

CHM 101 2018-2019

Learning Objectives:

Important applications of equilibria like

- pH
- Solubility
- Solubility of Ionic Solids

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What is pH?



The Simple Definition

- **pH** is a logarithmic measure of hydrogen ion (H^+) concentration

- originally defined by Danish biochemist Søren Peter Lauritz Sørensen in 1909

- **$pH = -\log[H^+]$**

where **log** is a base-10 logarithm and **$[H^+]$** is the concentration of hydrogen ions in moles per liter of solution.

- "p" stands for the German word for "power", *potenz*, so pH is an abbreviation for "power of hydrogen"

Understanding pH

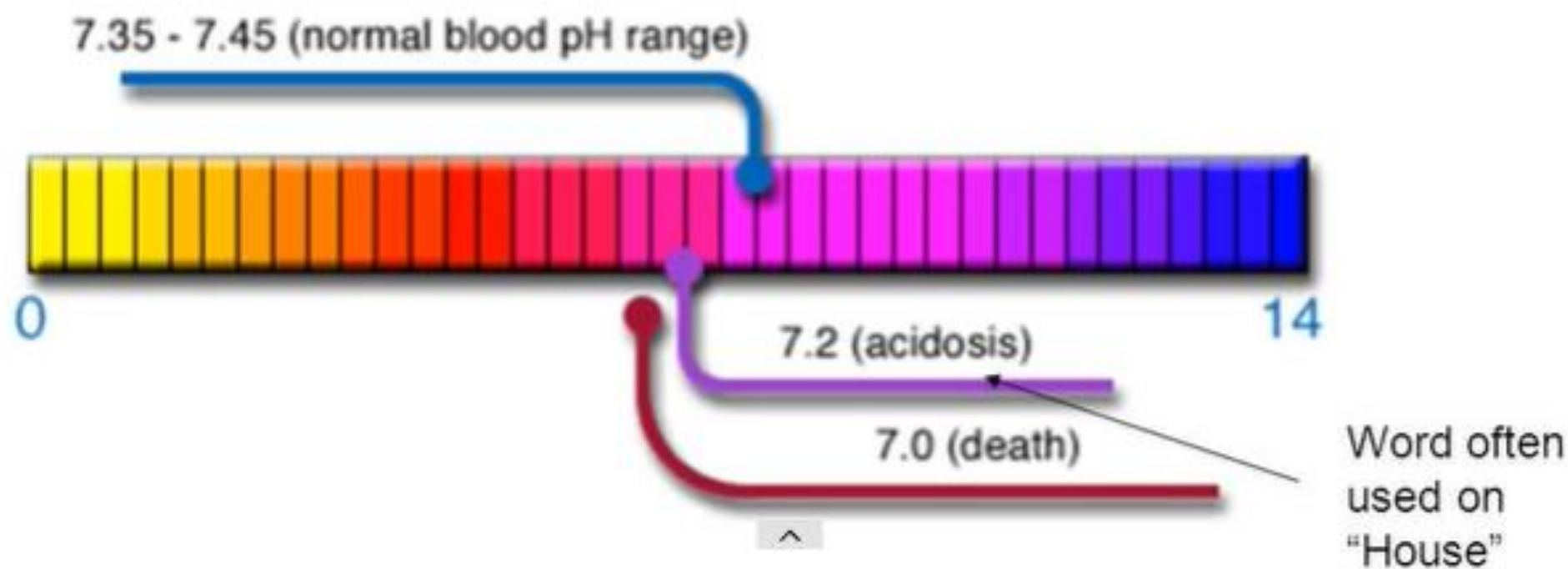
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- The hydrogen ion concentration in pure water around room temperature is about $1.0 \times 10^{-7} \text{ M}$.
- Which equals a pH of 7 is considered "neutral", because the concentration of hydrogen ions(H^+) is exactly equal to the concentration of hydroxide (OH^-) ions produced by dissociation of the water.
- Do you see why the pH is 7?



What's Normal

- The pH level of blood is the most important balance system of the body. Look at the blood pH as shown below.*



What's Normal

- Any drop in pH, no matter how slight, is the **beginning of a disease state and affects when and how we age.**
- All other organs and fluids will fluctuate in their range in order to keep the blood at a strict pH between 7.35 and 7.45 (slightly alkaline).
- This process is called homeostasis: The body makes constant adjustments in tissue and fluid pH to maintain this very narrow pH range in the blood.

PH & its Applications

COMMON PH VALUES AROUND US

- pH of cheese is between 4.8–6.4.
- pH of bananas is between 4.5–5.2.
- pH of grapes is between 3.5–4.5.
- pH of lime juice is between 2.0–2.4.

IMPORTANCE OF PH

- Our body works within the **pH range of 7.0 to 7.8.**
- Living organisms can survive only in a narrow range of pH change.
- When pH of rain-water is less than 5.6, it is called **acid rain.**
- When acid rain flows into the rivers, it lowers the **pH of the river water.**
- The survival of aquatic life in such rivers becomes difficult.

PH IN DIGESTIVE SYSTEM -

- The pH in the human digestive tract varies greatly.
- The pH of saliva is usually between 6.5 - 7.5. The fundic or upper portion of the stomach has a pH between 4.0 - 6.5,
- lower portion of the stomach secrete **hydrochloric acid (HCl) and pepsin** until it reaches a pH between 1.5 - 4.0

PH METER

- **A pH Meter is a scientific instrument that measures the hydrogen-ion concentration (or pH) in a solution, indicating its acidity or alkalinity.**
- **The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode.**

PH IN GROWING CROPS - DEFINITION

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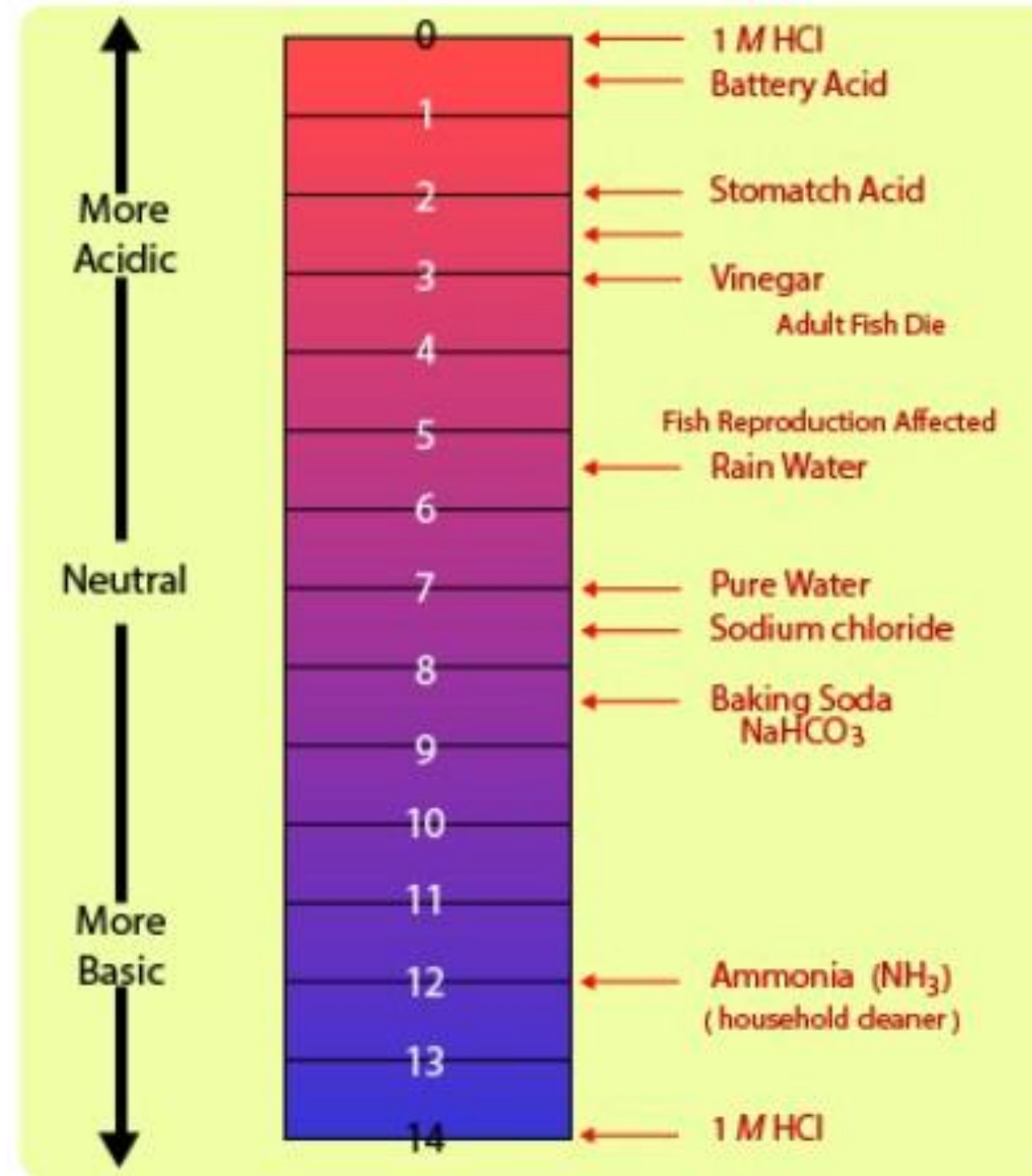
- **pH is a scale that chemists use to measure acidity. Values below 7 are considered acidic, values above 7 are alkaline (the opposite of acidic) and 7 is neutral.**
- **Most plants can tolerate a wide pH range in solution culture, but they cannot tolerate a wide range of acidity in the soil.**

RANGE OF PH SCALE

- The range of pH scale is from 0 to 14. The pH value from 0 to 7 indicates the acidic nature of solution whereas from 7 to 14 indicates the basic nature of solution. The intermediate value that is 7 indicates neutral nature of solution such as pure water.

Ammonia or Sodium Hydroxide show the pH value in the range 7-14, which reflects their basic nature.

On the contrary, acidic substances like vinegar, stomach acid, battery acid, coke etc show pH range from 0-7 that shows their acidic nature.



EFFECT OF PH ON PLANTS AND ANIMALS

- High levels of either acidity or alkalinity can be harmful to plants and animals.

Effect on Plants: Most of the plants do best when soil's pH is in the neutral range i.e. 6 to 7. Acidic soil can prevent certain nutrients from being absorbed by plants that are best absorbed **in alkaline soil**. In very alkaline soil, certain important micro-nutrients such as zinc and copper become **chemically unavailable to plants**.

