

18MBO23C-U1

PAPER – VI – PHYTOCHEMISTRY  
Unit – 1

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# Enthalpy

- We already know about enthalpy. Enthalpy is related to the amount of energy that is lost or gained by a system during a normal chemical process.
- We have seen both endothermic and exothermic processes in lab. Which do you think is favored by nature?
- Why?

$$\Delta H_{\text{vap}} \text{ and } \Delta H_{\text{fus}}$$

- Last unit we looked at the change in enthalpy associated with a chemical reaction and the energy flow as materials (mostly water) are heated.
- Today we're going to extend that lesson to include phase change.

$$\Delta H_{\text{vap}} \text{ and } \Delta H_{\text{fus}}$$

- If you put a thermometer in a glass of ice water, the temperature will read 273 K until all the ice melts. Only after all the ice melts will the temperature begin its crawl up to room temperature.
- For similar reasons, the temperature of boiling water will never exceed 373 K.
- Why is this?

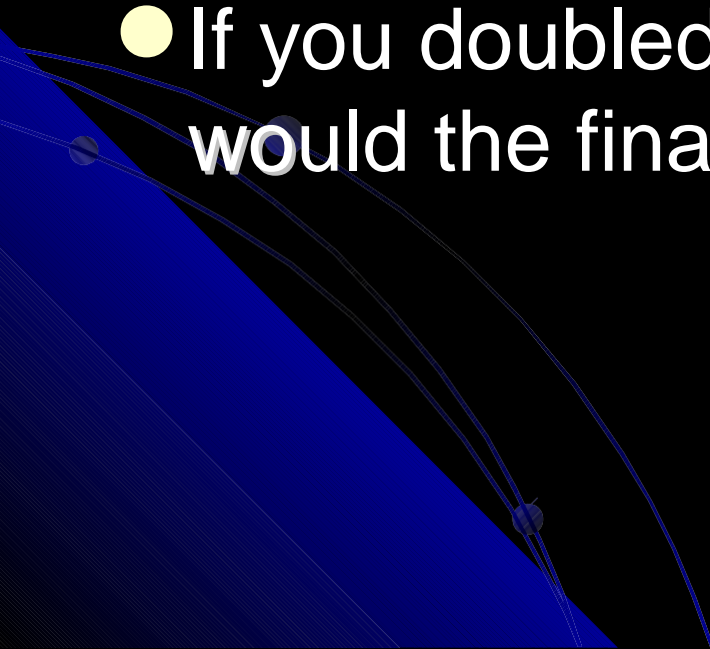
# $\Delta H_{\text{vap}}$ and $\Delta H_{\text{fus}}$

- Melting ice and boiling water are both endothermic processes and as such they both require energy.
- If any of the water were to increase in temperature that energy would immediately be transferred to the ice to cause it to melt.
- For water
  - $\Delta H_{\text{vap}} = 43.9 \text{ kJ/mol}$
  - $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$

# $\Delta H_{\text{vap}}$ and $\Delta H_{\text{fus}}$

- Examples, Given (for water)
  - $\Delta H_{\text{vap}} = 43.9 \text{ kJ/mol}$
  - $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$
- 1. How much energy is required to vaporize 10.0 g of water? (easy)
- 2. How much energy is required to melt 10.0 g of water? (easy)
- 3. How much energy would it take to raise the temperature of ice at 268 K to 378 K? (getting harder)

# Hard problems

- How much boiling water would you need to add to a cup with 100.0 g of ice and 100.0 g of water at equilibrium to get all the ice to melt? (hard)
  - If you doubled that amount of water what would the final temperature be? (hard)
- 

# A new look

- If 90.0 g of water at 300. K are added to 30.0 g of water at 350. K what will the final temperature be?

It sounds hard, but there's a trick:

Just make a weighted average:

$$(90.0 \cdot 300 + 30.0 \cdot 350) / 120 = 312.5$$



# The baseline approach

- Some problems will require a more sophisticated approach
- How many liters of steam at 1 atm and 373 K will it take to melt exactly 75.0 g of ice at STP?
- It sounds really hard, but it can be work quite simply with the baseline approach

# How to do it

- When the system reaches equilibrium all species will be liquid water at 273 K. That is our baseline.
- Next we find how much energy will be required to melt all that ice. That's easy
- That's how much energy it takes to get our ice to the baseline.
- Since heat gained by ice is going to equal heat lost by steam we now need to find how much energy is released when one mole of steam is brought down to baseline (273 K as a liquid)

# Steam

- What happens when 1 mole of steam is brought down to 273 K and remains a liquid?
  1. It condenses: 43.9 kJ will be released when this happens
  2. It cools from 373 K to 273 K
- This means that cooling a mole of water from boiling to freezing releases 75.2 kJ of energy.
- Add that to the heat released from the condensation process and you get  $43.9 + 75.2 = 119.1$  kJ/mol

# Finishing up

- If 119.1 kJ are released when one mole of steam is cooled to 273 K (as water) then how many moles of steam will be required to release the 25.1 kJ of energy required to melt our 75.0 g of ice?
- Easy ratio:

● Finally use  $PV=nRT$  to solve for the volume in liters.

(1 atm)

$$V = 6.46 \text{ L}$$



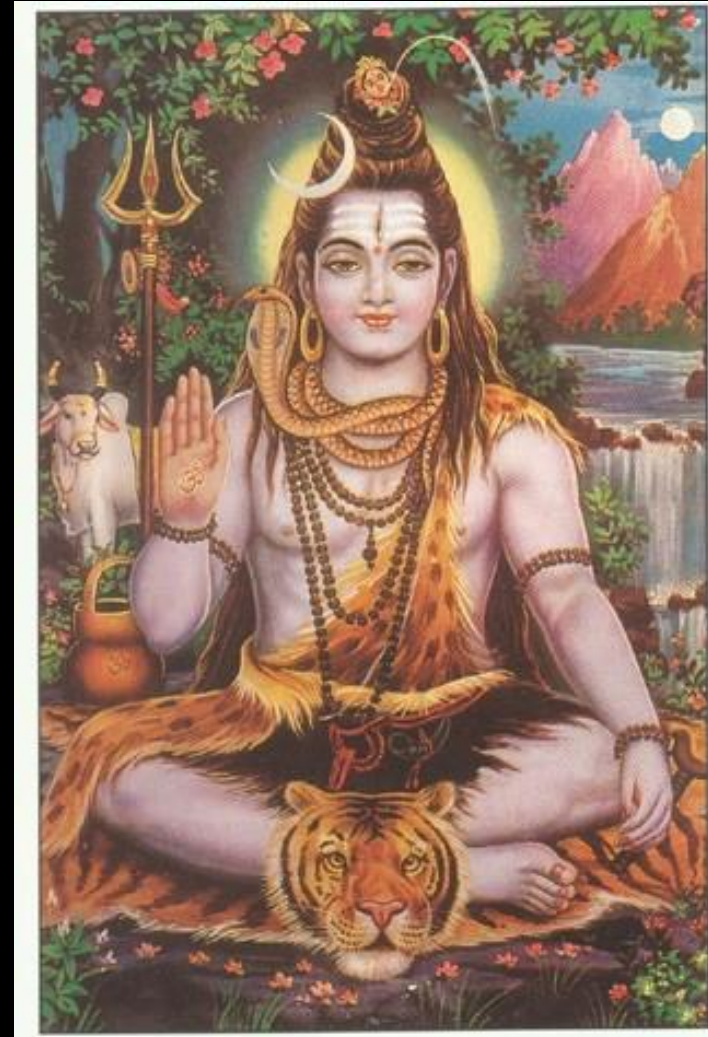
# Entropy



- If you thought that enthalpy was abstract, welcome to Entropy.
- Entropy can be thought of as the force in the universe that pushes everything toward disorder and chaos.
- The second law of thermodynamics states: In any spontaneous process there is always an increase in the entropy of the universe.

# Enter Shiva

- Shiva is the Hindu lord of chaos. He/she (in Hinduism he/she is a hermaphrodite) is the “lord of chaos”.  
Whenever a process produces an increase in Entropy Shiva is happy.



# Enthalpy vs. Entropy (Shiva)

- We know that the amount of energy in the universe is constant but the Entropy of the Universe is always increasing.

- Shiva is happy = ▪

Shiva's law

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For any reaction the change in entropy of the universe is going to be equal to the change in entropy of our system plus the change in entropy of the surroundings. If the change in entropy of the universe is positive ▪ and the reaction will happen spontaneously. If it's negative ▪ and it will not happen, end of story.



# What makes ▪

- Disorder!!! A gas his more scattered and spread out ▪
- Look on page 787
- Entropy is increased if there are more possible arrangements at the end of the reaction than before
- The mores spread out the better. Shiva is eagerly awaiting the **heat death** of the universe, when **maximum entropy** is achieved. This will **take a while**, fear not.



# Temperature

- Entropy is always increasing but we can manipulate entropy by changing the temperature.
- What has more disorder, ice or liquid water?
- Then why does ice ever form?



- So how can this happen????????????????

# Endo or exothermic?

- Is the freezing of water endothermic or exothermic?
- This release of energy from the system makes the surroundings more disordered. Hence,  $\Delta S_{\text{surr}} = +\#$ .

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

- As long as  $\Delta S_{\text{univ}}$  is  $+$  and it may proceed.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

- The sign of  $\Delta S_{\text{sys}}$  is easy to predict. If your system gets more orderly, the  $\Delta S_{\text{sys}}$  is negative  $\cdot$ , but if it gets more chaotic then  $\Delta S_{\text{sys}}$  is positive  $\cdot$ .
- But the system is only half the picture, the surroundings are important as well.
- When ice melts, it throws energy into the surroundings and makes them more chaotic  $\cdot$ .
- So the important question is:  
What causes freezing to take place at certain temperatures and not at other temperatures?

# $\Delta S_{\text{surr}}$ is T dependent

- The above equations are important.
- When water freezes  $\Delta S_{\text{sys}}$  becomes more ordered
- But the process is exothermic, which makes the surroundings more chaotic
- One term ( $\Delta S_{\text{sys}}$  or  $\Delta S_{\text{surr}}$ ) needs to dominate
- $\Delta S_{\text{sys}}$  is temperature dependent
  - At high temperatures  $\Delta S_{\text{sys}}$  becomes small and weak
  - At low temperatures  $\Delta S$  is large and dominates

$\Delta S_{\text{surr}}$  is T dependent



The reaction is spontaneous

# Gibbs free energy

- Gibbs free energy is defined as  
 $G = H - TS$  (does this look familiar?)
  - Where  $H$  = enthalpy
  - $T$  = temp (K)
  - $S$  = entropy
- The free energy equation can be rewritten:

$$\Delta G = \Delta H - T \Delta S$$

Note: that if  $\Delta G$  is negative, the reaction will occur spontaneously.

$$-(\Delta H - T \Delta S) = T(\Delta S_{\text{univ}}) = -\Delta G$$

# Let's look at a few examples

$$\Delta G = \Delta H - T \Delta S$$

$\Delta H$	$\Delta S$	$\Delta G$	Spontaneous ?
-	+	-	YES!!!!!!!
+	-	+	NO!!!!!!!
-	-	?	Depends on T
+	+	?	Depends on T

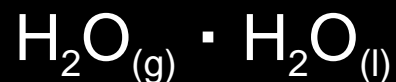
# Condensation

- When water condenses your system becomes more organized ▪
- However, condensation is exothermic and releases energy which makes the surroundings more disordered ▪
- This means that temperature determines if water will freeze
- But how do we calculate  $\Delta S$ ?



