**
HCl	HNO_3	LiOH	$Mg(OH)_2$
HBr	H_2SO_4[a]	NaOH	$Ca(OH)_2$
HI	$HClO_4$	KOH	$Sr(OH)_2$
		RbOH	$Ba(OH)_2$
		CsOH	

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[a] H_2SO_4 is a strong acid in its first ioniza[illegible] weak in its second ionization step.

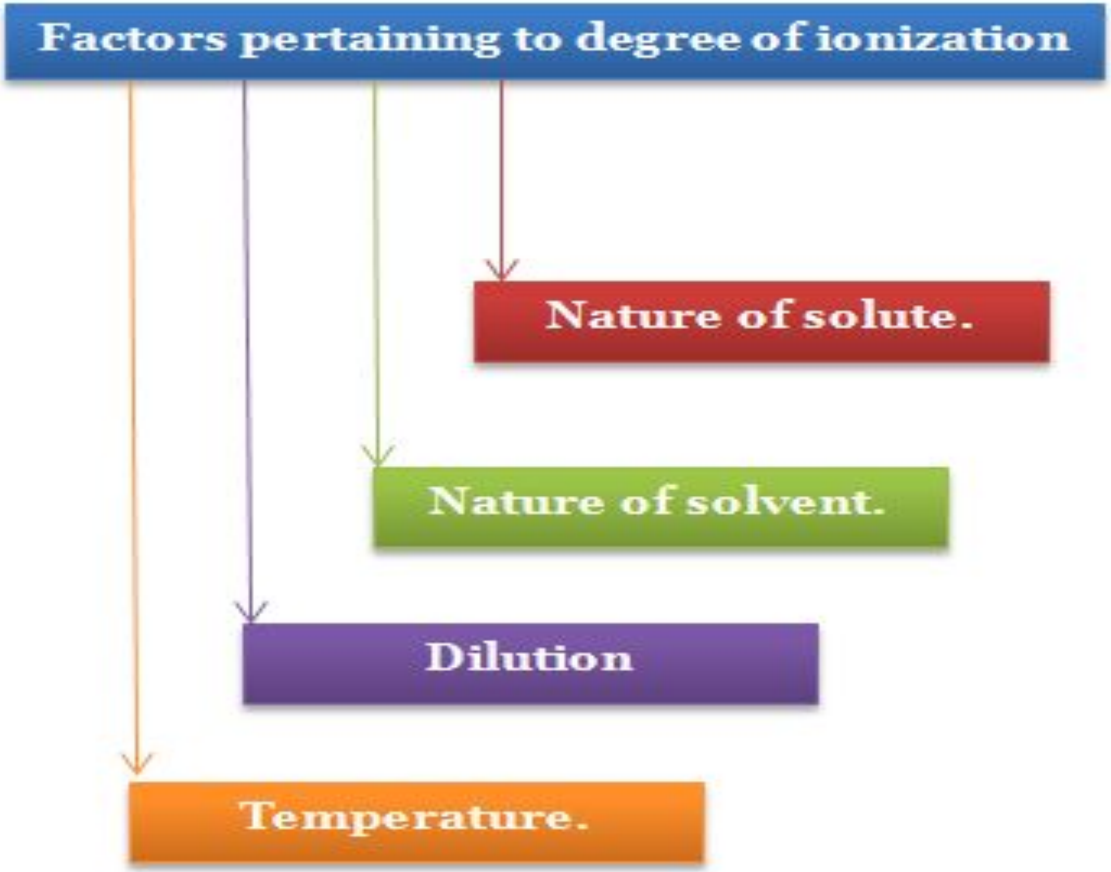
A pragmatic method of determining whether an acid is weak … just learn the strong acids!

Strength and properties of the electrolyte are described by the following values:

- **the degree (*α*) of ionization**
- and **the dissociation constant (K_{diss})** of the electrolyte.