Effect on Animals: Effect of pH is most observed for the animals that stay in water. Acidic water robs fish and other aquatic species of **sodium in the blood and oxygen in the tissues**. Additionally, it affects the **functioning of fish gills**. Acidic water also **poisons fish eggs**, as they will not hatch if water pH is too low. In addition to the direct effects on fish, acid water also **destroys ecosystems by killing organisms lower on the food chain**.

EFFECT OF PH ON TOOTH DECAY

- The saliva in a healthy mouth has a pH of 7.1.
- Certain foods increase the acidity of the mouth and reduce the pH level. Saliva helps neutralize the acid, **but the pH of saliva can become more acidic after eating acidic foods.** It can take between a few minutes to a few hours for the pH of the mouth to neutralize.
- In that time, **the lower pH of the mouth creates an optimal environment for bad bacteria, which eventually causes tooth decay.**

PH OF SOIL IN BACKYARD

- **Soil pH** is dictated by type of parent material from which soil is formed, rainfall, organic matter content among others.
- Soil in the backyard would mean it consists of kitchen garden growing grass, vegetables, trees etc., and it would have been supplied with some kind of organic amendments, fertilizers etc., over a period of time.
- **In such a scenario pH of acidic soils would improve and move towards neutral and pH of alkali soils would also move towards neutral.**

PH OF SALTS

- Salt can be made of either a weak acid and strong base, strong acid and weak base, strong acid and strong base, or a weak acid and weak base.
 1. Salts that are formed from strong bases and strong acids **will give a pH of 7 in their solution.**
 2. Salts that are formed from strong bases and weak acids **give a pH greater than 7 in their solution.**
 3. Salts that are formed from weak bases and strong acids **give a pH of less than 7 in their solution.**

pH in Chemistry

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- pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity, a_{H^+} in a solution.

$$\text{pH} = -\log_{10}(a_{\text{H}^+}) = \log_{10}\left(\frac{1}{a_{\text{H}^+}}\right)$$

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

For example,

- For a solution with a hydrogen ion activity of 5×10^{-6} (at that level, this is essentially the number of moles of hydrogen ions per litre of solution)
- There is $1/(5 \times 10^{-6}) = 2 \times 10^5$,
- Thus such a solution has a
- **pH of $\log_{10}(2 \times 10^5) = 5.3$**

pH depends on temperature

For instance at 0 °C the pH of pure water is about 7.47.

At 25 °C it is 7.00,

and at 100 °C it is 6.14.

Ion-selective electrodes,

- This definition of pH was adopted because **ion-selective electrodes**:
- **which are used to measure pH, respond to activity.**
- Ideally, electrode potential, E , follows the **Nernst equation**, which, for the hydrogen ion can be written as

$$E = E^0 + \frac{RT}{F} \ln(a_{\text{H}^+}) = E^0 - \frac{2.303RT}{F} \text{pH}$$

where E is a measured potential, E^0 is the standard electrode potential, R is the gas constant, T is the temperature in kelvins, F is the Faraday constant.

pH indicators

- Indicators may be used to measure pH, by making use of the fact that their color changes with pH.
- Visual comparison of the color of a test solution with a standard color chart provides a means to measure pH accurate to the nearest whole number.
- More precise measurements are possible if the color is measured spectrophotometrically, using a **colorimeter** or **spectrophotometer**.
- Universal indicator** consists of a mixture of indicators such that there is a continuous color change from about pH 2 to pH 10. Universal indicator paper is made from absorbent paper that has been impregnated with universal indicator. Another method of measuring pH is using an electronic **pH meter**

Average pH of common solutions

Substance	pH range	Type
Battery acid	< 1	Acid
Gastric acid	1.0 – 1.5	
Vinegar	2.5	
Orange juice	3.3 – 4.2	
Black coffee	5 – 5.03	
Milk	6.5 – 6.8	Neutral
Pure water	7	
Sea water	7.5 – 8.4	Base
Ammonia	11.0 – 11.5	
Bleach	12.5	
Lye	13.0 – 13.6	



Spectrophotometer



← **pH meter** →



Universal Indicator

pOH

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- **pOH is sometimes used as a measure of the concentration of hydroxide ions, OH⁻.**
- pOH values are derived from pH measurements. The concentration of hydroxide ions in water is related to the concentration of hydrogen ions by

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

where K_w is the **self-ionization** constant of water.

Taking **logarithms**

$$\text{pOH} = \text{p}K_{\text{w}} - \text{pH}$$

- So, at room temperature, $\text{pOH} \approx 14 - \text{pH}$.
- However this relationship is not strictly valid in other circumstances, such as in measurements of **soil alkalinity**.

Neutrality

- Neutrality is defined as the condition where $[H^+] = [OH^-]$ (or the activities are equal)

- Since **self-ionization of water** holds,
- the product of these concentration $[H^+] \times [OH^-] = K_w$, it can be seen that at neutrality

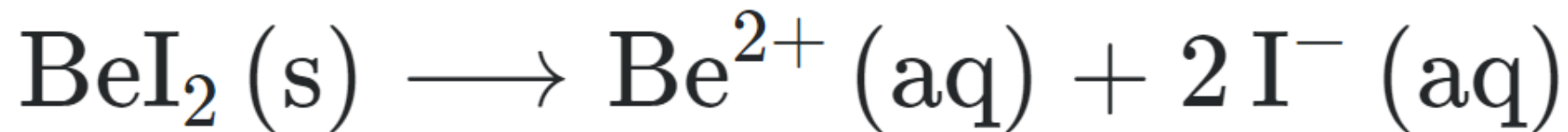
Therefore, $[H^+] = [OH^-] = \sqrt{K_w}$, or

$pH = pK_w/2$. pK_w is approximately 14

but depends on ionic strength and temperature, and so the pH of neutrality does also

Dissociation of Ionic Solids (& Compounds)

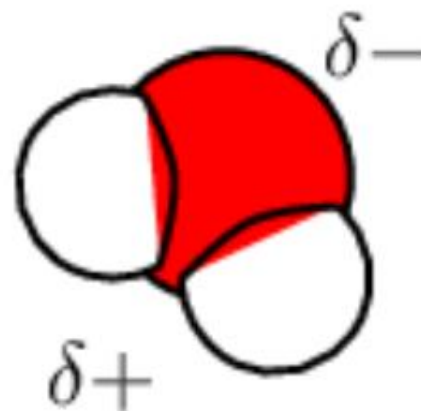
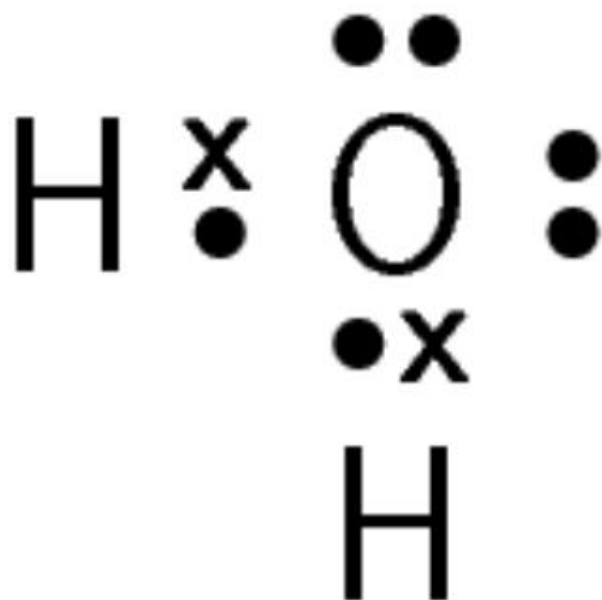
- **Dissociation** in chemistry is a general process in which molecules (or ionic compounds such as salts, or complexes) separate or split into smaller particles such as atoms, ions, or radicals, usually in a reversible manner.



Dissociation in water

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- Water is a **polar molecule**. If we represent water using Lewis structures we will get the following

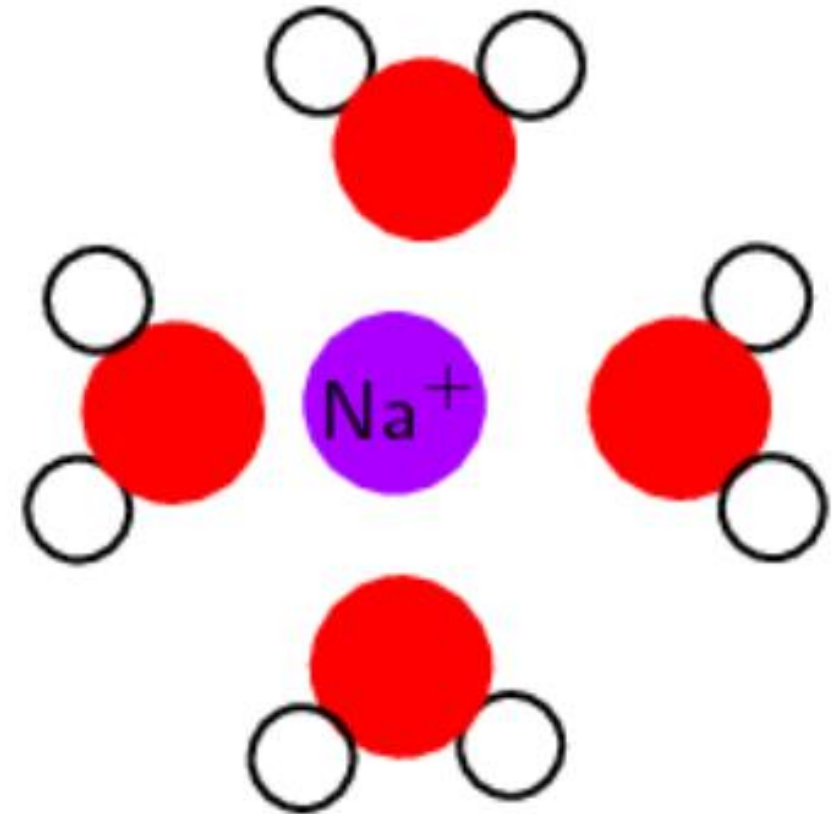
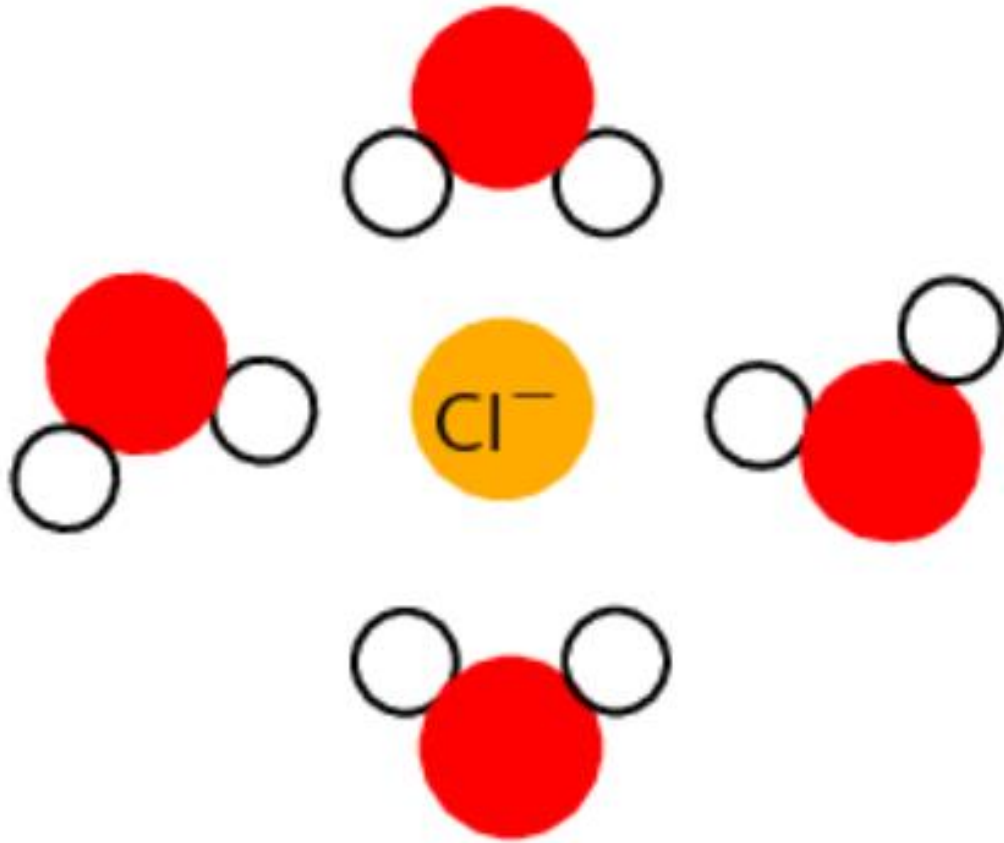