# Calculating $\Delta S$

- $\Delta S$  is calculated in a similar fashion to  $\Delta H$ .
- $\Delta S$  is looked up in the back of the book
  - Back to the example of the freezing water



$$\Delta S_{\text{reaction}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}} \text{ (Just like } \Delta H)$$

$$\Delta S_{\text{reaction}} = 69.96 - 188.7 = -118.7 \text{ J/mol} \cdot \text{K}$$

**NOTE:  $\Delta S$  is in Joules NOT kJ**



# Calculating $\Delta G$

- $\Delta S_{\text{reaction}} = 188.7 - 69.96 = -118.7$  ·
- Now that we have  $\Delta S$  all we need is  $T$  and  $\Delta H$  and we can find  $\Delta G$  using
- $\text{H}_2\text{O}_{(g)} \cdot \text{H}_2\text{O}_{(l)}$

$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$\Delta H_{\text{reaction}} = -286 - (-242) = -44 \text{ kJ/mol} \cdot$$

# Calculating $\Delta G$ (cont...)

- $\Delta S_{\text{reaction}} = -118.7 \text{ J/mol} \cdot \cdot -0.1187 \text{ kJ/mol}$

- $\Delta H_{\text{reaction}} = -44 \text{ kJ/mol}$

- Now we plug and chug. If  $T = 300 \text{ K}$  we would expect condensation to take place spontaneously.

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = -44 - (300)(-0.1187)$$

$$\Delta G = -8.39 \text{ kJ/mol}$$

- But what about @  $444 \text{ K}$ ???

$$\Delta G = -44 - (444)(-0.1187)$$

$$\Delta G = +8.7 \text{ kJ/mol}$$

# $\Delta G$ and Boiling point Temp

- $\Delta G$  can be used to predict boiling point.
  - At the boiling point  $\text{H}_2\text{O}_{(g)}$  and  $\text{H}_2\text{O}_{(l)}$  are in equilibrium, hence the reaction is spontaneous in both directions or in neither (take your pick)
  - Regardless  $\Delta G = 0$

- $\Delta S_{\text{reaction}} = -0.1187 \text{ kJ/mol} \cdot$

- $\Delta H_{\text{reaction}} = -44 \text{ kJ/mol} \cdot$

$$\Delta G = \Delta H - T \Delta S$$

$$0 = -44 - (T)(-0.1187)$$

$$T = 371 \text{ K} \rightarrow 98^\circ\text{C} \text{ (pretty close to water's BP)}$$



# 1. Physical Properties:

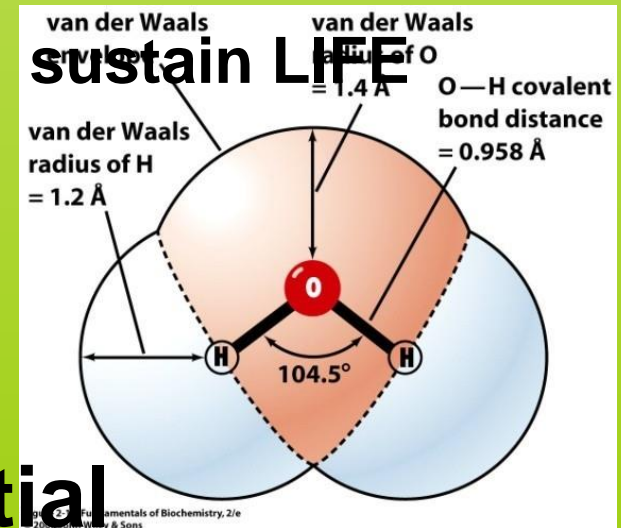
- Polar molecule
- Hydrophilic substances dissolve
- Hydrophobic substances aggregate
- Osmosis
- Diffusion

## **2. Chemical Properties :**

- Ionizes to  $O$  and  $OH$
- Acids and bases alter pH
- Buffers resists changes in pH

# Physical Properties of Water

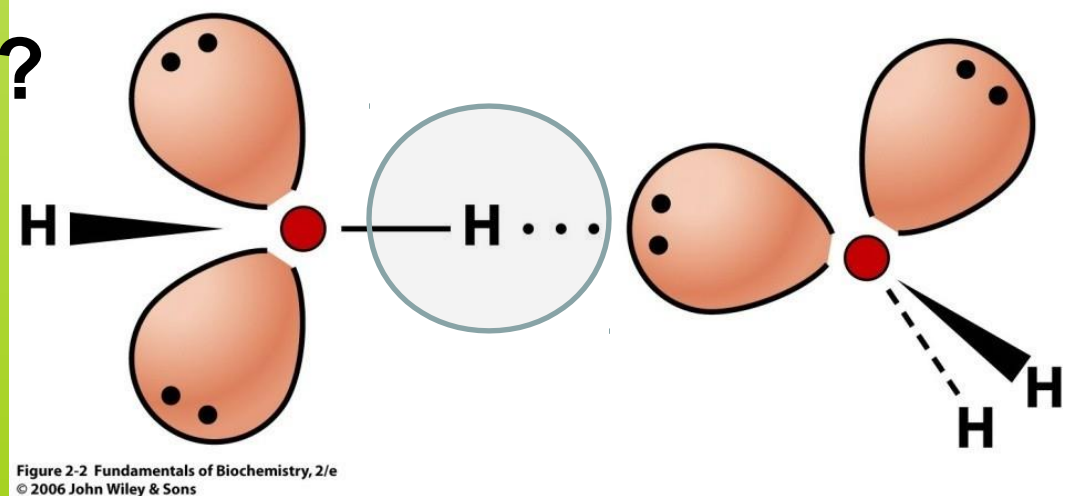
- Structure of water:
  - Consists of two H atoms bonded to an O atom.
  - Angle formed by the 3 atoms is  $104.5^\circ$ 
    - Most important angle
  - Tetrahedron structure:



- Polar molecule – has a partial negative charge on the oxygen and a partial positive charge on the

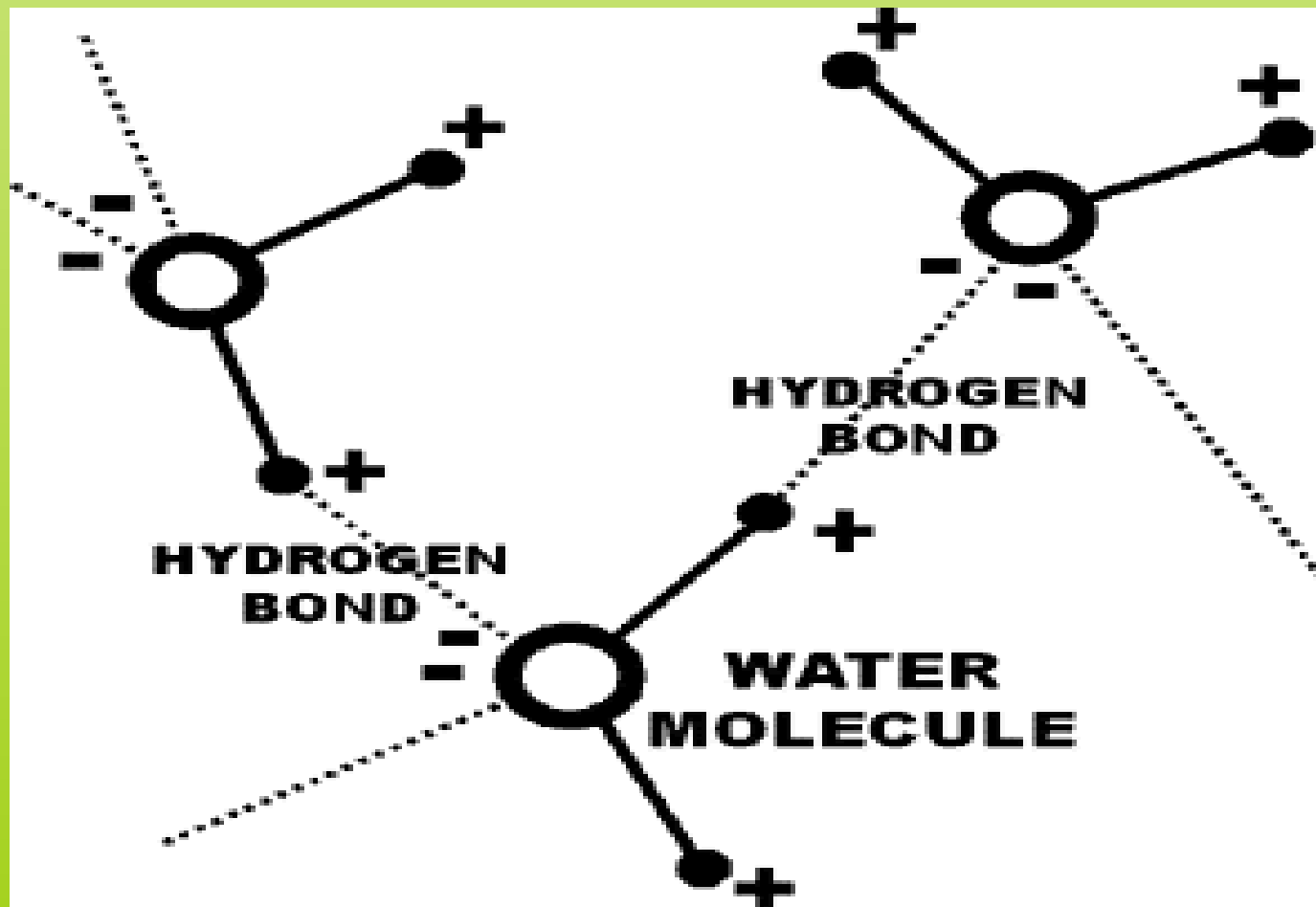


- The electrostatic attractions between the dipoles of water are important for water as a solvent.
- How do water molecules join together?



## The structure of ice and its implications for life on earth . . .

- Increase in hydrogen bonding therefore increase in strength.



**- WATER MOLECULES ARE POLAR DUE TO PARTIAL CHARGES. THEY WILL LINE-UP DUE TO ATTRACTION AND REPULSION OF THESE PARTIAL CHARGES.**

**Amphipathic compounds** contain regions that are:

- **Polar** (or charged) and regions that are **Nonpolar**.