Degree of ionization '*α*' may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions:

$$\alpha = \frac{n\ \ (number\ of\ molecules\ dissociated\ \ \mathrm{int}\,o\ ions)}{N\ \ (Total\ \ number\ of\ \ molecules)} \cdot 100\%$$

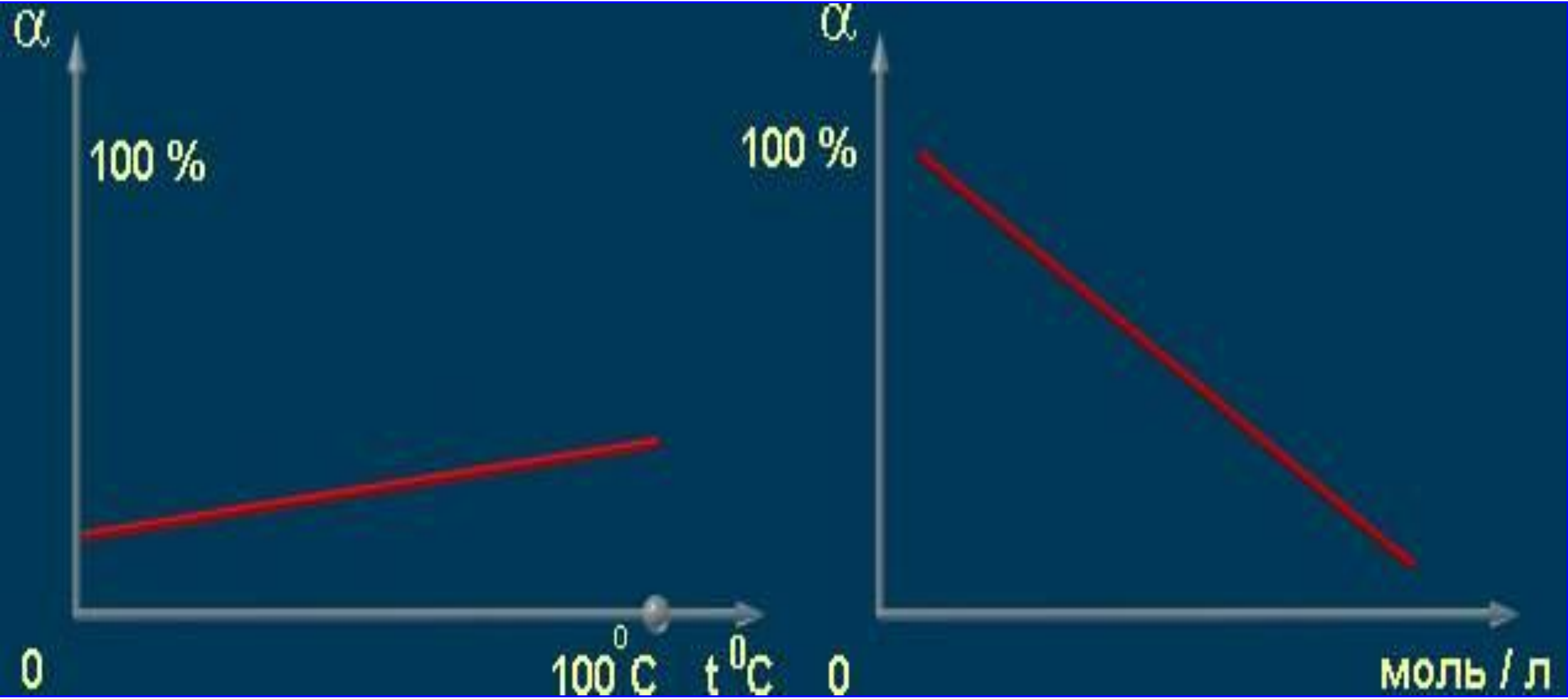


Factors pertaining to degree of ionization

- Nature of solute.
- Nature of solvent.
- Dilution
- Temperature.