Dissociation of sodium chloride in water

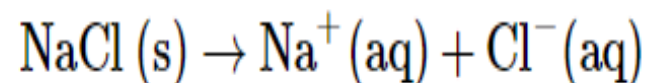
- It is the polar nature of water that allows ionic compounds to dissolve in it.
- In the case of sodium chloride (NaCl) for example, the positive sodium ions (Na^+) are attracted to the negative pole of the water molecule, while the negative chloride ions (Cl^-) are attracted to the positive pole of the water molecule.
- When sodium chloride is dissolved in water, the polar water molecules are able to work their way in between the individual ions in **the lattice**.
- The water molecules surround the negative chloride ions and positive sodium ions and pull them away into the solution.

This process is called dissociation

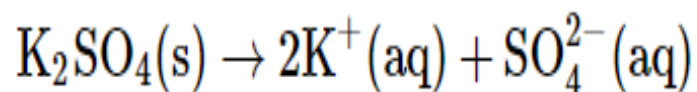
Sodium chloride dissolves in water



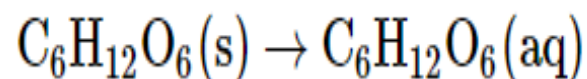
The dissolution of sodium chloride can be represented by the following equation:



The dissolution of potassium sulfate into potassium and sulfate ions is shown below as another example:

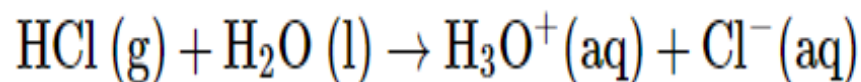


Remember that **molecular** substances (e.g. covalent compounds) may also dissolve, but most will not form ions. One example is glucose.



There are exceptions to this and some molecular substances *will* form ions when they dissolve. Hydrogen chloride for example can ionise to hydrogen and chloride ions.

form



For Acids , Bases & Ionic Solids

Electrolyte

Acids, Bases, and ionic compounds

pH between 0 and 7

Acid

pH between 7 and 14

Base

Turns litmus paper pink

Acid

Turns litmus paper blue

Base

Calculating pH for Acids , Bases & Ionic Solids

- [pH] or potential of Hydrogen, is measured on a scale from 0 to 14. **0 being the most ACIDIC, while 14 being the most BASIC**
- To find pH from the concentration of H_3O^+ (or just simply H^+) you need to do the following:

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

The $[\text{H}_3\text{O}^+]$ or $[\text{H}^+]$ is just the concentration (in molarity)

If you have the concentration of OH^- , however, simply find the pOH by:

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

- After you get this number, you do the following:

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

Related questions

pH has a great importance in agriculture because:

Correct Answer

- A** soil is often tested to determine whether acidic or basic fertilizers are required for particular crop.
 - B** for large number of qualitative and quantitative analysis.
 - C** both a and b
 - D** none of the above
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The pH of soil A is 7.5 while that of soil B is 4.5. Which of the two soils, A or B, should be treated with powdered chalk to adjust its pH and why?

Answer

Soil B should be treated with powdered chalk to adjust its pH. Soil B is acidic in nature so its treated with powdered chalk to reduce its acidity.

pH of an aqueous solution of NaCl at 85°C should be:

A 7

B > 7

C < 7

D 0

Answer

Correct option is ☒ C < 7

As $T \uparrow$, $pK_W \downarrow$

$\text{pH of salts} = \frac{pK_W}{2}$ As they are neutral.

$pK_W \downarrow \rightarrow \frac{pK_W}{2} \downarrow \quad \text{pH} \downarrow$

$\text{pH} < 7$

- The **importance of water pH** is to keep your body in balance and to regulate metabolic processes. A diet high in acidity will lead to weight gain, slower immune response, and susceptibility to disease, while a diet too alkaline will lead to inability to metabolize key nutrients.

The pH of D_2O and H_2O at 298 K is:

A 7.0, 7.0

B 7.35, 7.0

C 7.0, 6.85

D 6.85, 7.35

Answer

Correct option is **B** 7.35, 7.0

In case of D_2O the bonds are readily broken as compared to water. Hence, the ionic product of D_2O is less than that of water. Hence, pH of D_2O is more, i.e. 7.35 and of water is 7.

How many times a 0.1 M strong monobasic acid solution should be diluted so that pH of the resulting solution is tripled?

A 50

B 10

C 25

D 100

E 1000

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$$pH = -\log [\text{conc}]$$

$$pH = -\log (10^{-1})$$

$$pH = 1 \quad \text{if } pH = 3 \Rightarrow 100 \text{ times}$$

$$3 = -\log 10^{-x}$$

$$3 = x \log 10 \quad x = 3$$

YouTube video player

OR

Given that

Monobasic acid = 0.1M

Let consider the acid is HCl

then,

$$H^+ = 0.1$$

$$pH = -\log(0.1) = 1$$

According to question the resulting pH after dilution should be tripled.

means $pH = 3$

$$[H^+] = 10^{-3}$$

Assume if V ml of 0.1M solution were taken initially then, volume required to get 0.001M concentration

$$M_1 V_1 = M_2 V_2$$

$$0.1V = 0.001V_2$$

$$V_2 = 100V$$

100 times dilution is required.

Option D is correct.

pH of water is 7 so it is:

A acidic

B neutral

C basic

D none of these

Fresh milk has a pH of 6. On changing into curd, its pH becomes :

A more than 6

B less than 6

C does not change

D 7

Which of the following has the greatest concentration of H^+ ion?

A 1 M HCl solution

B 1 M H_3PO_2 solution

C 1 M H_2SO_4 solution

D 1 M H_2CO_3 solution

Answer

- **Correct option is C**
- **1 M H₂SO₄ solution**
- **Given concentration of all the acidic solutions is equal.
However, H₂SO₄ being the strongest acid will dissociate completely
thus giving highest concentration of H⁺ ions.**

Our body works within the pH range of:

A 6 - 6.5

B 7 - 7.8

C 8 - 9

D 6.5 - 7

Give one example each of a salt which gives an aqueous solution having:

- (a) pH less than 7
- (b) pH equal to 7
- (c) pH more than 7

Answer

(a) Ammonium chloride (NH_4Cl) has a pH less than 7 since it is made of strong acid and weak base.

(b) Sodium chloride (NaCl) has a pH equal to 7 since it is made of strong acid and strong base.

(c) Sodium carbonate (Na_2CO_3) has a pH more than 7 since it is made of a weak acid and a strong base.

For a weak base BOH, $K_b = 10^{-4}$. Calculate pH of 10^{-4} M BOH solution.

(Take $\log 6.2 = 0.79$)

A 10

B 9.79

C 8

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D None of these

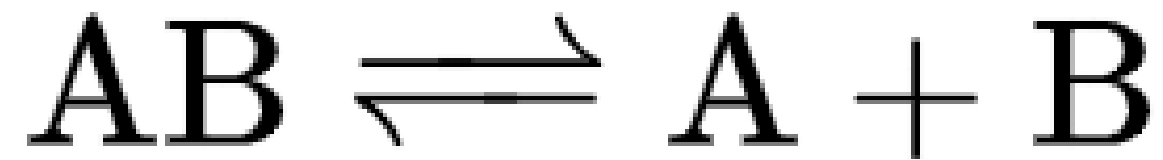
Answer

Correct option is ☒ B less than 6

Fresh milk is less acidic with 6 but the milk bacteria lactose dehydrogenase converts it into curd by producing lactic acid which increases the acidity of milk making it less than 6.

pH balance disorders

- A blood pH imbalance can lead to two conditions: **acidosis and alkalosis**.
- **Acidosis** refers to having blood that's too acidic, or a blood pH of less than 7.35. **Alkalosis** refers to having blood that's too basic, or a blood pH of higher than 7.45.
- There are different types of acidosis and alkalosis based on the underlying cause.
- When acidosis or alkalosis is caused by a lung disorder or issue with exhalation, it's referred to as "**respiratory.**" When acidosis or alkalosis is caused by a problem with the functioning of the kidneys, it's referred to as "**metabolic.**"



the dissociation constant K_d

$$K_d = \frac{[A][B]}{[AB]}$$

Similar Concepts in dissociation

DEFINITION

Dissociation

Dissociation is a general process in which ionic compounds separate into smaller ions, usually in a reversible manner.

DEFINITION

Dissolution

Dissolution or dissolving is the process where ionic crystals break up into ions in water.

DEFINITION

Hydration

Hydration is the process where ions become surrounded with water molecules.