- When an amphipathic compound is mixed with water, the polar hydrophilic region interacts favorably with the solvent and tends to dissolve.
- but the nonpolar, hydrophobic region tends to avoid contact with the water.

- These stable structures of amphipathic compounds in water are called **micelles**, May contain hundreds or thousands of molecules.
- Many biomolecules are amphipathic; e.g Proteins, pigments, certain vitamins, and the sterols and phospholipids of membranes all have polar and nonpolar surface regions

# water

- The general importance of water:
  - Sustain life
  - How?
- Importance of water in Biochemistry
  - 1.Biological molecules → shape and function.
  - 2.Biochemical reactions (transport within cells).
  - 3.Participates in chemical reactions eg. Ionic components of water →  $H^+$  and  $OH^-$ .
- Understanding physical and chemical properties

# Water is the most important food

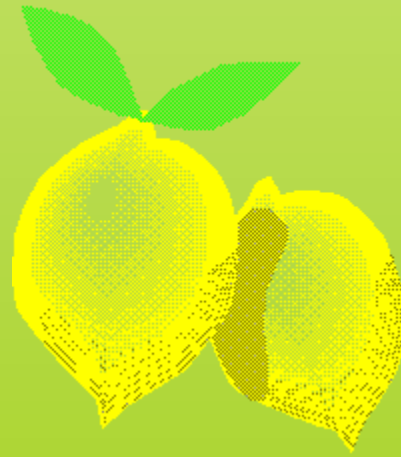
- Human being= **70 %** water
- Cells 85 %
- Heart 79 %
- Lungs 79 %
- Bones 22 %
- Brain 75 %
- Skin 72 %
- Liver 68 %
- Muscle 76 %
- Kidney 83%
- Intestine 75 %
- Spleen 76 %
- Body fat 10 %

# pH and pHScale



# Acids and Bases

- Some of our favorite foods make our tongue curl up because they are SOUR.



# Bitter!



- Some foods have a “bite” of their own because they’re somewhat bitter.
- **WHY?**

# Acidic/Basic

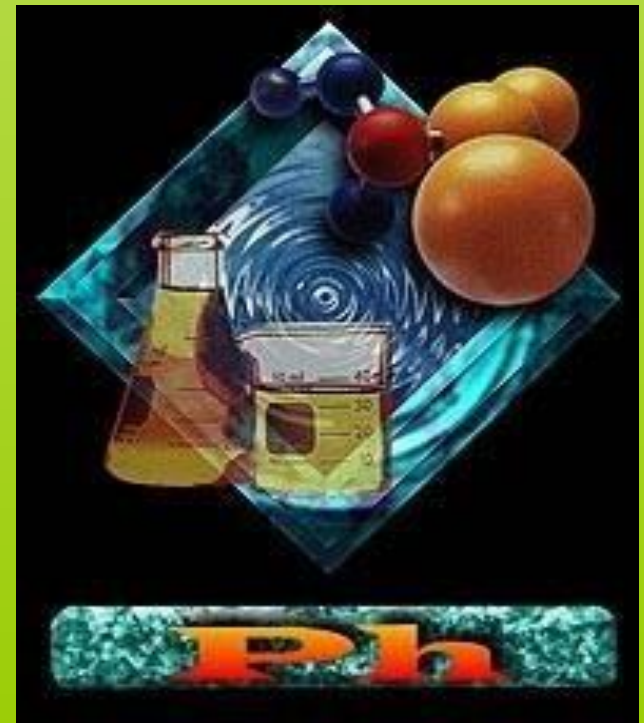
- There is a scientific reason for this:
- These foods are either acidic or basic.
- Other substances besides foods have these characteristics.

# Acids and Bases

- Chemicals may be classed as acids or bases.
- Things that are neither acids nor bases are neutral.
- pH measures how acidic or basic a solution is.

- A special name is given to the acid or base characteristic that a substance has:
- It is called: pH
- “p” stands for potential and “H” stands for hydrogen; hence, the potential of a substance to attract hydrogen ions

pH



# Reminder: So, what is acid?

- An acid is any compound that yields hydrogen ions (H<sup>+</sup>) or hydronium ions (H<sub>3</sub>O<sup>+</sup>) when dissolved in water.

Carbonic, citric, and phosphoric acids

carbonic acid



phosphoric acid



citric acid

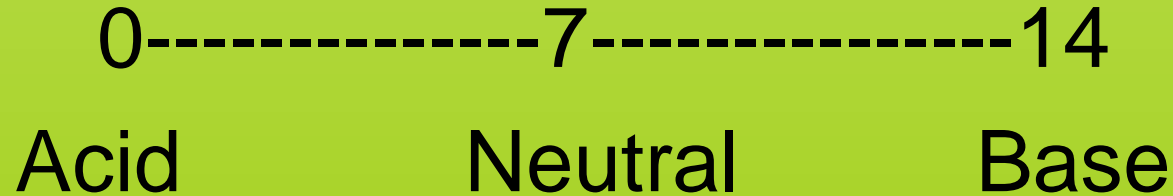
$$\begin{array}{ccccccc} & \text{O} & & \text{OH} & & \text{O} & \\ & || & & | & & || & \\ \text{HO} & - \text{C} & - \text{CH}_2 & - \text{C} & - \text{CH}_2 & - \text{C} & - \text{OH} \\ & & & | & & & \\ & & & \text{C} = \text{O} & & & \\ & & & | & & & \\ & & & \text{OH} & & & \end{array}$$

CARBONATED WATER, HIGH FRUCTOSE CORN SYRUP AND/OR SUCROSE, CARAMEL COLOR, PHOSPHORIC ACID, NATURAL FLAVORS, CAFFEINE.

C. Ophardt, c. 2003

# Acid

- Any substance which has a pH of value of less than 7 is considered an acid



# Reminder: What is a base?

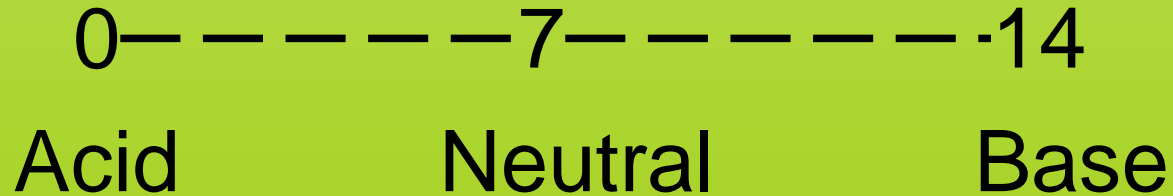
- A base is any compound that yields hydroxide ions ( $\text{OH}^-$ ) when dissolved in water.





# Base

- Any substance which has pH value greater than 7 is a base



# Properties:

## ACIDS

- Sour taste
- Can burn skin
- Contains more  $H_3O^+$  than  $OH^-$

## BASES

- Bitter taste
- Can burn skin
- Contains more  $OH^-$  than  $H_3O^+$
- Feels slippery/soapy

What is a common property of Acids and Bases?

They both can burn!