Values of the degree of dissociation (ex)depends upon the following factors

1. nature of solute
2. nature of solvent
3. concentration
4. temperature



When temperature is increased, degree of ionization increase too

When concentration is increased, degree of ionization decrease

Dissociation is reversible process. Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e., $A_xB_y \rightarrow x\,A^+ + y\,B^-$

Applying the law of mass action to above equilibrium, we have constant ***K*** is known as ***ionization constant*** :

$$K_{diss} = \frac{[A^+]^x \cdot [B^-]^y}{[A_xB_y]}$$

$$a)\ H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$$

$$K_{дисс} = \frac{[H^+]^3 \cdot [PO_4^{3-}]}{[H_3PO_4]}$$

$$b)\ Cu(OH)_2 \rightarrow Cu^{2+} + 2OH^-$$

$$K_{дисс} = \frac{[Cu^{2+}] \cdot [OH^-]^2}{[Cu(OH)_2]}$$

- **For strong electrolytes** α>0,3 (30%) and they having high value of K_{diss}
- **For weak electrolytes** α<0,3 (0 – 30%) and those having low constant value of K_{diss}

OSTWALD'S DILUTION LAW

- This law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and $\lambda/\lambda\infty$ does not give an accurate value of 'α'.
- When the concentration of ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, law of mass action cannot be strictly applied in the case of strong electrolytes.
- **For strong electrolytes:**

$$K_{diss} = \frac{\alpha^2 \cdot C_M}{1-\alpha}$$

where K is dissociation constant and C is molar concentration of the solution.

OSTWALD'S DILUTION LAW

- **For weak electrolytes (Kdiss=const and (1 – α) ≈ 1):**

$$K_{diss} = \alpha^2 \cdot C_M \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_{diss}}{C_M}}$$

Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

“**For a weak electrolyte, the degree of ionisation is inversely proportional to the square root of molar concentration or directly proportional to the square root of volume containing one mole of the solute**.” **This is called Ostwald’s dilution law.**

IONIC REACTIONS

A chemical equation which shows dissociation of electrolyte and written as dissociated ions of electrolyte is known as **ionic equation**.

Double Replacement (Metathesis) Reactions involve swapping ions in solution:

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

Metathesis reactions will lead to a change in solution if one of three things occurs:

- **An insoluble solid is formed** (When a chemical reaction forms such a solute, the insoluble solute comes out of solution and is called a ***precipitate***),
- **Weak acids are formed** (H_2SO_3, CH_3COOH),
- **An insoluble gas is formed** (H_2S, CO_2, SO_2, NH_3),
- **Neutralization reaction**

IONIC REACTION

Irreversible reaction

- **Precipitate(↓)**

  $BaCl_2 + Na_2SO_4 = \mathbf{BaSO_4}\downarrow + 2NaCl$

- **Gas reaction**

  $Na_2S + 2HCl = \mathbf{H_2S}\uparrow + 2NaCl$

- **Weak electrolytes are formed**

  $2CH_3COOK + H_2SO_4 = \mathbf{2CH_3COOH} + K_2SO_4$

- **Complex compounds are formed**

  $Hg(NO_3)_2 + 4KJ = \mathbf{K_2[HgJ_4]} + 2KNO_3$

Acid–Base Reactions: Neutralization

Neutralization is the (usually complete) reaction of an acid with a base. The products of this neutralization are *water* and a ***salt***.

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Acid–Base Reactions: Net Ionic Equations

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{H_2O} + \mathrm{NaCl}$$

- In the reaction above, the HCl, NaOH, and NaCl all are strong electrolytes and dissociate completely.
- The actual reaction occurs between ***ions***.

Na^+ and Cl^- are *spectator* ions.

$$\mathrm{H^+} + \cancel{\mathrm{Cl^-}} + \cancel{\mathrm{Na^+}} + \mathrm{OH^-} \rightarrow \mathrm{H_2O} + \cancel{\mathrm{Na^+}} + \cancel{\mathrm{Cl^-}}$$