Recap -----Revision

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Table of Common Ions

Common Positive Ions (Cations)

Monovalent		Divalent		Trivalent	
Hydronium (aqueous)	H ₃ O ⁺	Magnesium	Mg ²⁺	Aluminium	Al ³⁺
Hydrogen (proton)	H ⁺	Calcium	Ca ²⁺	Antimony III	Sb ³⁺
Lithium	Li ⁺	Strontium	Sr ²⁺	Bismuth III	Bi ³⁺
Sodium	Na ⁺	Beryllium	Be ²⁺		
Potassium	K ⁺	Manganese II	Mn ²⁺		
Rubidium	Rb ⁺	Barium	Ba ²⁺		
Cesium	Cs ⁺	Zinc	Zn ²⁺		
Francium	Fr ⁺	Cadmium	Cd ²⁺		
Silver	Ag ⁺	Nickel II	Ni ²⁺		
Ammonium	NH ₄ ⁺	Palladium II	Pd ²⁺		
Thalium	Tl ⁺	Platinum II	Pt ²⁺		
Copper I	Cu ⁺	Copper II	Cu ²⁺		
		Mercury II	Hg ²⁺		
		Mercury I	Hg₂²⁺		
		Iron II	Fe ²⁺	Iron III	Fe ³⁺
		Cobalt II	Co ²⁺	Cobalt III	Co ³⁺
		Chromium II	Cr ²⁺	Chromium III	Cr ³⁺
		Lead II	Pb ²⁺		
		Tin II	Sn ²⁺		

Table 5.2 • Common Acids and Bases

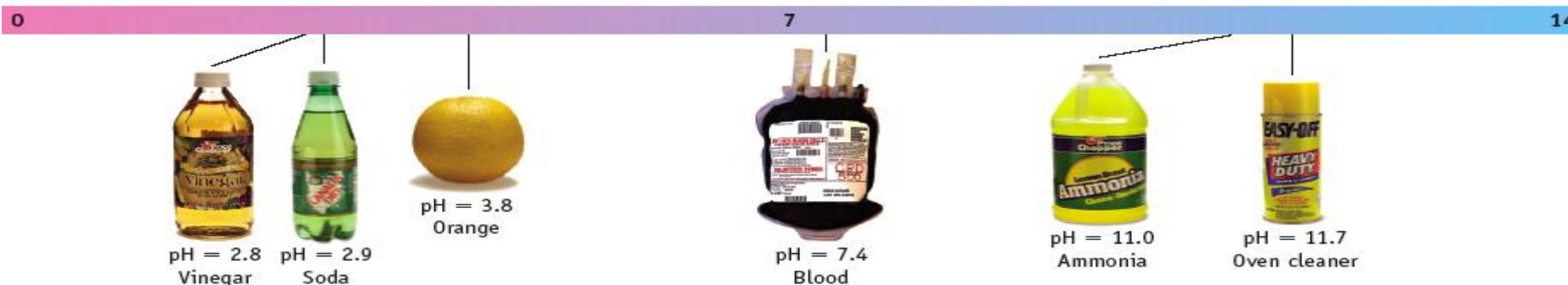
Strong Acids (Strong Electrolytes)		Strong Bases (Strong Electrolytes)	
HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrobromic acid	NaOH	Sodium hydroxide
HI	Hydroiodic acid	KOH	Potassium hydroxide
HNO ₃	Nitric acid		
HClO ₄	Perchloric acid		
H ₂ SO ₄	Sulfuric acid		
Weak Acids (Weak Electrolytes) *		Weak Base (Weak Electrolyte)	
H ₃ PO ₄	Phosphoric acid	NH ₃	Ammonia
H ₂ CO ₃	Carbonic acid		
CH ₃ CO ₂ H	Acetic acid		
H ₂ C ₂ O ₄	Oxalic acid		
C ₄ H ₆ O ₆	Tartaric acid		
C ₆ H ₈ O ₇	Citric acid		
C ₉ H ₈ O ₄	Aspirin		

You should know the
strong acids & bases

*These are representative of hundreds of weak acids.

pH, a Concentration Scale

pH: a way to express acidity -- the concentration of H^+ in solution.



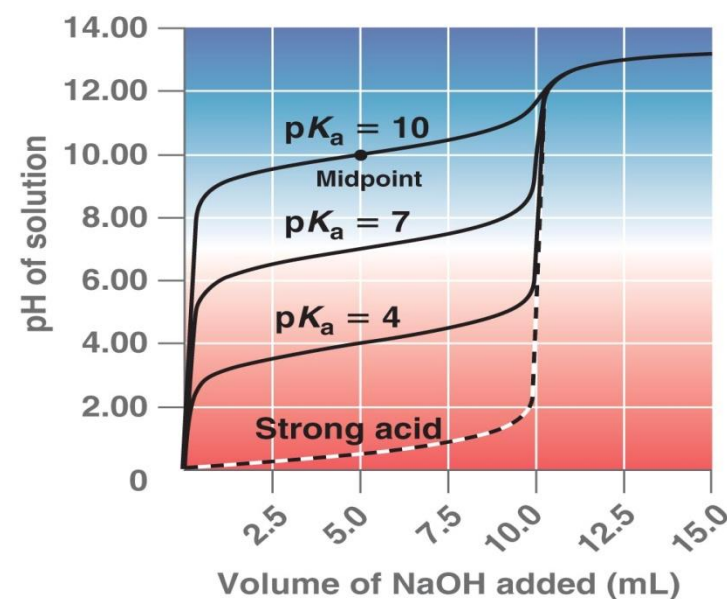
Low pH: high $[\text{H}^+]$

High pH: low $[\text{H}^+]$

$$\text{pH} = \log (1/ [\text{H}^+]) = - \log [\text{H}^+]$$

Acid	Formula	pH at half equivalence point
Acetic	CH_3COOH	4.7
Nitrous	HNO_2	3.3
Hydrofluoric	HF	3.1
Hypochlorous	HClO	7.4
Hydrocyanic	HCN	9

Acidic solution	pH < 7
Neutral	pH = 7
Basic solution	pH > 7



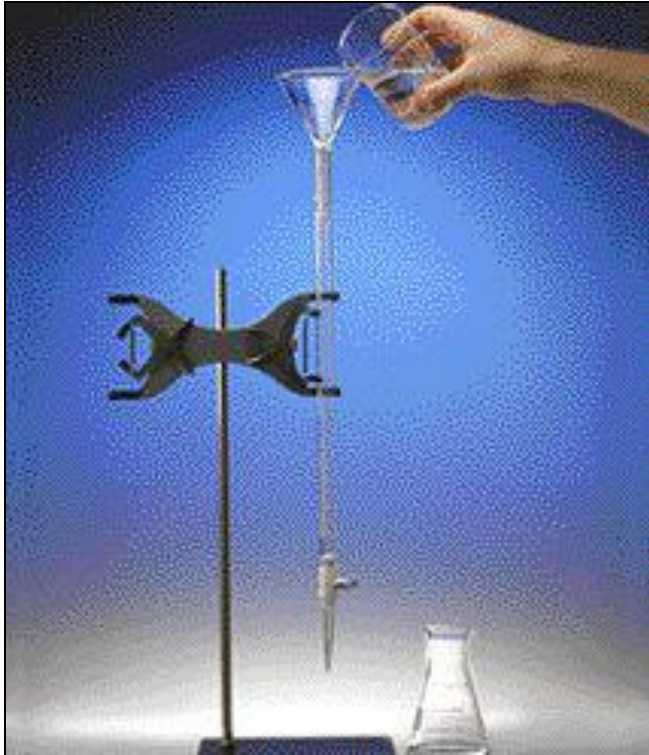
pH, a Concentration Scale

- A convenient way to express the acidity and basicity of a solution is the pH and pOH scales.
- The pH of an aqueous solution is defined as:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

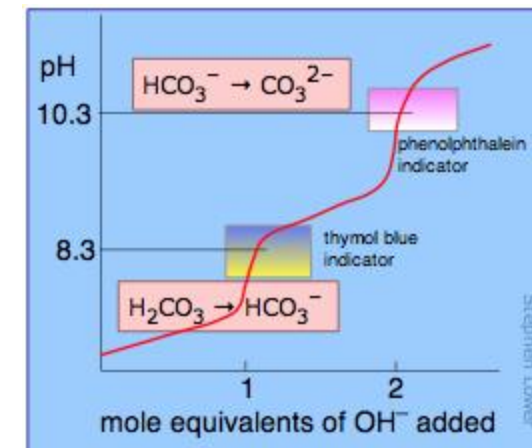
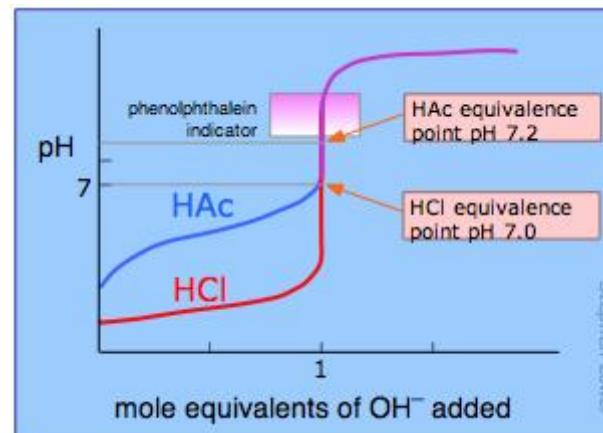
Acid	Formula	pH
Acetic	CH_3COOH	4.7
Nitrous	HNO_2	3.3
Hydrofluoric	HF	3.1
Hypochlorous	HClO	7.4
Hydrocyanic	HCN	9