- Some substances are not really an acid or a base: For example, pure water



# pH

In the expression for  $[\text{H}_3\text{O}^+]$

$$1 \times 10^{-\text{exponent}}$$

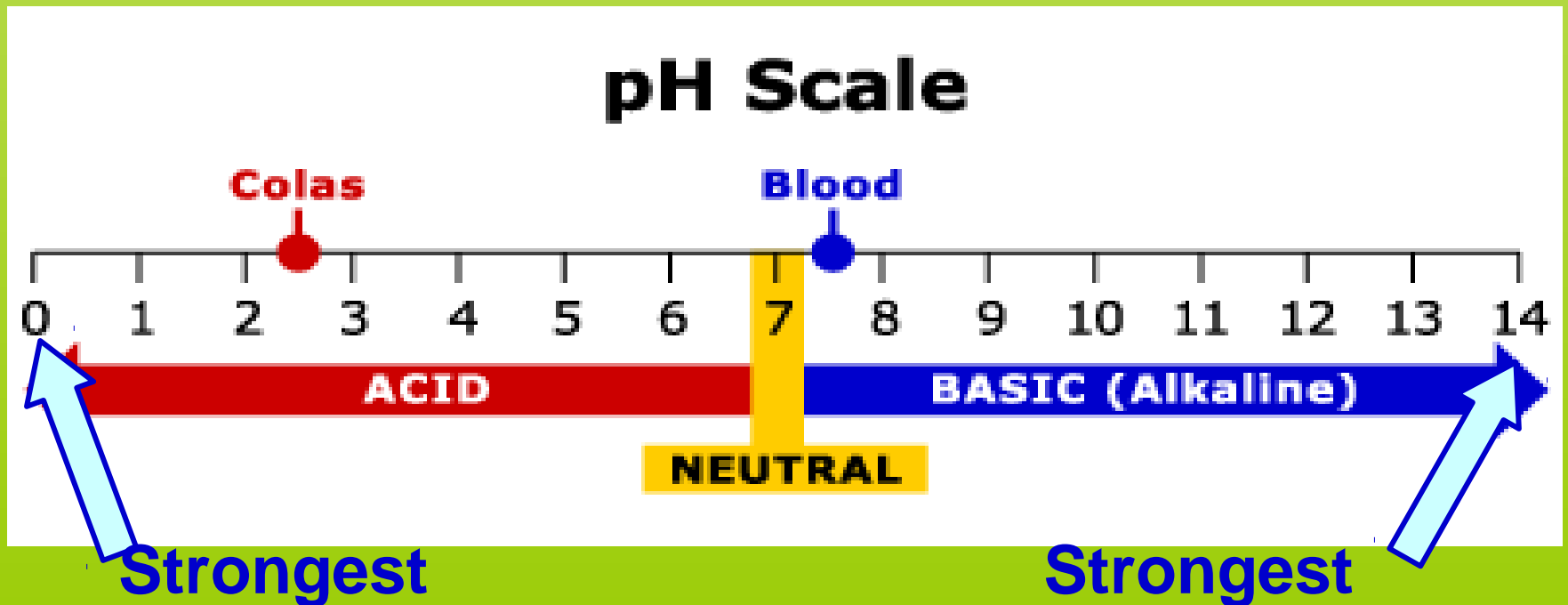
the exponent = pH



$$[\text{H}_3\text{O}^+] = 1 \times 10^{-\text{pH}} \text{ M}$$

# pH SCALE

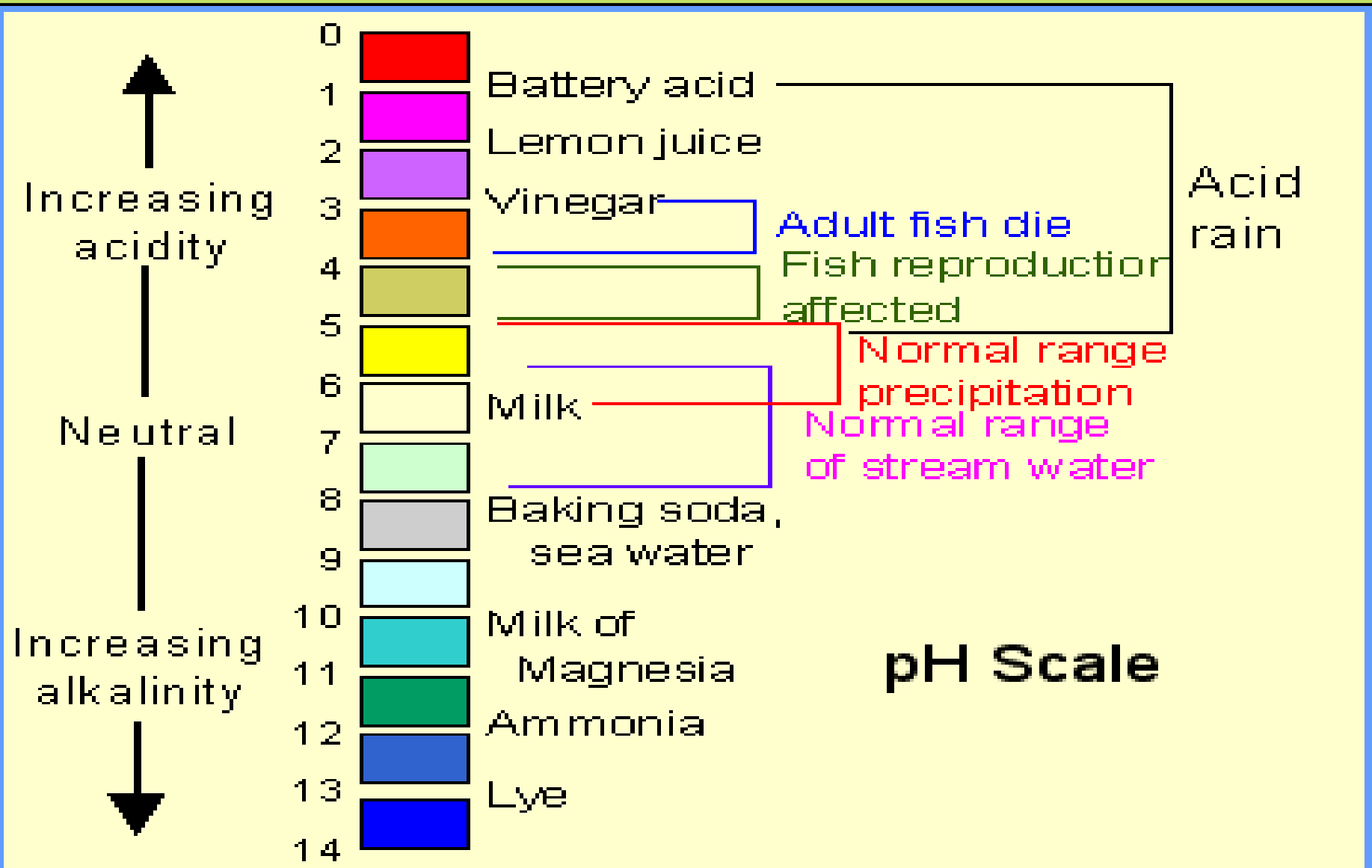
A scale of values that show how basic or acidic a substance is based on an assigned number



# The pH Scale

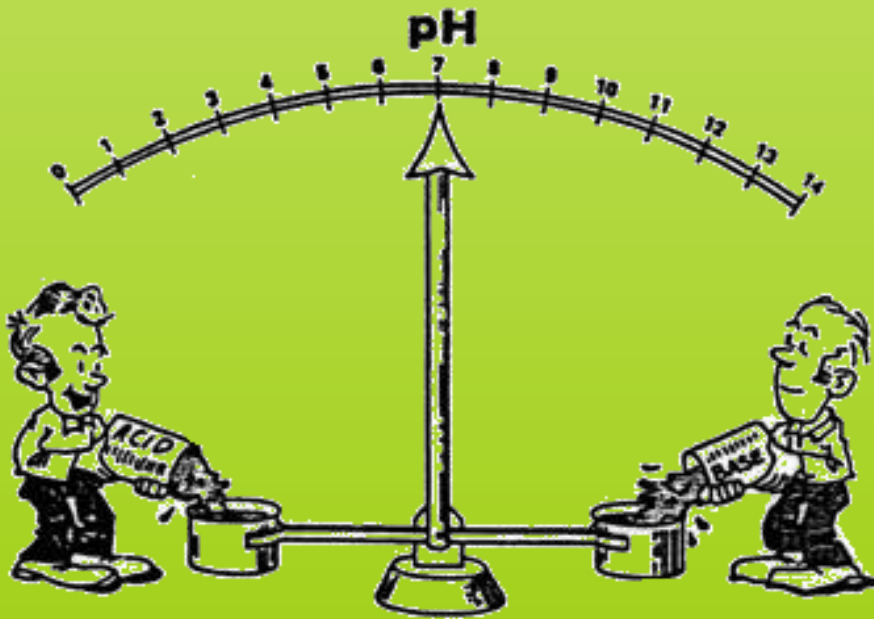
- pH scale ranges from 0 -14
- pH 7 is neutral; neither acid nor base
- Pure water is pH 7
- Low pH (0-6.9) = acid
- High pH (7.1-14) = base
- The closer to the ends of the scale, the stronger the solution is

# The pH Scale



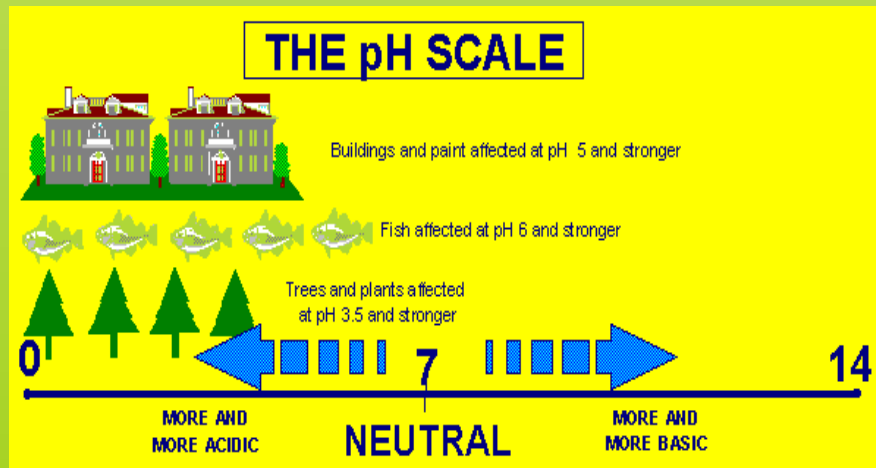
# Which way is more acidic?

- A pH of more than 7 means the solution is basic. The less pH, the more acidic the solution is. The more pH, the more basic the solution is.





# Acidity and the pH Scale



- The pH scale is logarithmic and as a result, each whole pH value below 7 is ten times more acidic than the next higher value. For example, a pH of 4 is ten times more acidic than a pH of 5 and 100 times more acidic than a pH of 6.

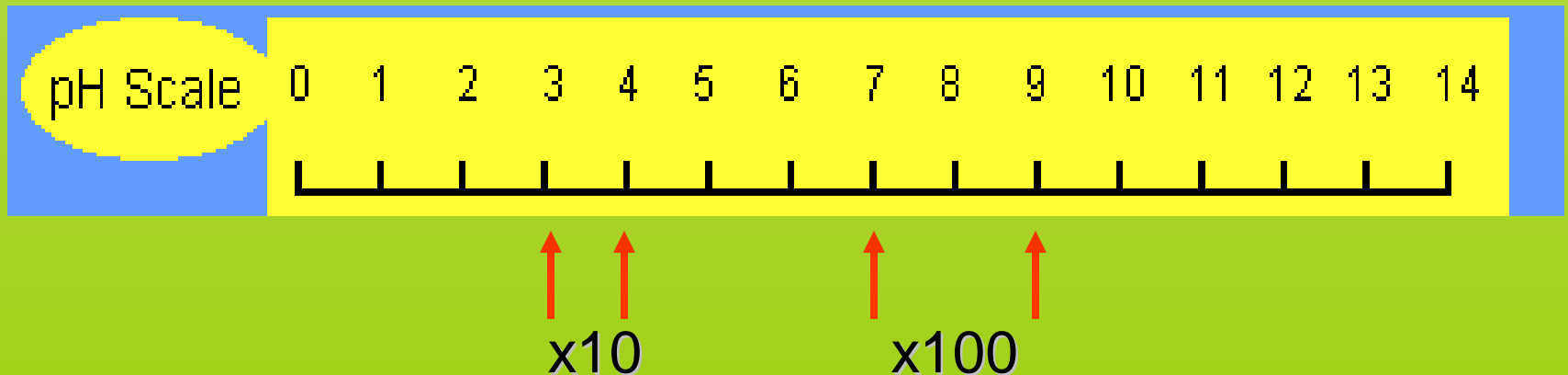
# The other way also...

- The same holds true for pH values above 7, each of which is ten times more alkaline (another way to say basic) than the next lower whole value. For example, a pH of 10 is ten times more alkaline than a pH of 9.



# The pH Scale

- Careful measurement is important
- A mistake of *one* pH unit means *10 times* too much or too little!

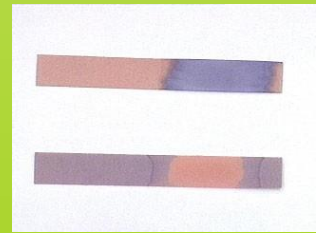


# INDICATORS

Indicators are chemical dyes that turn different colours when they are placed in acidic and alkaline (basic) solutions

**TYPES OF INDICATORS:**

**Litmus Paper**



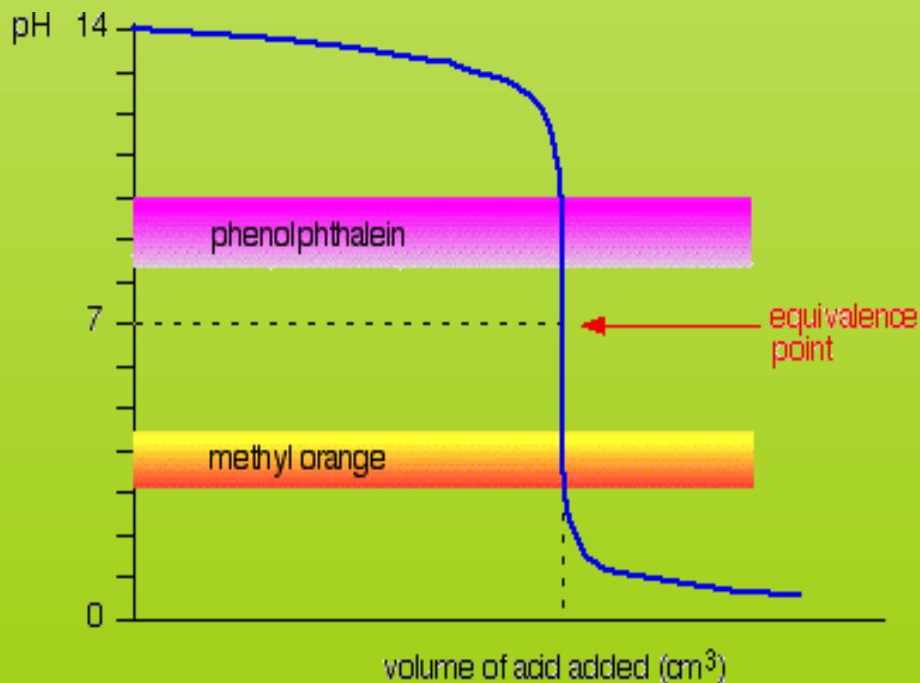
**Universal Indicator**

**Bromophenol Blue**

**Phenolphthalein**



# How do you measure pH in real life?



- Indicators have are very useful they change color depending on the pH of the solution they are in. Each pH indicator is defined by a useful pH range. For example Phenolphthalein changes from colorless at 8.0 to pink at 10.0. And Bromthymol Blue has a useful range from 6.0 (yellow) to 7.6 (blue).