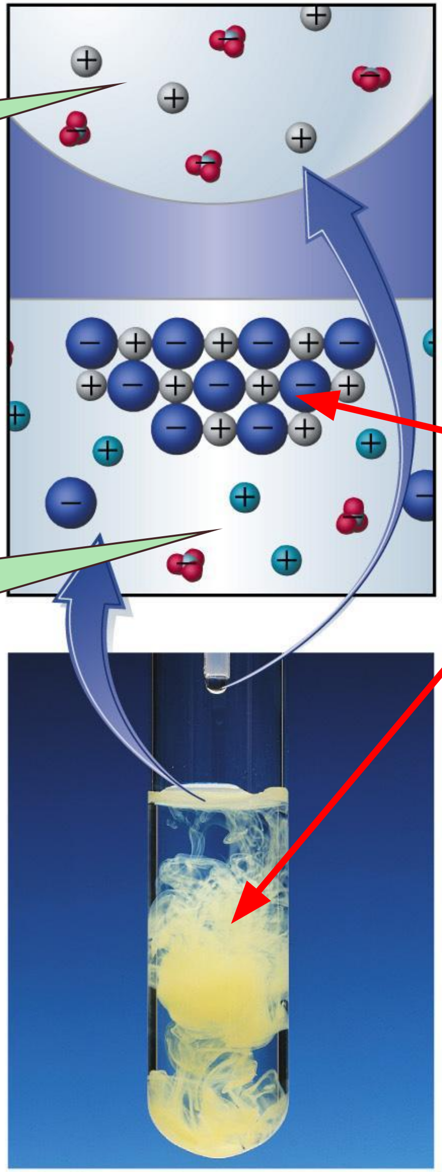
$$\mathrm{H^+} + \mathrm{OH^-} \rightarrow \mathrm{H_2O}$$

A ***net ionic*** equation shows the species actually involved in the reaction.

Reactions that Form Precipitates

- There are limits to the amount of a solute that will dissolve in a given amount of water.
- If the maximum concentration of solute is less than about 0.01 M, we refer to the solute as *insoluble* in water.
- When a chemical reaction forms such a solute, the insoluble solute comes out of solution and is called a ***precipitate***.

Silver Iodide Precipitation



A solution containing silver ions and nitrate ions, when added to …

… a solution containing potassium ions and iodide ions, forms …

… a precipitate of silver iodide.

What is the net ionic equation for the reaction that has occurred here? (Hint: what species actually reacted?)