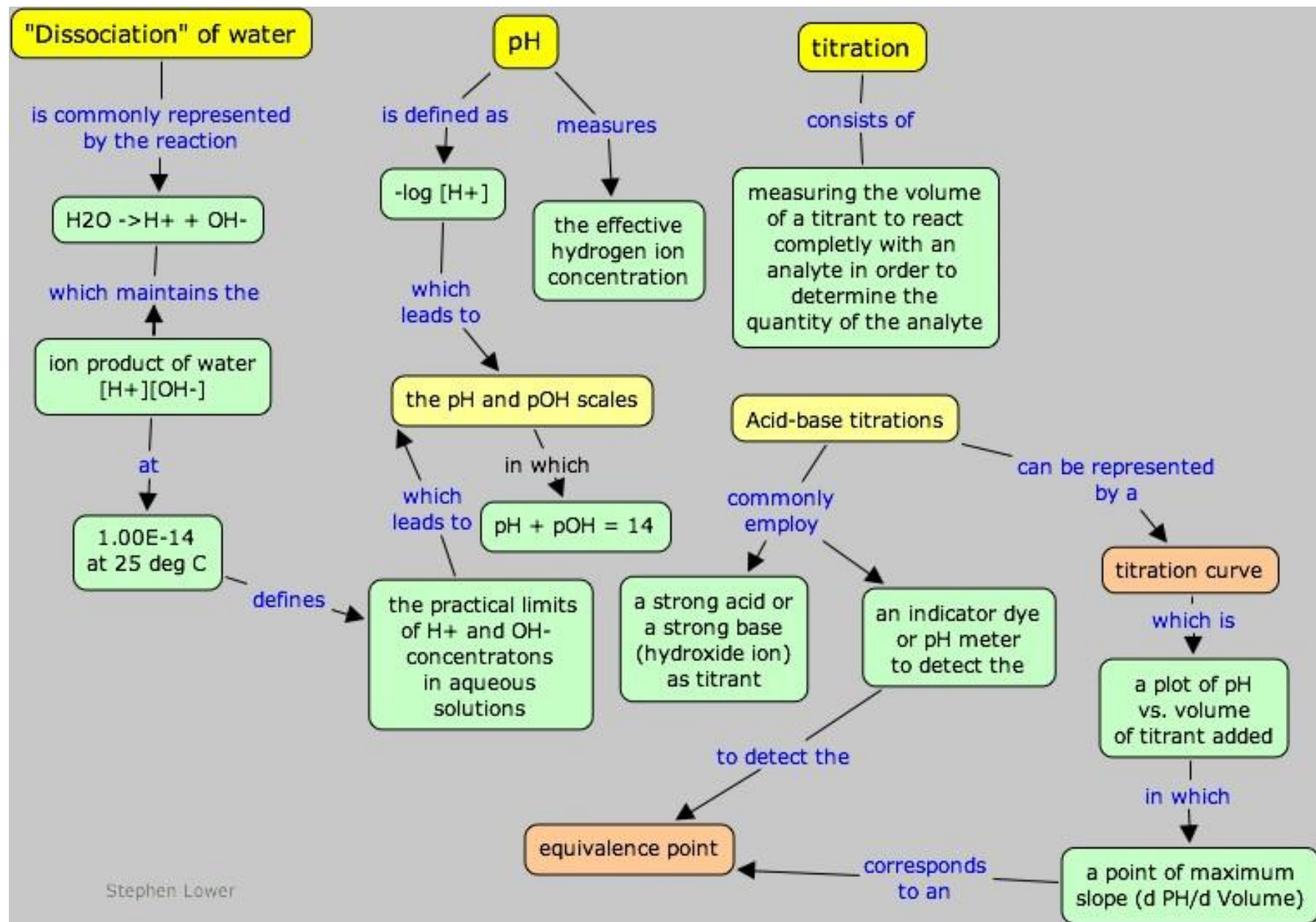
Titration



1. Add solution from the buret.
2. Reagent (base) reacts with compound (acid) in solution in the flask.
3. Indicator shows when exact stoichiometric reaction has occurred.
4. Net ionic equation
$$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$$
5. At equivalence point
moles H^+ = moles OH^-

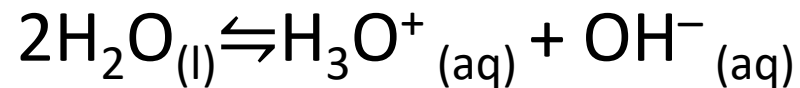
Titrant
Equivalence Point
Primary Standard
End Point
Secondary Standard
Titration





Autoionization of Water

- Because water is amphoteric, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:



- Equilibrium constant K for this reaction can be written as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

- When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of hydronium ion and hydroxide ion are equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M} \quad [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M} = K_w$$

$$\text{pH} = \text{pOH} = 7 \quad \text{pH} + \text{pOH} = \text{p}K_w = 14$$

$$K_c [\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

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New Topic

Lecture Outline

Solubility and Complexation Equilibria

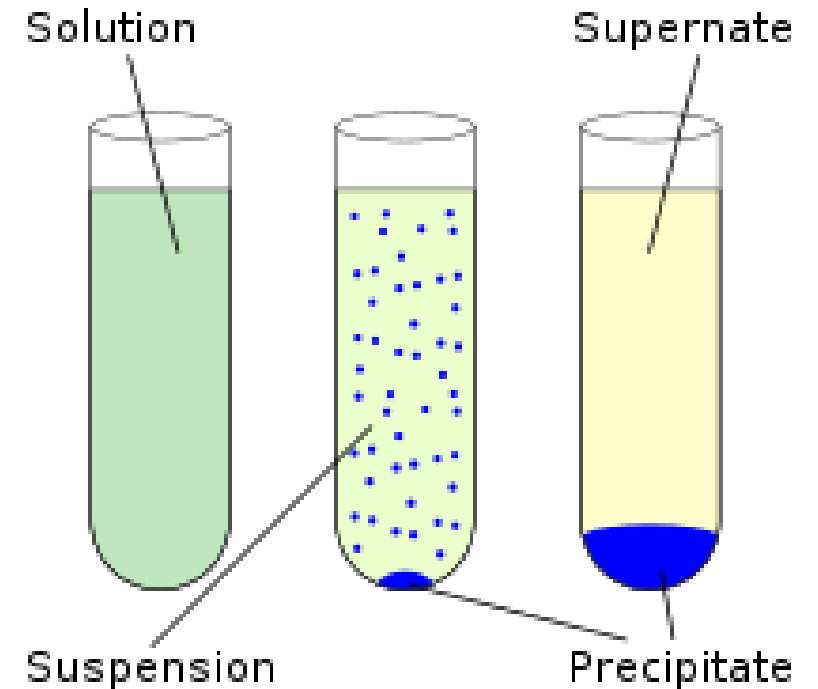


CHAPTER OBJECTIVES

- To be able to calculate the solubility of an ionic compound from its K_{sp}
- To understand the factors that determine the solubility of ionic compounds
- To be able to describe complex-ion formation quantitatively
- To understand why the solubility of many compounds depends on pH

What is **Solubility**

- **Solubility** is the property of a solid, liquid or gaseous chemical substance **called solute** to dissolve in a solid, liquid or gaseous solvent.
- The solubility of a substance fundamentally depends on the physical and chemical properties of the solute and solvent as well as on temperature, pressure and presence of other chemicals (including changes to the **pH**) of the solution



- Solubility may be stated in various units of concentration such as molarity, molality, mole fraction, mole ratio, mass (solute) per volume (solvent) and other units.
- A number of other descriptive terms are also used to qualify the extent of solubility for a given application. For example, [U.S. Pharmacopoeia](#) gives the following terms:

Term	Mass parts of solvent required to dissolve 1 mass part of solute
Very soluble	<1
Freely soluble	1 to 10
Soluble	10 to 30
Sparingly soluble	30 to 100
Slightly soluble	100 to 1000
Very slightly soluble	1000 to 10,000
Practically insoluble or insoluble	$\geq 10,000$

Determining the Solubility of Ionic Compounds

Definition of TERMS: The Solubility Product, K_{sp}

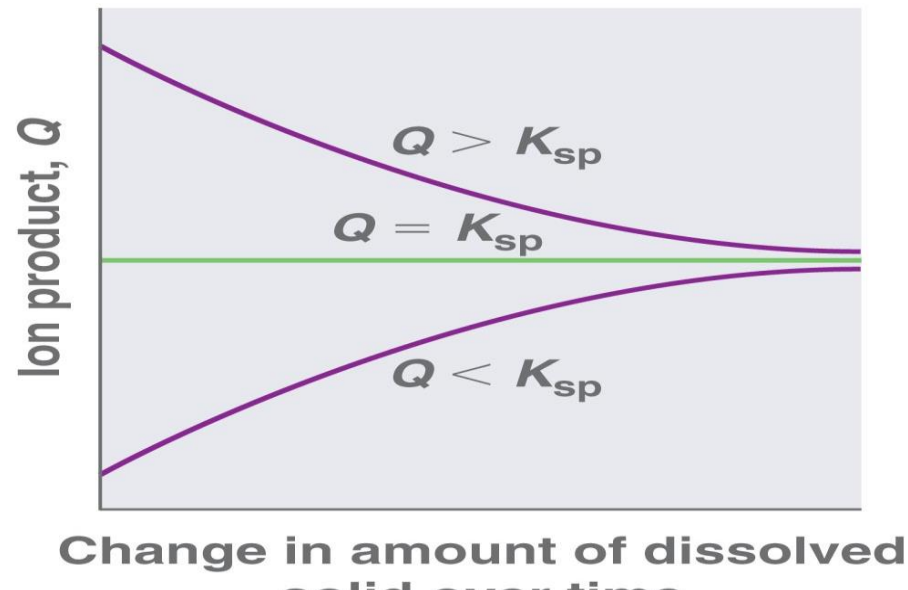
- When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions.
- The equilibrium constant for the dissolution of a sparingly soluble salt is the solubility product of the salt, K_{sp} .
- The concentration of a pure solid is a constant and does not appear in the equilibrium constant expression.
- Solubility products are determined experimentally by either directly measuring the concentration of one of the component ions or by measuring the solubility of the compound in a given amount of water.
- K_{sp} is defined in terms of molar concentrations of the component ions.

Definition of TERMS: The Ion Product

- The ion product (Q) of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression.
- The ion product describes concentrations that are *not* necessarily equilibrium concentrations, whereas K_{sp} describes **equilibrium** concentrations.
- The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product **is a way to determine if a solution is unsaturated, saturated, or supersaturated and whether a precipitate will form when solutions of two soluble salts are mixed.**

Definition of TERMS: The Ion Product

- **Three possible conditions for an aqueous solution of an ionic solid**
 1. $Q < K_{sp}$: the solution is unsaturated, and more of the ionic solid will dissolve
 2. $Q = K_{sp}$: the solution is saturated and at equilibrium
 3. $Q > K_{sp}$: the solution is supersaturated, and ionic solid will precipitate



Definition of TERMS: The Common Ion Effect and Solubility

- **Solubility product expression**

- Equilibrium concentrations of cation and anion are inversely related

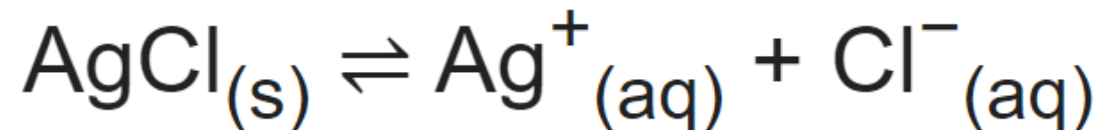
- As the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases, and vice versa

- K_{sp} is constant

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Solubility of ionic compounds in water

- Some ionic compounds (**salts**) dissolve in water, which arises because of the attraction between positive and negative charges.
- For example, the salt's positive ions (e.g. Ag^+) attract the partially negative oxygens in H_2O . Likewise, the salt's negative ions (e.g. Cl^-) attract the partially positive hydrogens in H_2O .
- Note: oxygen is partially negative because it is more **electronegative** than hydrogen, and vice versa



Solubility product, K_{sp} .