# How about those **test papers**?



- Another way to test pH levels are with commercial calibrated test papers. These test papers are impregnated with pH indicators. pH is determined by immersing the strip in the liquid to be tested and comparing its color with a standard color chart provided with the pH paper.

# How Does It Work?

- The paper is treated with chemicals that change color to show the pH.
- When the paper touches the substance being tested, it turns a specific color to tell if the substance is an acid or a base.

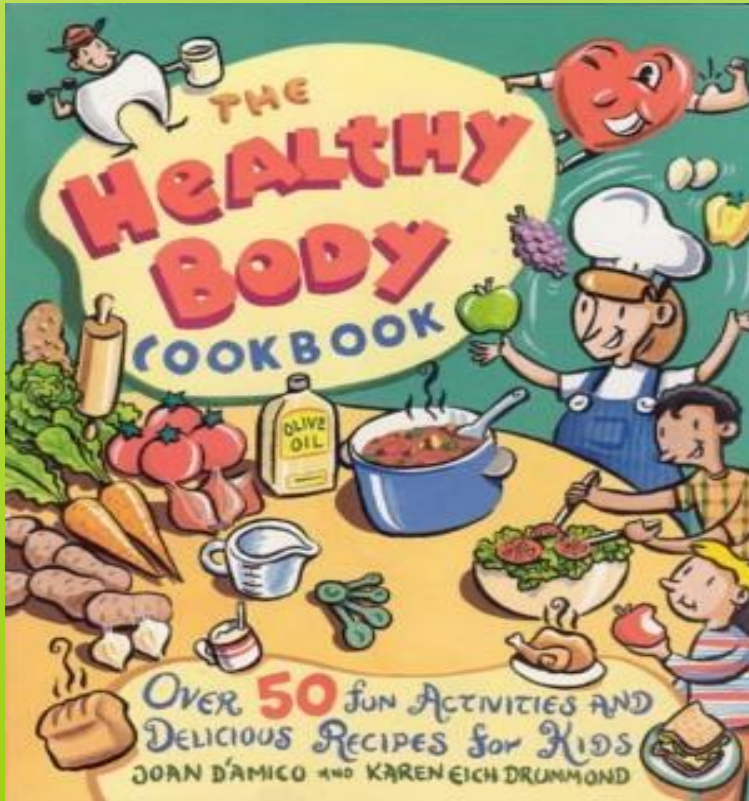


# To Use pH Paper

- Place the edge of the pH paper into the mixture.
- Observe the color change of the pH paper
- Match the resulting color to the colors listed on the outside of the pH paper package.
- The colors match with a correlated pH number.
- The number is the pH value of the sample.



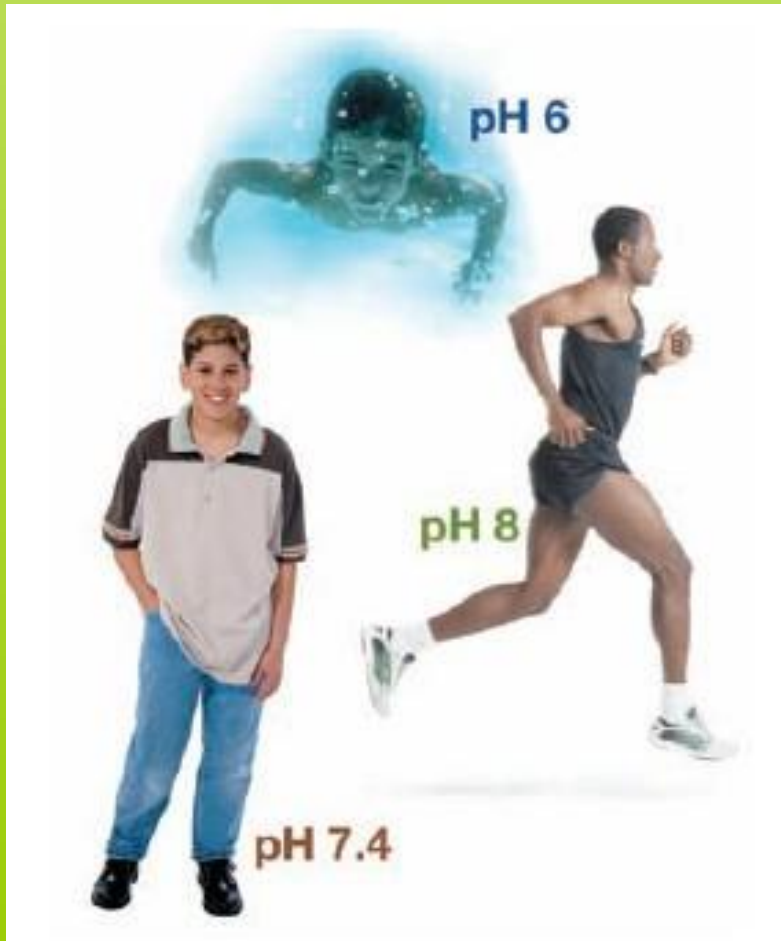
# So why is pH important to me?



- We learned some ways to test pH. But why should we really care about pH?
- Well Our bodies are alkaline by design and acid by function. Maintaining proper alkalinity is essential for life, health, and vitality. So basically, an imbalance of alkalinity creates a condition favorable to the growth of bacteria, yeast and other unwanted organisms. All leading biochemists and medical physiologists have recognized pH as the most important aspect of a balanced and healthy body.

# pH and blood

- The pH of your blood is normally within the range of 7.3–7.5.
- Holding your breath causes blood pH to drop.
- High blood pH can be caused by hyperventilating.



**EX.**

You have a glass of orange juice that has a pH of 3. What can you conclude about the orange juice?

It is an **ACID**



**EX.**

You have some drain cleaner that has a pH of 13.5. What can you conclude?

It is a **BASE**



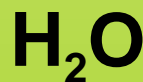
**EX.**

You have some distilled water. What can you conclude about the pH?

It is **NEUTRAL**, so **pH = 7**

**EX.**

Which of the following substances would definitely have a **pH under 7**?



pH under 7 = **ACIDS**



# pH Scale



X 10 x 10 x 10 x 10....and so on

**EX.**

If substance A has a pH of 1 & substance B has a pH of 3, which is **MORE ACIDIC?**

**ANSWER:**

**Substance A** – it is actually **100** times more acidic!!!

# EX.

Rank from **most** acidic to **least** acidic:

- Vinegar pH 2
- Bleach pH 13
- Milk pH 6.5
- Coffee pH 5



Vinegar

Most acidic

Coffee



Milk



Bleach



Least acidic

# EX.

Rank from **least** basic to **most** basic:

- Blood pH 7.4
- Sea Water pH 8
- Bananas pH 5
- Drain Cleaner pH 13.5



**Bananas**

Least Basic

**Blood**



**Sea Water**



**Drain Cleaner**



Most Basic

# pH

**A. The  $[\text{H}_3\text{O}^+]$  of tomato juice is  $1 \times 10^{-4}$  M.**

**What is the pH of the solution?**

**1) -4**

**2) 4**

**3) 8**

**B. The  $[\text{OH}^-]$  of an ammonia solution is**

**$1 \times 10^{-3}$  M. What is the pH of the solution?**

**1) 3**

**2) 11**

**3) -11**



# Learning Check pH5

The pH of a soap is 10. What is the  $[\text{H}_3\text{O}^+]$  of the soap solution?

1)  $1 \times 10^{-4} \text{ M}$

2)  $1 \times 10^{10} \text{ M}$

3)  $1 \times 10^{-10} \text{ M}$



THE  
END



# Buffers



# Definition

□ “Buffers are compounds or mixtures of compounds that by their presence in the solution resist changes in the pH upon the addition of small quantities of acid or alkali.”



# Necessity of a buffer system:

- Sometimes it is necessary that a solution of a definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If solution comes in contact with air, it will absorb  $\text{CO}_2$  and becomes acidic. On the other hand, if solution is stored in a glass bottle, alkaline impurities from the glass may alter its pH. Due to these reasons, pharmaceutical solutions are buffered as the buffer solutions are capable of maintaining pH at some fairly constant value when even small amounts of acid or base are added.



# Types of buffers:

Generally buffers are of two types;

- ▣ Acidic buffers

- ▣ Basic buffers



## Acidic Buffers:

An acidic buffer is a combination of weak acid and its salt with a strong base.

i.e. Weak acid & salt with strong base (conjugate base).

▣ EXAMPLES:







# Basic Buffers:

A basic buffer is a combination of weak base and its salt with a strong acid.

i.e. Weak base & salt with strong acid (conjugate acid).

## EXAMPLES:







## **Phosphate Buffers (Double salt buffers):**

**Besides the two general types of buffers (i.e. acidic & basic), a third appears to exist. This is buffer system composed of two salts:**

- ▣ Monobasic potassium phosphate ( $\text{KH}_2\text{PO}_4$ )**
- ▣ Dibasic potassium phosphate ( $\text{K}_2\text{HPO}_4$ ).**

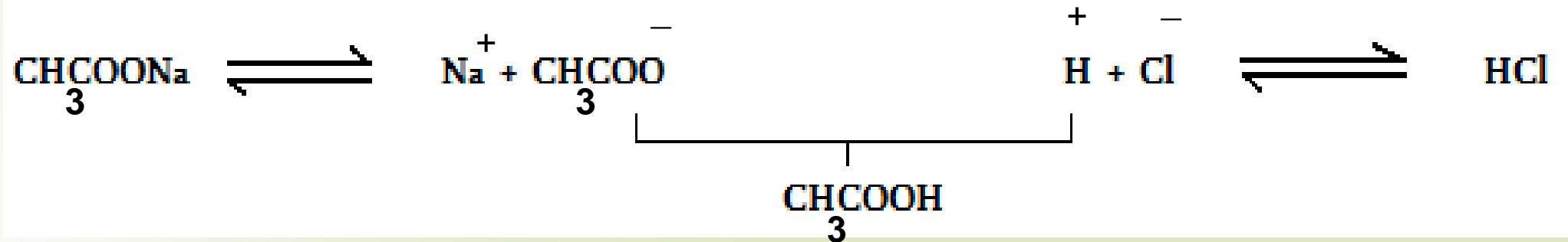



# Buffer action

The resistance of a buffer solution to a change in pH is known as buffer action.