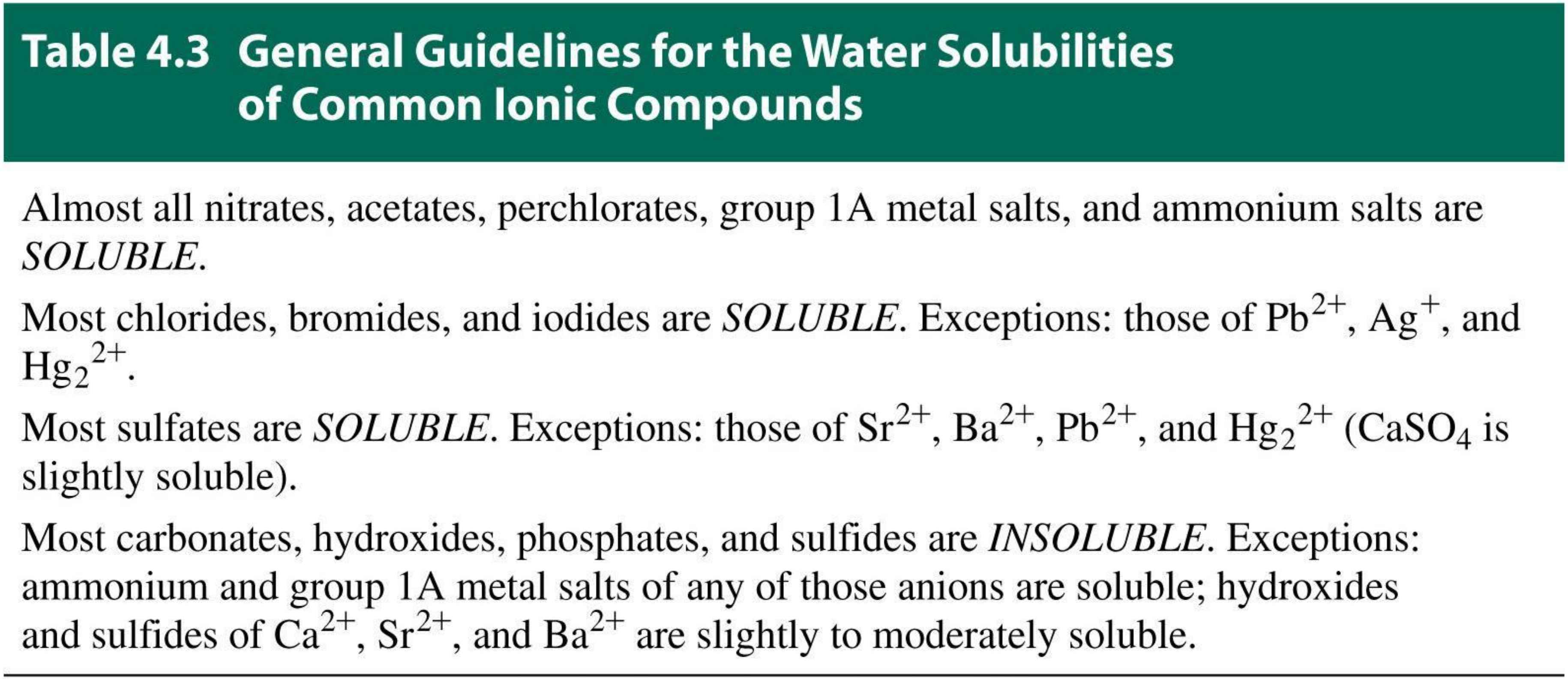


Table 4.3 General Guidelines for the Water Solubilities of Common Ionic Compounds

Almost all nitrates, acetates, perchlorates, group 1A metal salts, and ammonium salts are *SOLUBLE*.

Most chlorides, bromides, and iodides are *SOLUBLE*. Exceptions: those of Pb^{2+}, Ag^{+}, and Hg_2^{2+}.

Most sulfates are *SOLUBLE*. Exceptions: those of Sr^{2+}, Ba^{2+}, Pb^{2+}, and Hg_2^{2+} ($CaSO_4$ is slightly soluble).

Most carbonates, hydroxides, phosphates, and sulfides are *INSOLUBLE*. Exceptions: ammonium and group 1A metal salts of any of those anions are soluble; hydroxides and sulfides of Ca^{2+}, Sr^{2+}, and Ba^{2+} are slightly to moderately soluble.

- With these guidelines we can predict precipitation reactions.
- When solutions of sodium carbonate and iron (III) nitrate are mixed, a precipitate will form.
- When solutions of lead acetate and calcium chloride are mixed, a precipitate will form.

Table 4.4 Some Precipitation Reactions of Practical Importance

Reaction in Aqueous Solution	Application
$Al^{3+}(aq) + 3\,OH^{-}(aq) \longrightarrow Al(OH)_3(s)$	Water purification. (The gelatinous precipitate carries down suspended matter.)
$Al^{3+}(aq) + PO_4^{3-}(aq) \longrightarrow AlPO_4(s)$	Removal of phosphates from wastewater in sewage treatment.
$Mg^{2+}(aq) + 2\,OH^{-}(aq) \longrightarrow Mg(OH)_2(s)$	Precipitation of magnesium ion from seawater. (First step in the Dow process for extracting magnesium from seawater.)
$Ag^{+}(aq) + Br^{-}(aq) \longrightarrow AgBr(s)$	Preparation of AgBr for use in photographic film.
$Zn^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + S^{2-}(aq) \longrightarrow ZnS(s) + BaSO_4(s)$	Production of *lithopone*, a mixture used as a white pigment in both water paints and oil paints.
$H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow CaHPO_4 \cdot 2\,H_2O(s)$	Preparation of calcium hydrogen phosphate dihydrate, used as a polishing agent in toothpastes.