- However, there is a limit to how much salt can be dissolved in a given volume of water.
- This amount is given by the solubility product, K_{sp} .
- This value depends on the type of salt (AgCl vs. NaCl, for example), temperature, and the common ion effect.

Calculation of Solubility

- One can calculate the amount of AgCl that will dissolve in 1 liter of water.
- Some algebra is required:

$$K_{sp} = [Ag^+] \times [Cl^-]$$

(definition of solubility product)

- $K_{sp} = 1.8 \times 10^{-10}$ (from a table of solubility products)
- $[Ag^+]$ and $[Cl^-]$ are conc of Silver and Chloride ions respectively

Interpretation

- $[\text{Ag}^+] = [\text{Cl}^-]$, in the absence of other silver or chloride salts,
- $[\text{Ag}^+]^2 = 1.8 \times 10^{-10}$
- $[\text{Ag}^+] = 1.34 \times 10^{-5}$
- Meaning of the result: 1 liter of water can dissolve 1.34×10^{-5} moles of AgCl(s) at room temperature.
- Compared with other types of salts, AgCl is poorly soluble in water. In contrast, table salt (NaCl) has a higher K_{sp} and is, therefore, more soluble.

Factors That Affect Solubility

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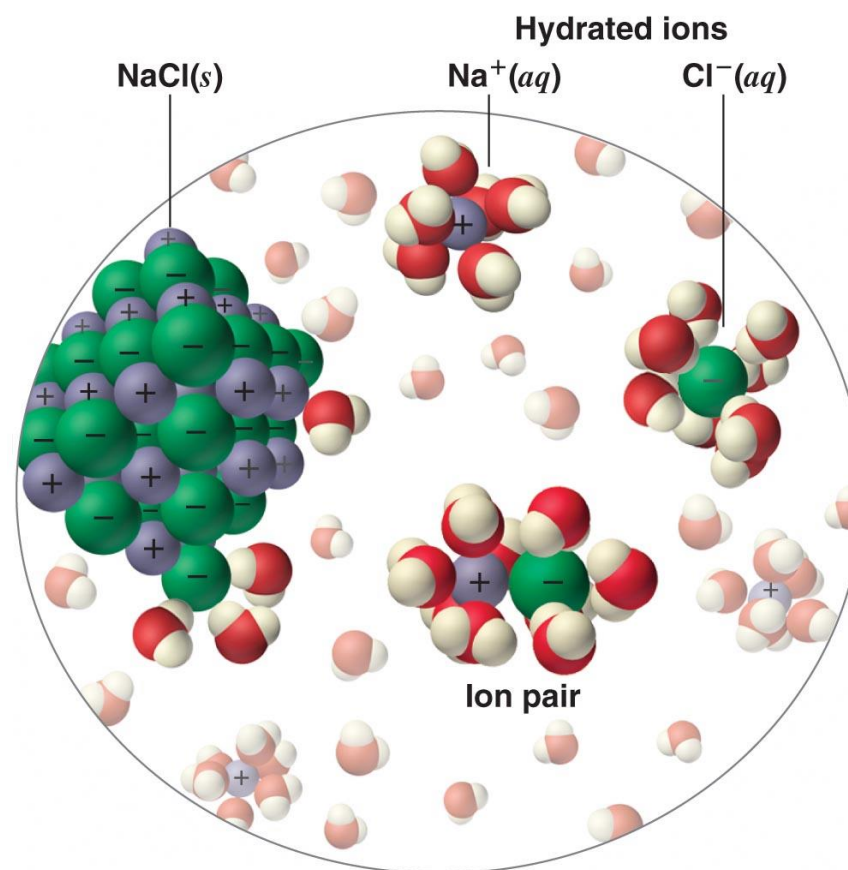
Factors That Affect Solubility

- The solubility product of an ionic compound describes the concentrations of *ions* in equilibrium with a solid.
- There are **four reasons** that the solubility of a compound may be other than expected:
 1. Ion-pair formation
 2. Incomplete dissociation of molecular solutes
 3. Formation of complex ions
 4. Changes in pH

(O level concepts...: Temperature, Pressure, Polarity and rate of dissolution)

Ion-Pair Formation

- An **ion pair** consists of a cation and anion that are in intimate contact in solution, rather than separated by solvent.



Ion-Pair Formation

- Ions in an ion pair are held together by the same attractive electrostatic forces as for ionic solids.
 - Ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions.
 - The ion pair is a species intermediate between the ionic solid (in which each ion participates in many cation-anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

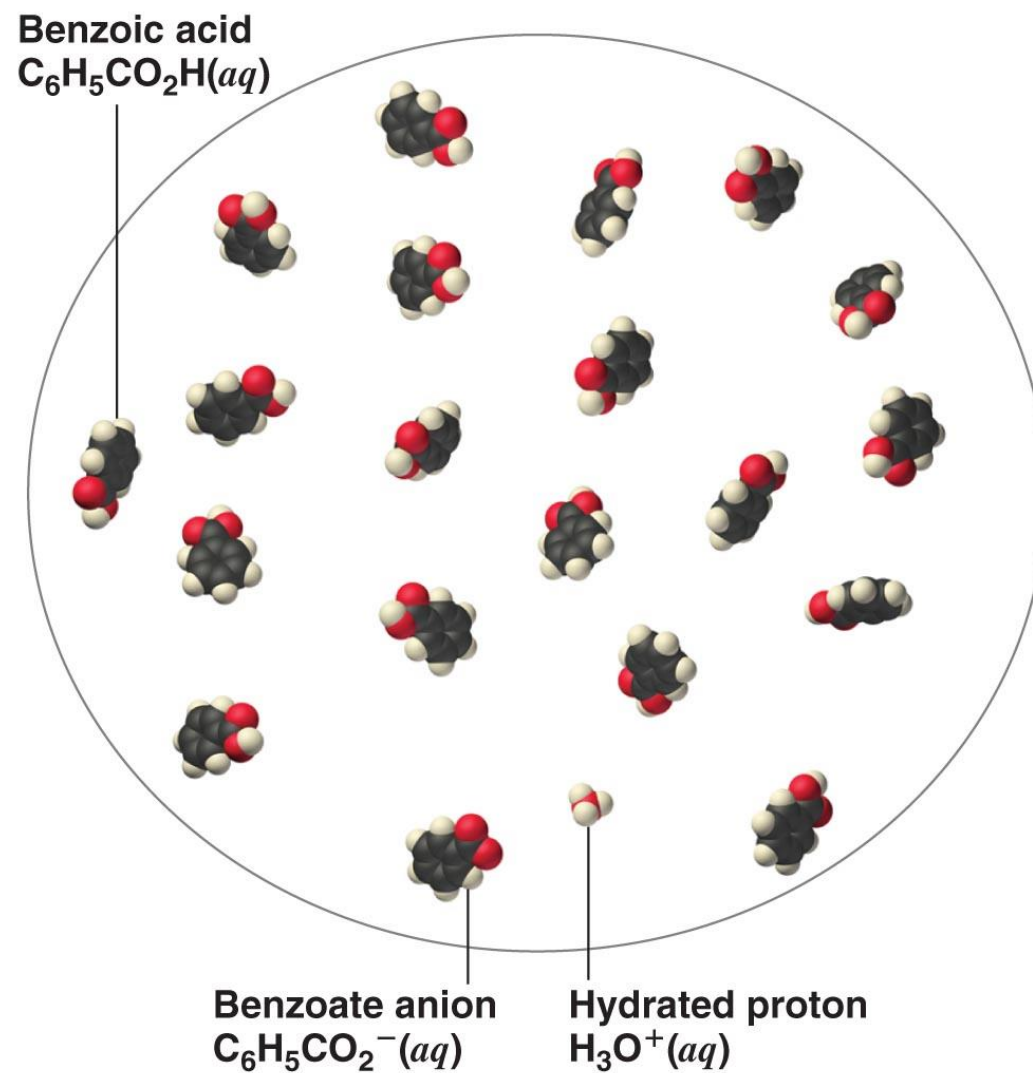
Ion-Pair Formation

- Ion pairs
 - A second equilibrium must be included to describe the solubility of salts that form ion pairs.
 - An ion pair is represented by the symbols of the individual ions separated by a dot, to indicate that they are associated in solution ($\text{Ca}^{2+} \cdot \text{SO}_4^{2-}$).
 - The formation of an ion pair is a dynamic process, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.
 - Ion-pair formation has a major effect on the measured solubility of a salt and is most important for salts that contain M^{2+} and M^{3+} ions; it is unimportant for salts that contain monocations.

Incomplete Dissociation

- A molecular solute may be more soluble than predicted by the measured concentrations of ions in solution due to **incomplete dissociation**.
 - Common for weak organic acids
 - Weak acids do not dissociate completely into their constituent ions (H^+ and A^-) in water
 - The molecular (undissociated) form of a weak acid (HA) is quite soluble in water
 - Many carboxylic acids have a limited solubility in water

Incomplete Dissociation



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Complex-Ion Formation

Complex-Ion Formation

- Metal ions in aqueous solution are *hydrated*—surrounded by a shell of four to six water molecules.
- A hydrated ion is one kind of **complex ion**, molecules or ions that contain at least one lone pair of electrons. , a species formed between a central metal ion and one or more surrounding **ligands (Note the definition)**
- A complex ion forms from a metal ion and a ligand because of a Lewis acid-base interaction.
 - The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base.
 - Small, highly charged metal ions have the greatest tendency to act as Lewis acids and to form complex ions.



The Formation Constant

- The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**.
- Equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression.
- The larger the value of K_f , the more stable the product.

The Effect of Complex-Ion Formation on Solubility

- The solubility of a **sparingly soluble salt increases** if a ligand that forms a stable complex ion is added to the solution.
- The formation of a complex ion by the addition of a **complexing agent increases the solubility of a compound**.
- **Complexing agents** are molecules or ions that increase the solubility of metal salts by forming soluble metal complexes. (Note the definition)

Other examples of complexing agents are: EDTA, Ammonia, phosphates, phosphonates, polycarboxylates, and zeolites

Solubility and pH

Solubility and pH

- Solubility of many compounds depend strongly on the pH of the solution
 - The anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution.
 - The solubility of simple binary compounds such as oxides and sulfides are dependent on pH.