# Mechanism of Action of acidic buffers:

- Consider a buffer system of  $\text{CH}_3\text{COOH}$  (Weak electrolyte) and  $\text{CH}_3\text{COONa}$  (Strong electrolyte). There will be a large concentration of  $\text{Na}^+$  ions,  $\text{CH}_3\text{COONa}^-$  ions, and undissociated  $\text{CH}_3\text{COOH}$  molecules.
- When an acid is added
- If a strong acid (HCl) is added in  $\text{CH}_3\text{COOH} / \text{CH}_3\text{COONa}$  buffer, the changes that will occur may be represented as:

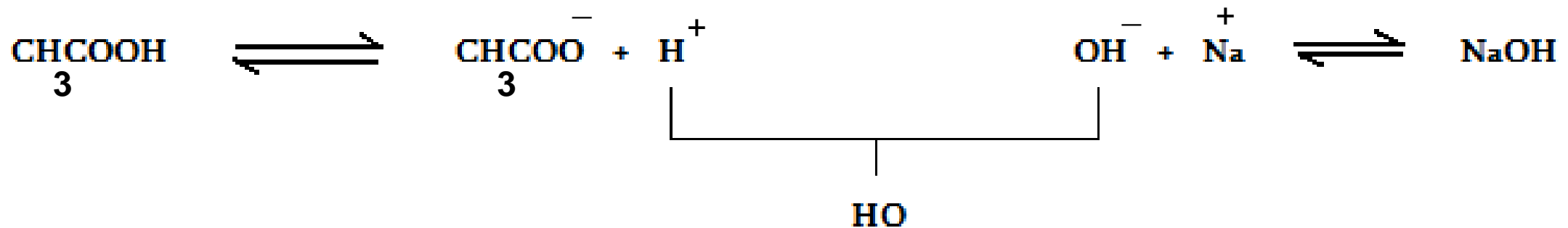




□ The hydrogen ions yielded by the HCl are quickly removed as unionized acetic acid, and the hydrogen ion concentration is therefore only slightly affected (because acetic acid produced is very weak as compared to HCl added).

When a base is added

- ▮ If a strong base (NaOH) is added in CH<sub>3</sub>COOH / CH<sub>3</sub>COONa buffer, the changes that will occur may be represented as:



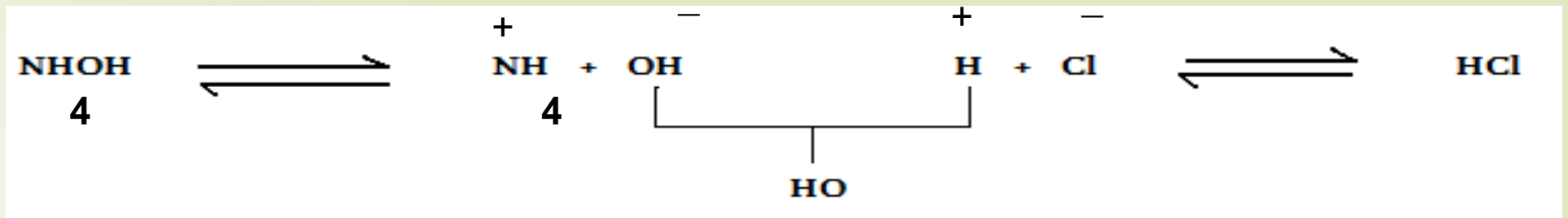
The hydroxyl ions yielded by the NaOH are therefore removed as water. The supply of hydrogen ions needed for this purpose being constantly provided by the dissociation of acetic acid.

# Mechanism of Action of basic buffers:

Consider a buffer system of  $\text{NH}_4\text{OH}$  (Weak electrolyte) and  $\text{NH}_4\text{Cl}$  (Strong electrolyte). There will be a large concentration of  $\text{NH}_4^+$  ions,  $\text{Cl}^-$  ions, and undissociated  $\text{NH}_4\text{OH}$  molecules.

**When an acid is added**

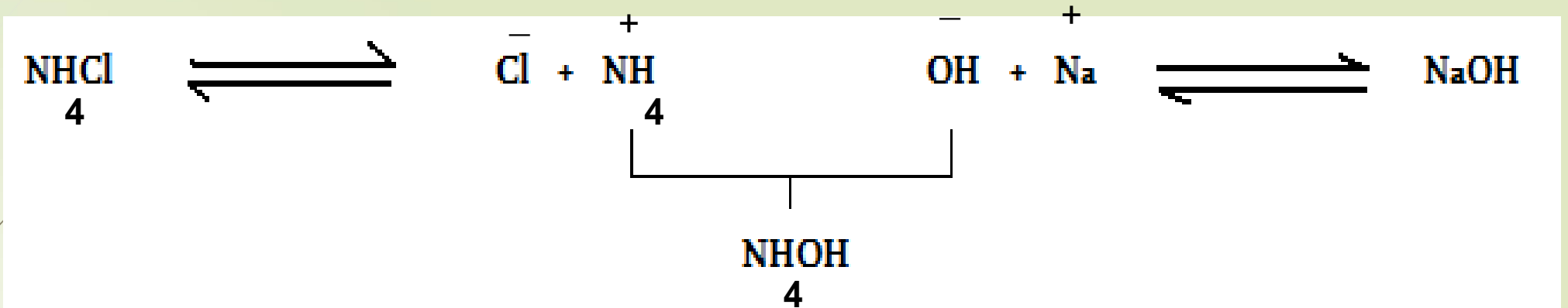
If a strong acid (HCl) is added in  $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$  buffer, the changes that will occur may be represented as:



The hydrogen ions yielded by the HCl are therefore removed as water. The supply of OH ions needed for this is constantly provided by the ammonium hydroxide.

*When a base is added*

If a strong base (NaOH) is added in  $\text{NH}_4\text{OH} / \text{NH}_4\text{Cl}$  buffer, the changes that will occur may be represented as:



The hydroxyl ions yielded by the NaOH are therefore quickly removed as unionized ammonium hydroxide and the pH of solution is only slightly affected.

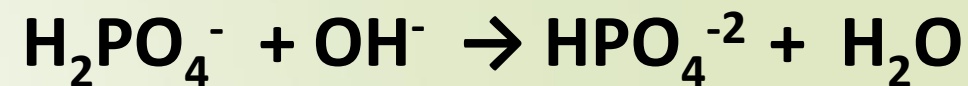
## Mechanism of Action of phosphate buffers:

In  $\text{KH}_2\text{PO}_4 / \text{K}_2\text{HPO}_4$  buffer system,  $\text{H}_2\text{PO}_4^-$  serves as weak acid and  $\text{HPO}_4^{2-}$  serves as conjugate base.

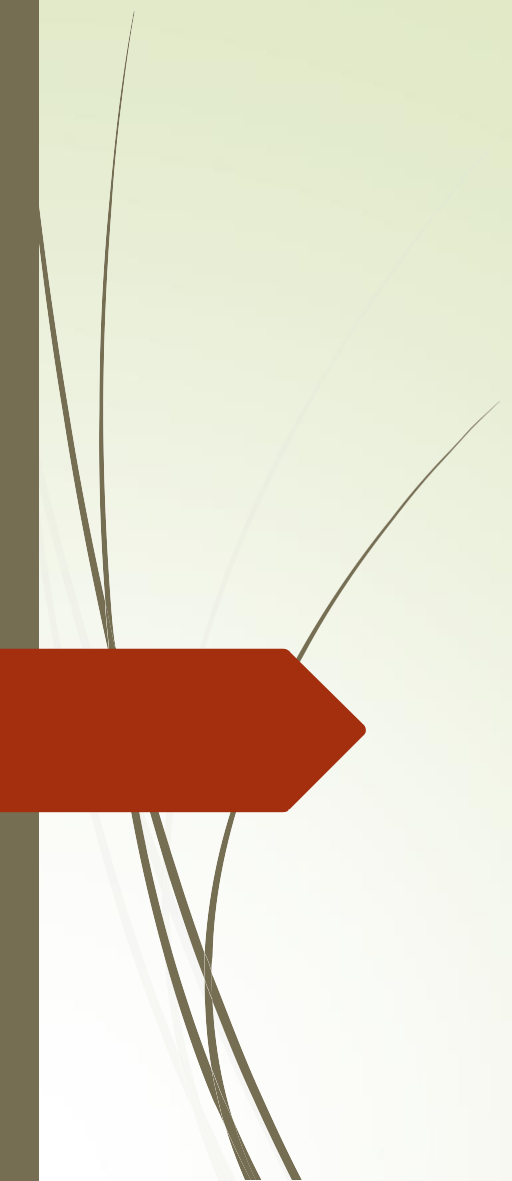
When hydronium ions are added, then



When hydroxyl ions are added to this buffer, the following reaction takes place;







# **BUFFER EQUATION**

## **(Henderson – Hasselbalch equation)**

# For Acid Buffers:

The pH of acid buffer can be calculated from the dissociation constant,  $K_a$  of the weak acid and the concentrations of the acid and salt used.


□ The dissociation expression of the weak acid can be represented as:



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

□ Or

$$\square [\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \text{----- (1)}$$



**□ A weak acid is only slightly dissociated, and its dissociation is further depressed by the addition of the salt (XA) which provides  $A^-$  ion (common ion effect) as a result the equilibrium concentration of the unionized acid is nearly equal to the initial concentration of the acid. The equilibrium concentration of  $A^-$  is assumed to be equal to the initial concentration of the salt added since it is completely dissociated. Therefore, in above equation (1), we represent concentration of  $A^-$  by salt concentration.**

▮  $[H^+] = K_a \cdot [Acid] / [Salt]$  -----(2)

▮ Taking log on both sides, we get:

▮  $\log[H^+] = \log K_a + \log [Acid] / [Salt]$

▮ multiplying both sides by -ve sign,

▮  $-\log[H^+] = -\log K_a - \log [Acid] / [Salt]$

▮ As  $-\log[H^+] = pH$  &  $-\log K_a = pka$

▮  $pH = pka - \log[Acid] / [Salt]$  OR

**$pH = pka + \log[Salt] / [Acid]$  ----- (3)**

Eq. (3) is called as Henderson – Hasselbalch equation.