The Effect of Acid-Base Equilibria on the Solubility of Salts

- Examining the effect of pH on the solubility of a representative salt, M^+A^- , where A^- is the conjugate base of the weak acid HA
 - When the salt dissolves in water, this reaction occurs:
$$MA_{(s)} \rightleftharpoons M^+_{(aq)} + A^-_{(aq)} \quad K_{sp} = [M^+] [A^-]$$
 - The anion can also react with water in a hydrolysis reaction:
$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HA_{(aq)}$$
 - If a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA, which decreases $[A^-]$ and which in turn decreases the magnitude of the ion product, $Q = [M^+] [A^-]$
 - More MA will dissolve until $Q = K_{sp}$

Solubility and Partition Phenomena

Contents

Solubility

- Definitions
- Factors influencing solubility
- The effect of pH on solubility
- The effect of pressure
- Influence of solvents on solubility

Contents

Partition Phenomena

- Partition concepts
- For weak electrolytes as solutes
- Drug absorption
- pH partition hypothesis
- Site of drug partitioning

Definitions

- **Solubility** is the **concentration of a solute** when the solvent has dissolved all the solute that it can at a given **temperature**

표 9-1 미국약전에서 용해도의 정의			
Description Forms (Solubility Definition)	Parts of Solvent Required for One Part of Solute	Solubility Range (mg/mL)	Solubility Assigned (mg/mL)
Very soluble (VS)	<1	> 1000	1000
Freely soluble (FS)	From 1 to 10	100 – 1000	100
Soluble	From 10 to 30	33 – 100	33
Sparingly soluble (SPS)	From 30 to 100	10 – 33	10
Slightly soluble (SS)	From 100 to 1000	1 – 10	1
Very slightly soluble (VSS)	From 1000 to 10,000	0.1 – 1	0.1
Practically insoluble (PI)	>10,000	< 0.1	0.01

Factors influencing solubility

- **Dissolution of a crystal**

1. A solute (drug) molecule is removed from its crystal
2. A cavity for the molecule is created in the solvent
3. The solute molecule is inserted into this cavity

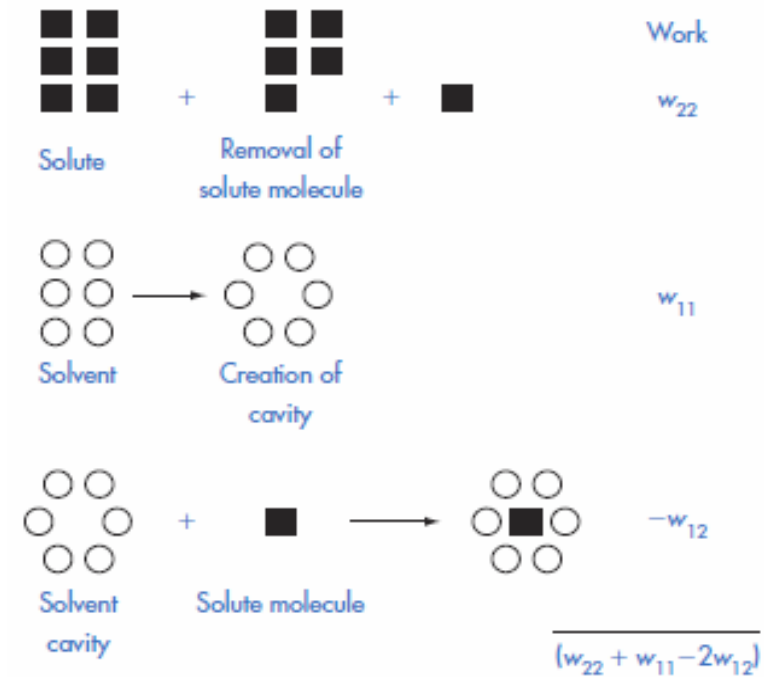


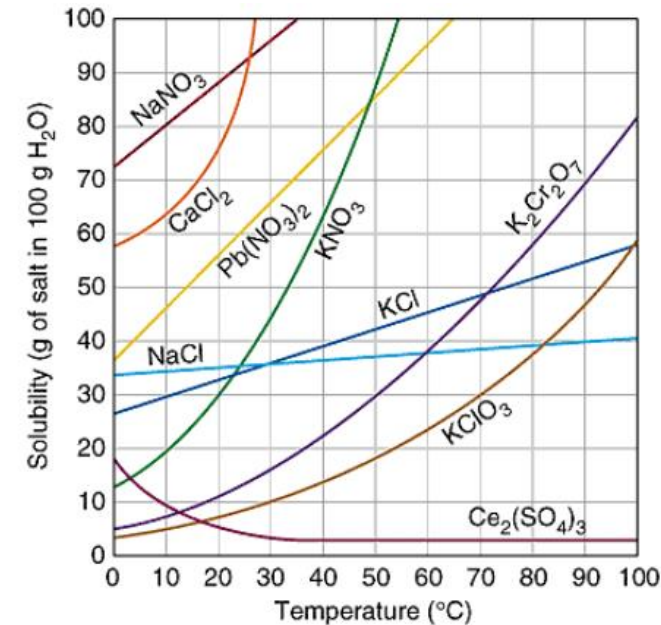
Figure 5.1 Diagrammatic representation of the three processes involved in the dissolution of a crystalline solute: the expression for the work involved is $w_{22} + w_{11} - 2w_{12}$ (solute-solvent interaction in the last stage is $-2w_{12}$ as bonds are made with one solute and two solvent molecules).

Factors influencing solubility

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- **Temperature & Pressure**

- Solubility is an equilibrium value that is dependent on a given **temperature and pressure**
- **Solubility does not depend on how fast a substance dissolves in the solvent**



Factors influencing solubility

- **Temperature**

- **Heat of solution (ΔH_{soln})**

- The enthalpy change associated with the dissolution of a substance in a solvent

* Table. Heat of solution

Solute	ΔH_{soln} (25°C) kcal/mole
HCl	- 17.96
NaOH	- 10.6
CH ₃ COOH	- 0.36
NaCl	+ 1.0
KMnO ₄	+ 10.4
Mannitol	+ 5.26
KI	+ 4.3

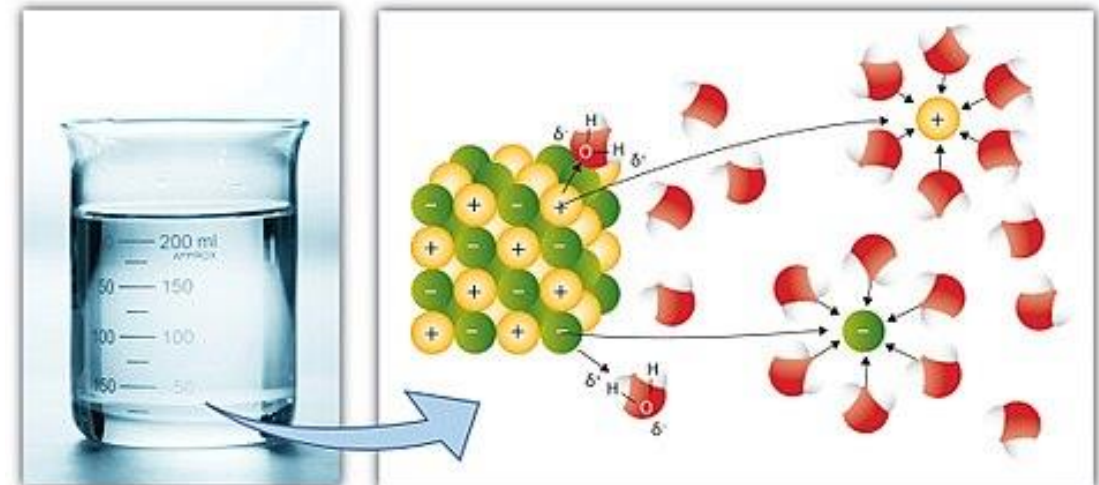
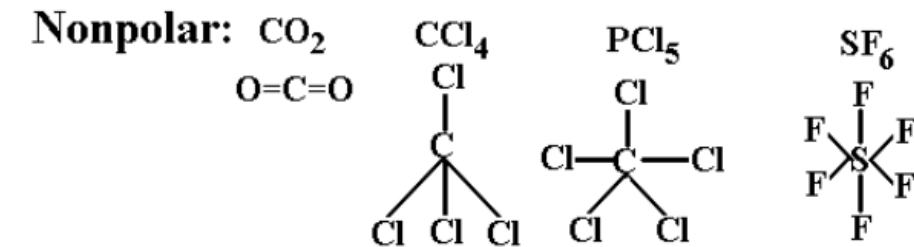
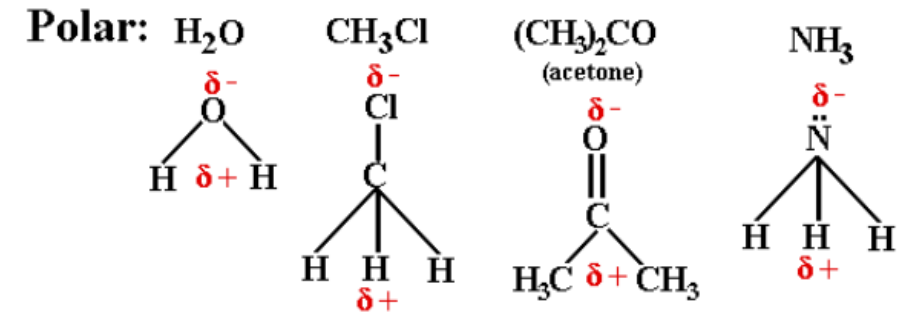
Factors influencing solubility

- **Chemical structure**

- **Dipole moment**

- A measure of polarity

Molecules that have a high dipole moment are more soluble in polar solvents such as water



Factors influencing solubility

- **Chemical structure**

- **Dielectric properties**

- Related to the ability to store charge
 - How a substance interacts with solvents

* Table 6-5 Dielectric Constants of Some Solvents at 25°C

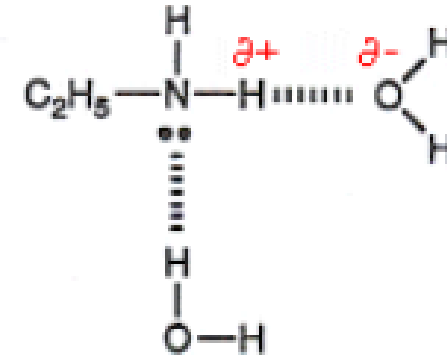
Solvent	Dielectric constant
Water	78.5
Glycerin	40.1
Propylene glycol	32.01
Methanol	31.5
Acetone	19.1
PEG 400	12.5
Cottonseed oil	6.4
Ether	4.3

Factors influencing solubility

- **Chemical structure**

- **Hydrogen bonding**

- The attractive interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine
- Major factor on solubility in water



- Amines with small alkyl groups are very soluble in water. This is because hydrogen bonding occurs between the amine and water molecules

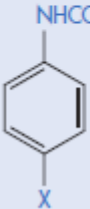
Factors influencing solubility

- **Chemical structure**

- **Hydrogen bonding**

- The attractive interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine
- Major factor on solubility in water

*

Table 5.5 The effect of substituents on solubility of acetanilide derivatives in water		
Derivative	X	Solubility (mg dm ⁻³)
	H	6.38
	Methyl	1.05
	Ethoxyl	0.93
	Hydroxyl	13.9
	Nitro	15.98
	Aceto	9.87

- The presence of hydroxyl groups or nitro groups can markedly increase the solubility.

Factors influencing solubility

- A high melting point means low water solubility
- *cis* (z) Isomer is more soluble than *trans* (e) isomer

*

Table 5.3 Correlation between melting points of sulfonamide derivatives and aqueous solubility

Compound	Melting point (°C)	Solubility
Sulfadiazine	253	1 g in 13 dm ³ (0.077 g dm ⁻³)
Sulfamerazine	236	1 g in 5 dm ³ (0.20 g dm ⁻³)
Sulfapyridine	192	1 g in 3.5 dm ³ (0.29 g dm ⁻³)
Sulfathiazole	174	1 g in 1.7 dm ³ (0.59 g dm ⁻³)

Table 2. Solubility^a of Maleic Anhydride, Maleic Acid, and Fumaric Acid, g/100 g Solution

Solvent	Maleic anhydride (g/100 g solvent)	Maleic acid ^b	Fumaric acid
water at ^c			
25°C		44.1	0.70
40°C		52.9	1.05
60°C		58.9	2.34
97.5°C		79.7	
100°C			8.93

The effect of pH on solubility

- **Acidic drugs (HA)**
 - **Total saturation solubility of drug S, the solubility of the undissociated species HA S_0**

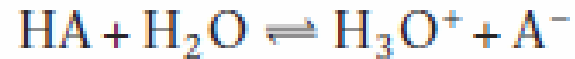
$$S = S_0 + (\text{concentration of ionised species})$$

By changing the pH of the solution, you can change the charge state of the solute. If the pH of the solution is such that a particular molecule carries no net electric charge, the solute often has minimal solubility and precipitates out of the solution.

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The effect of pH on solubility

- **Acidic drugs (HA)**



- **The dissociation constant K_a**

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

- **According to previous page, $[\text{HA}] = S_0$, $[\text{A}^-] = S - S_0$**

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{A}^-]}{S_0}$$

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{S - S_0}{S_0}$$

The effect of pH on solubility

- **Acidic drugs (HA)**
 - Taking logarithms,

$$pH - pK_a = \log\left(\frac{S - S_0}{S_0}\right)$$

- $[A^-] = S - S_0, S_0 = [HA]$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

<Henderson-Hasselbalch Equation>

The effect of pH on solubility

- **Basic drugs (RNH_2)**
 - **Total saturation solubility of drug S , the solubility of the undissociated species RNH_2 S_0**

$$S = S_0 + (\text{concentration of ionised species})$$

The rate at which a drug goes into the solution when it is dissolved in an acidic or a basic medium is proportional to the **solubility** of the drug. Many drugs have different solubilities at different pHs. These **pH-dependent solubility** differences lead to **pH- -dependent** dissolution profiles.

The effect of pH on solubility

- **Basic drugs (RNH₂)**



- **The dissociation constant K_b**

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

- **According to previous page, [RNH₂] = S₀, [RNH₃⁺] = S – S₀**

$$\frac{K_b}{[\text{OH}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{S - S_0}{S_0}$$

The effect of pH on solubility

- **Basic drugs (RNH₂)**
 - Taking logarithms,

$$pK_a - pH = \log\left(\frac{S - S_0}{S_0}\right)$$

$$pH - pK_a = \log\left(\frac{S_0}{S - S_0}\right)$$

- **[RNH₃⁺] = S - S₀, S₀ = [RNH₂]**

$$pH = pK_a + \log \frac{[RNH_2]}{[RNH_3^+]}$$

<Henderson-Hasselbalch Equation>

The effect of Pressure

- **Henry's Law**

$$C_2 = \sigma p$$

C_2 = concentration of the dissolve gas (g/l)

p = partial pressure (mm of the undissolvegas)

σ = inverse of the Henry's law constant, K

- In a dilute solution at constant temperature, the concentration of dissolved gas is proportional to the partial pressure of the gas above the solution at equilibrium

Influence of (Co)Solvents on Solubility

- **Strong electrolytes**
 - Strong acids and bases and all salts are soluble in water
 - The polar nature of water attracts the ions
- **Weak electrolytes**
 - Weak acids and bases with high molecular weight are not soluble in water
 - Cosolvents such as alcohol, propylene glycol and polyethylene glycol are required for solubility

Influence of Solvents on Solubility

- **Cosolvents**
 - **Solubility enhancements caused by co-solvent addition occur because of changes in the bulk properties of the isotropic solution**

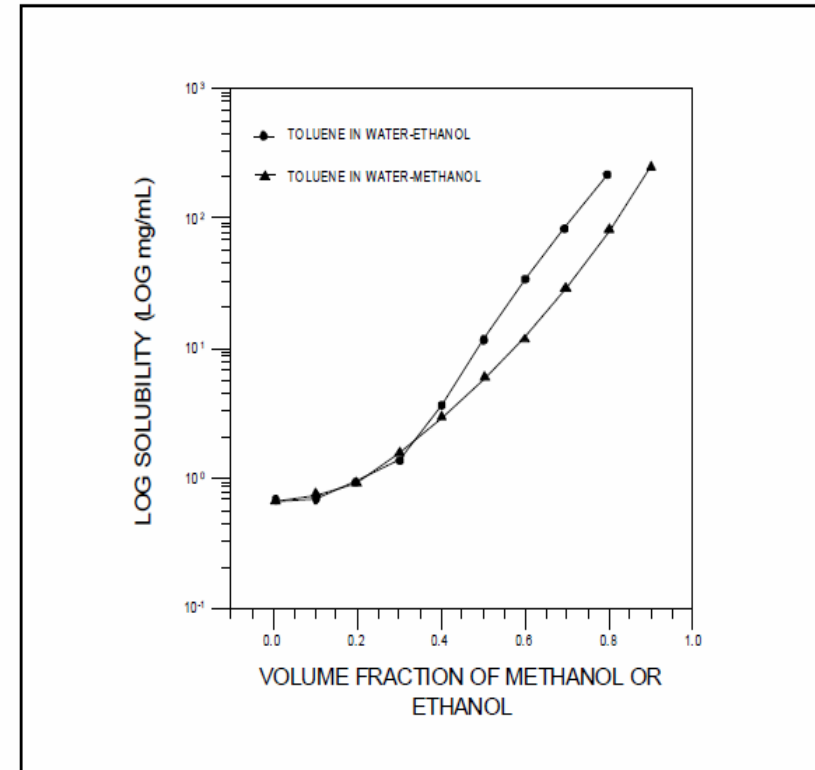


Figure 3. Solubility of toluene in water-ethanol and water-methanol mixtures (From Yalkowski, S. H., "Solubility of organic solutes in mixed aqueous solvent," Final Report to the R. S. Kerr Research Lab., U.S. EPA, contract CR811852-01-0, 1985).

Water Solubility of Ionic Compounds

SOLUBLE COMPOUNDS

Almost all salts of Na^+ , K^+ , NH_4^+

Salts of nitrate, NO_3^-
chlorate, ClO_3^-
perchlorate, ClO_4^-
acetate, CH_3CO_2^-

If one ion from the “Soluble Compound” list is present in a compound, the compound is water soluble.

EXCEPTIONS

Almost all salts of Cl^- , Br^- , I^-

Halides of Ag^+ , Hg_2^{2+} , Pb^{2+}

Compounds containing F^-

Fluorides of Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+}

Salts of sulfate, SO_4^{2-}

Sulfates of Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+}

INSOLUBLE COMPOUNDS

Most salts of carbonate, CO_3^{2-}
phosphate, PO_4^{3-}
oxalate, $\text{C}_2\text{O}_4^{2-}$
chromate, CrO_4^{2-}

EXCEPTIONS

Most metal sulfides, S^{2-}

Salts of NH_4^+ and the alkali metal cations

Most metal hydroxides and oxides

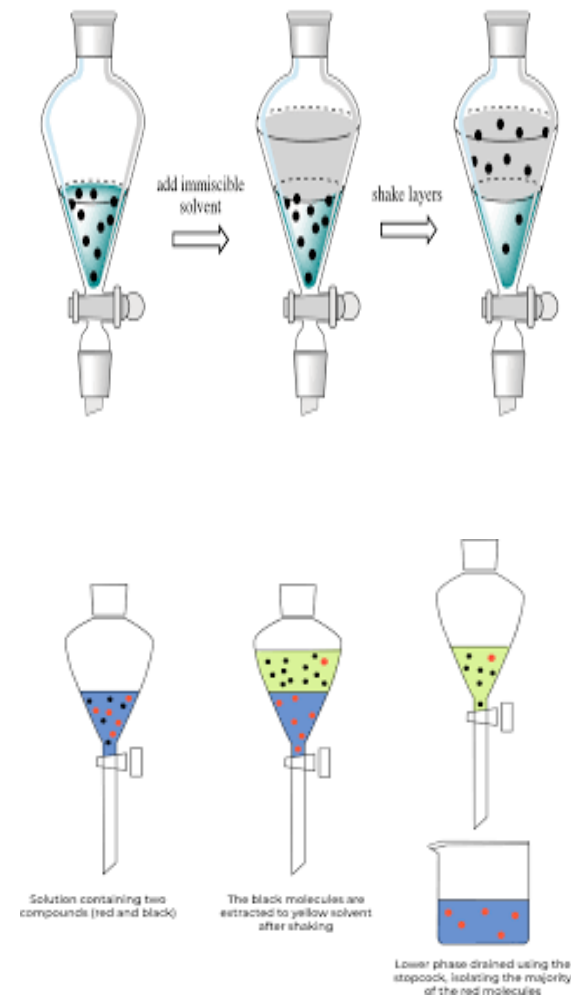
$\text{Ba}(\text{OH})_2$ is soluble

Other Applications of Solubility

- Solubility is of fundamental importance in a large number of **scientific disciplines and practical applications**, ranging from
- ore processing and nuclear reprocessing to
- the use of medicines,
- and the transport of pollutants.
- In separation techniques

Application of Solubility : liquid–liquid extraction

- The synthesis of benzoic acid from phenylmagnesium bromide and dry ice. Benzoic acid is more soluble in an organic solvent such as dichloromethane or diethyl ether, and when shaken with this organic solvent in a separatory funnel, will preferentially dissolve in the organic layer. The other reaction products, including the magnesium bromide, will remain in the aqueous layer, clearly showing that separation based on solubility is achieved. This process, known as liquid–liquid extraction, is an important technique in synthetic chemistry.



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**Wishing the best in
CAT and examination**