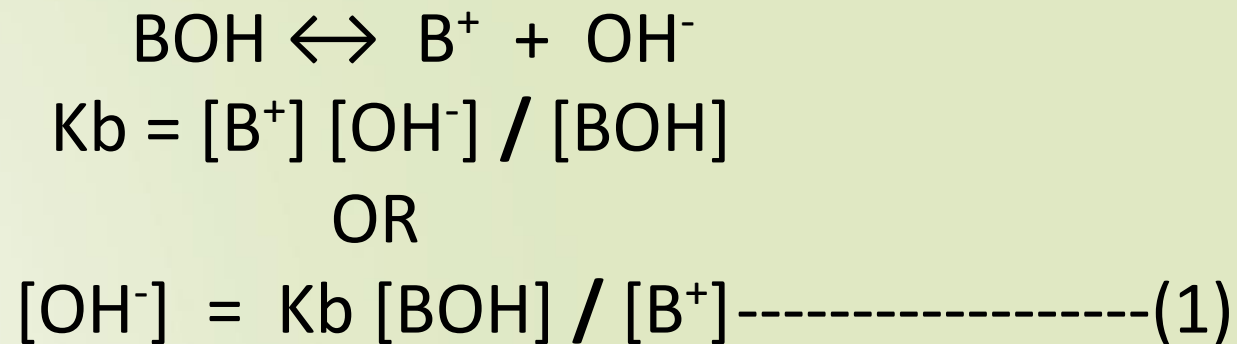
It helps in calculating the pH value of buffer solution,



if the concentrations of acid as well as that of the salt are known.

## For Basic Buffers:


Buffer equation for basic buffer can be calculated in same way as that for acidic buffers.

Consider a basic buffer composed of a mixture of weak base (BOH) and its salt (BA). The dissociation constant for base can be written as,





□ A weak base is only slightly dissociated, and its dissociation is further depressed by the addition of the salt (BA) which provides  $B^+$  ion (common ion effect) as a result the equilibrium concentration of the unionized base is nearly equal to the initial concentration of the base. The equilibrium concentration of  $B^+$  is assumed to be equal to the initial concentration of the salt added since it is completely dissociated. Therefore, in above equation (1), we represent concentration of  $B^+$  by salt concentration.


$$[\text{OH}^-] = K_b \cdot [\text{Base}] / [\text{Salt}] \text{-----(2)}$$

Taking log on both sides, we get:

$$\log[\text{OH}^-] = \log K_b + \log [\text{Base}] / [\text{Salt}]$$

multiplying both sides by -ve sign,

$$-\log[\text{OH}^-] = -\log K_b - \log [\text{Base}] / [\text{Salt}]$$

As  $-\log[\text{OH}^-] = \text{pOH}$  &  $-\log K_b = \text{p}K_b$

$$\text{pOH} = \text{p}K_b - \log [\text{Base}] / [\text{Salt}]$$

Or


$$\text{pOH} = \text{p}K_b + \log[\text{Salt}] / [\text{Base}] \text{----- (3)}$$

## Significance of Henderson – Hasselbalch equation:

By this equation, the pH of a buffer solution can be calculated from the initial concentrations of the weak acid and the salt provided when  $K_a$  is given. However, the Henderson equation for a basic buffer will give pOH, and so pH can be calculated as;

$$pK_w = pH + pOH$$

or

$$pH = pK_w - pOH$$

$$pH = 14 - pOH$$

Also, the dissociation constant of a weak acid ( $pK_a$ ) or a weak base ( $pK_b$ ) can be calculated by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.



### EXAMPLE:

- ▮ Calculate the pH of a buffer solution containing 0.03 moles/litre of acetic acid and 0.1 moles/litre of sodium acetate. pka for CH<sub>3</sub>COOH is 4.57.

### Solution:

- ▮ Conc. Of acid = 0.03 M

- ▮ Conc. Of salt = 0.1 M

- ▮ So,

- ▮  $\text{pH} = \text{pka} + \log [\text{salt}] / [\text{acid}]$

- ▮  $= 4.57 + \log 0.1 / 0.03$

- ▮  $= 4.57 + 0.52$

- ▮  $= 5.09$

- ▮ **Result** → The pH of the buffer solution containing 0.03 M of acetic acid and 0.1 M of sodium acetate is 5.09.

▮ **EXAMPLE:**

▮ Calculate the pH of a buffer solution containing 0.25 moles / litre of formic acid (HCOOH) and 0.10 moles / litre of sodium formate (HCOONa).  $K_a$  for formic acid is  $1.8 \times 10^{-4}$ .

▮ **Solution:**

▮ Conc. Of acid = 0.25 M

▮ Conc. Of salt = 0.10 M

▮  $K_a = 1.8 \times 10^{-4}$

▮ & pka is

▮  $pka = -\log ka = -\log 1.8 \times 10^{-4}$

▮  $= -(\log 1.8 \times 10^{-4}) = -(\log 1.8 + \log 10^{-4}) = -[0.25 + (-4)] = -(-3.75) = \underline{3.75}$

▮ So,

▮  $pH = pka + \log [salt] / [acid]$

▮  $= 3.75 + \log 0.10 / 0.25 = 3.75 - 0.397 = 3.34$

▮ **Result** → The pH of a buffer solution containing 0.25 M of formic acid and 0.10 M of sodium formate is 3.34.

# BUFFER CAPACITY

- ▮ The buffer capacity of a buffer solution is “a measure of its magnitude of its resistance to change in the pH on an addition of an acid or a base.”
- ▮ Buffer capacity is also referred as *buffer index*, *buffer value*, *buffer efficiency* or *buffer coefficient*.
- ▮ The buffer capacity represented by ‘ $\beta$ ’ may also be defined as:
  - ▮ “The ratio of the increment (amount added) of strong acid or base to the small change in pH ( $\Delta\text{pH}$ ) brought about by this addition”.
- ▮  $\beta = \Delta A \text{ or } \Delta B / \Delta\text{pH}$
- ▮
- ▮ Where,  $\Delta A$  or  $\Delta B$  represents the small increment (in gram equivalents / litre of strong acid or base added) to the buffer to bring about a pH change of  $\Delta\text{pH}$ .
- ▮ According to the above equation, a solution has a buffer capacity of 1 when one litre of it requires one gram equivalent of a strong acid or base to change the pH by one unit. So, smaller the pH change in a solution upon the addition of an acid or base, greater is the buffer capacity and vice versa.

# Prepare a buffer solution of pH 5 from acetic acid $\text{CH}_3\text{COOH}$ & $\text{CH}_3\text{COONa}$ . pka of $\text{CH}_3\text{COOH}$ is 4.7.

Required pH = 5

pka = 4.7

Molar concentration of acid required = 1M, Molar concentration of base required = x M = ?

▮ So, by putting above information in equation, we get:

$$\text{pH} = \text{pka} + \log[\text{Salt}] / [\text{Acid}]$$

$$5 = 4.7 + \log [x] / [1]$$

$$5 - 4.7 = \log x - \log 1$$

$$\text{as } \log 1 = 0,$$

$$0.3 = \log x$$

$$x = \log^{-1} 0.3 \quad (\log^{-1} \text{ means anti-log})$$

$$x = 2$$

▮ **Result** → in order to prepare buffer solution of pH 5, acetic acid  $\text{CH}_3\text{COOH}$  & sodium acetate  $\text{CH}_3\text{COO}$  must be mixed in a ratio of 1M : 2M



# **APPLICATIONS OF BUFFERS:**



# In biological systems:

- ▣ The pH of blood is maintained at about 7.4 by two buffer systems. That are;
- ▣ a) primary buffers : these are present in plasma. The plasma contains;
- ▣ carbonic acid / carbonate & acid /alkali sodium salt of phosphoric acid.
- ▣ b) secondary buffers: these are present in erythrocytes which are;
- ▣ oxy-haemoglobin / haemoglobin & acid / alkali potassium salts of phosphoric acid.



## **In pharmaceutical systems:**

- ▮ Buffers are widely used in the field of pharmacy as ingredients in most of the pharmaceutical formulations in order to adjust the pH of the product to that required for maximum stability.

## **In parenteral preparations (i.e. injections):**

- ▮ In case of parenteral preparations, pH should be considered carefully as large deviations of pH may lead to serious consequences. The ideal pH of a parenteral product is 7.4, which is pH of blood. The most commonly used buffers in parenteral products (injections) are *acetate, phosphate, citrate and glutamate*.



## In ophthalmic preparations (i.e. eye preparations):

- ▮ Buffers are generally used in ophthalmic preparations to maintain the pH within the physiological pH range of lacrimal fluid (i.e. eye fluid). The lacrimal fluid has a pH in rang 7 – 8 , but it has good buffering capacity and can tolerate preparations having pH values between 3.5 – 10.5 with little discomfort. Out side this range (i.e. 3.5 – 10.5), increase lacrimation may occur with other complications.
- ▮ The buffering agents most commonly used in ophthalmic preparations include *borate, carbonate and phosphates*.

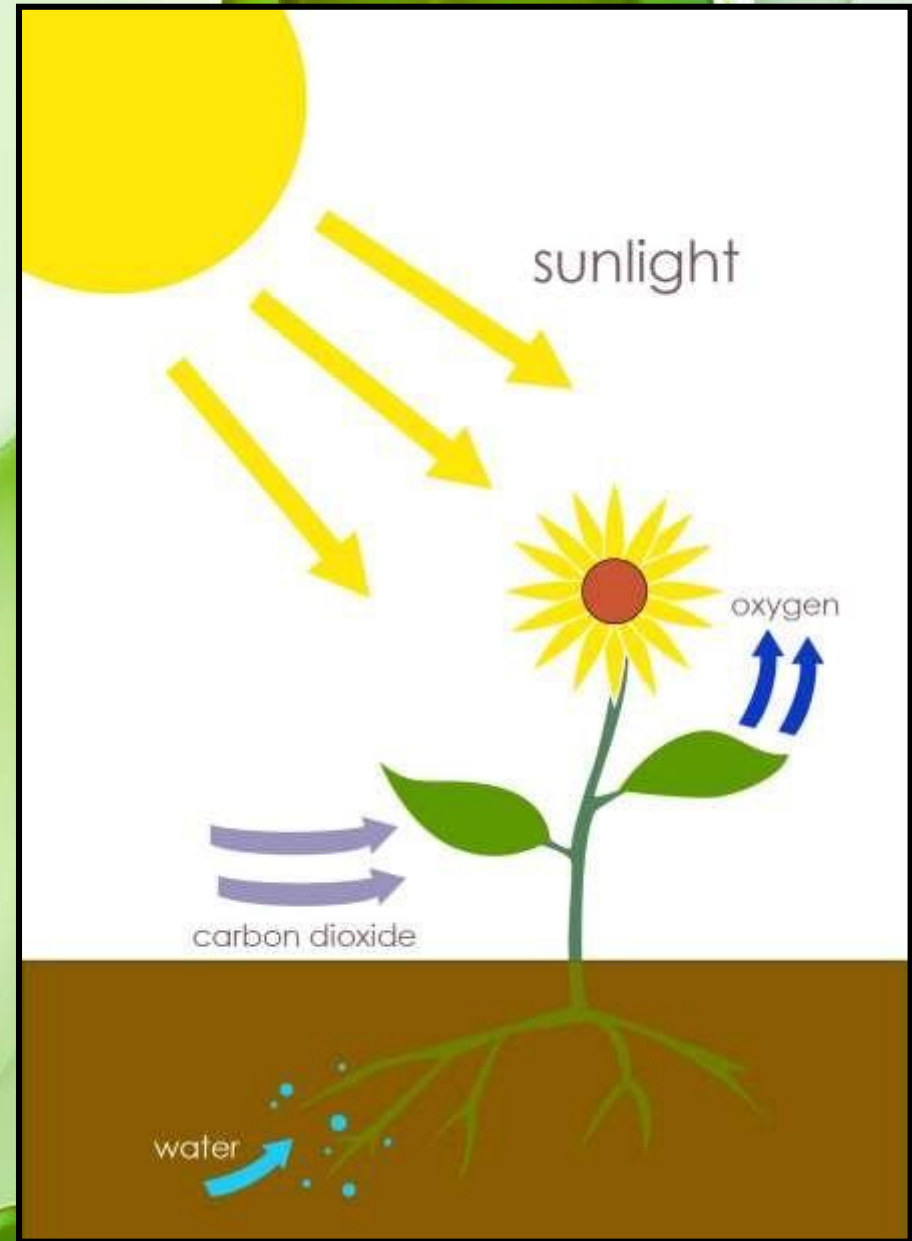
## In ointments and creams:

- ▮ Topical products (which are used on skins) such as ointments and creams are also buffered to ensure stability of the formulation. The most commonly used buffers in ointments and creams are citric acid / its salts & phosphoric acid / its salts.



# CONCEPT OF ENERGY IN ECOSYSTEM

- Energy is the capacity to do work.
- Biological activities require consumption of energy which ultimately comes from sun.
- Except for the deep-sea hydrothermal ecosystem, sun is only the source of energy for all ecosystem on Earth.
- Of the total incident solar radiation less than 60% of it is **photosynthetically active radiation (PAR)**.
- Solar energy of sun is transformed into chemical energy(Adenosine triphosphate) by the process of photosynthesis, then it is stored in plant tissues and then transformed into mechanical and heat form of energy during metabolic activities.



# Components of the energy flow in Ecosystem

- Sun – The energy used for all plant life processes is derived from solar radiations and all animals are further dependent on plants. About 34% of the sunlight reaching the Earth's atmosphere is reflected back (by clouds and dust), 10% is held by ozone layer, water vapour and other atmospheric gases. The rest 56% reaches the earth's surface and out of that only 2 to 10% is used by plants and the remaining is absorbed as heat by water or ground.





- Producers – The green plants in the ecosystem-terminology are called producers. In a terrestrial ecosystem major producers are herbaceous and woody plants. Likewise, primary producers in an aquatic ecosystem are various species like phytoplankton, algae and higher plants.

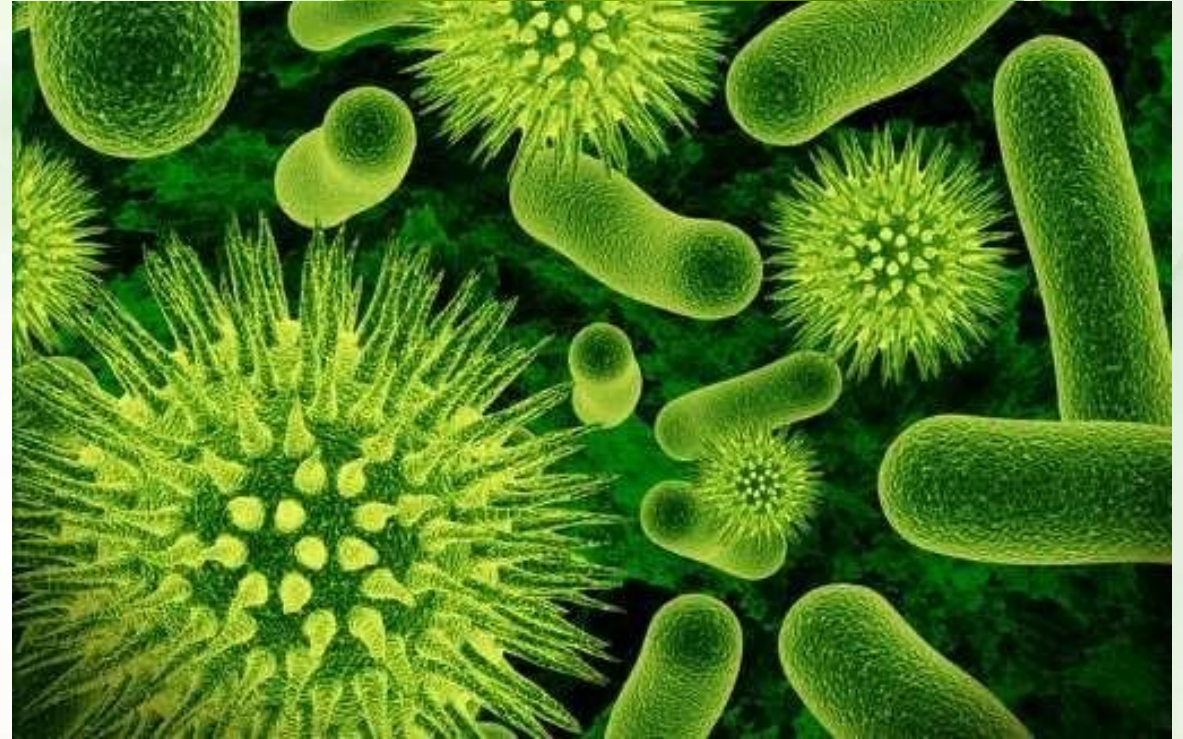


- Consumers – All animals depend on plants (directly or indirectly) for their food needs. Hence, they are called consumers and also heterotrophs.



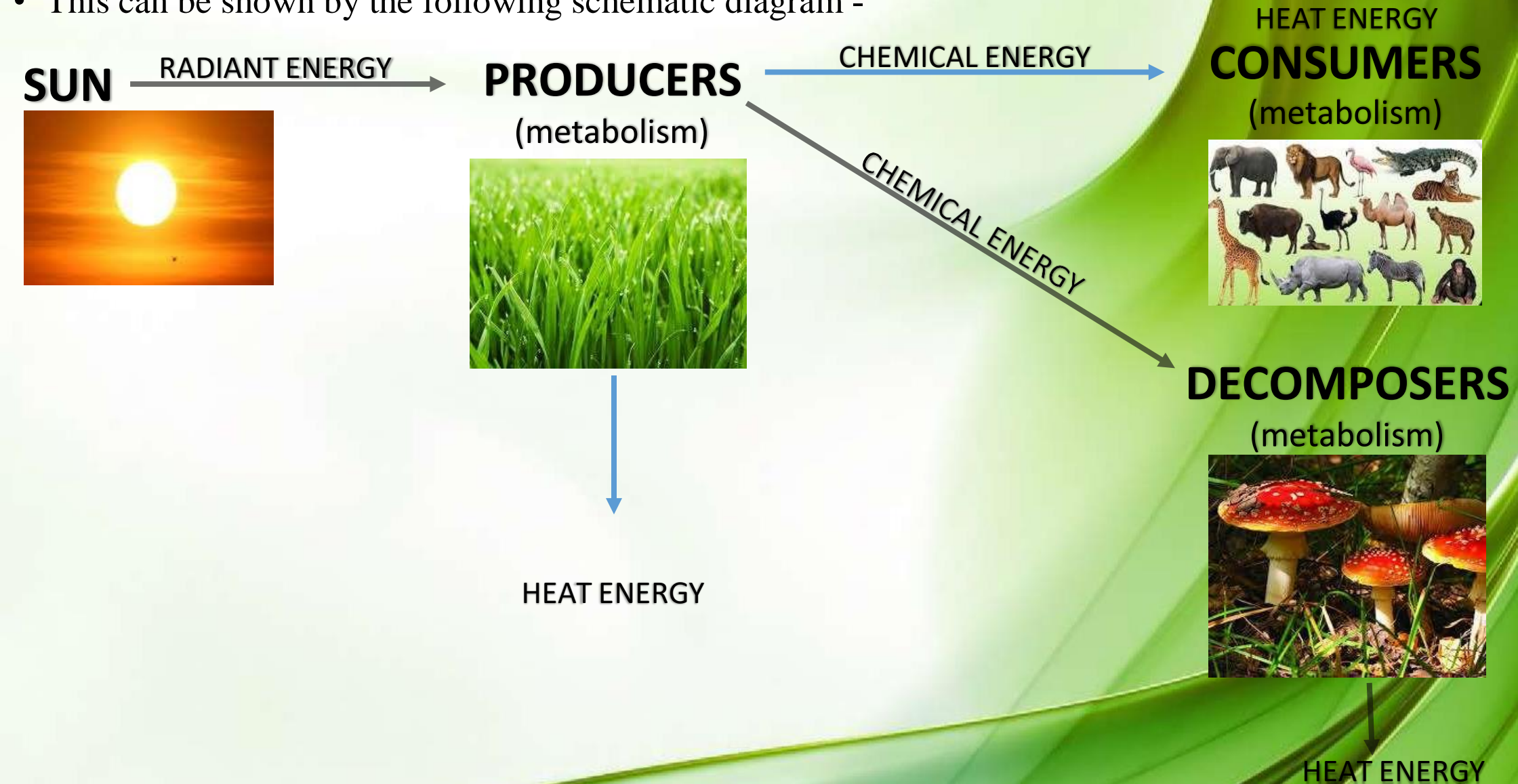


- Decomposers – The heterotrophic organisms, mainly fungi and bacteria, which meet their energy and nutrient requirements by degrading dead organic matter or detritus are called decomposers. They are also known as **saprotrophs**.





- Plants capture only 2 to 10 % of the PAR and this small amount of energy sustains the entire living world!
- So, it is very important to know how solar energy captured by plant flows through different organisms of an ecosystem.
- This can be shown by the following schematic diagram -



# ECOLOGICAL ENERGETICS

- Ecological energetics include energy transformation which occur within the ecosystems.
- In ecological energetics, we consider –
  - i. Quantity of energy reaching an ecosystem per unit of area per unit time.
  - ii. Quantity of energy trapped by green plants and converted to a chemical form (photosynthesis).
  - iii. The quantity and path of energy flow from green plants to organisms of different trophic levels over a period of time in a known area ( energy flow from producers to consumers).



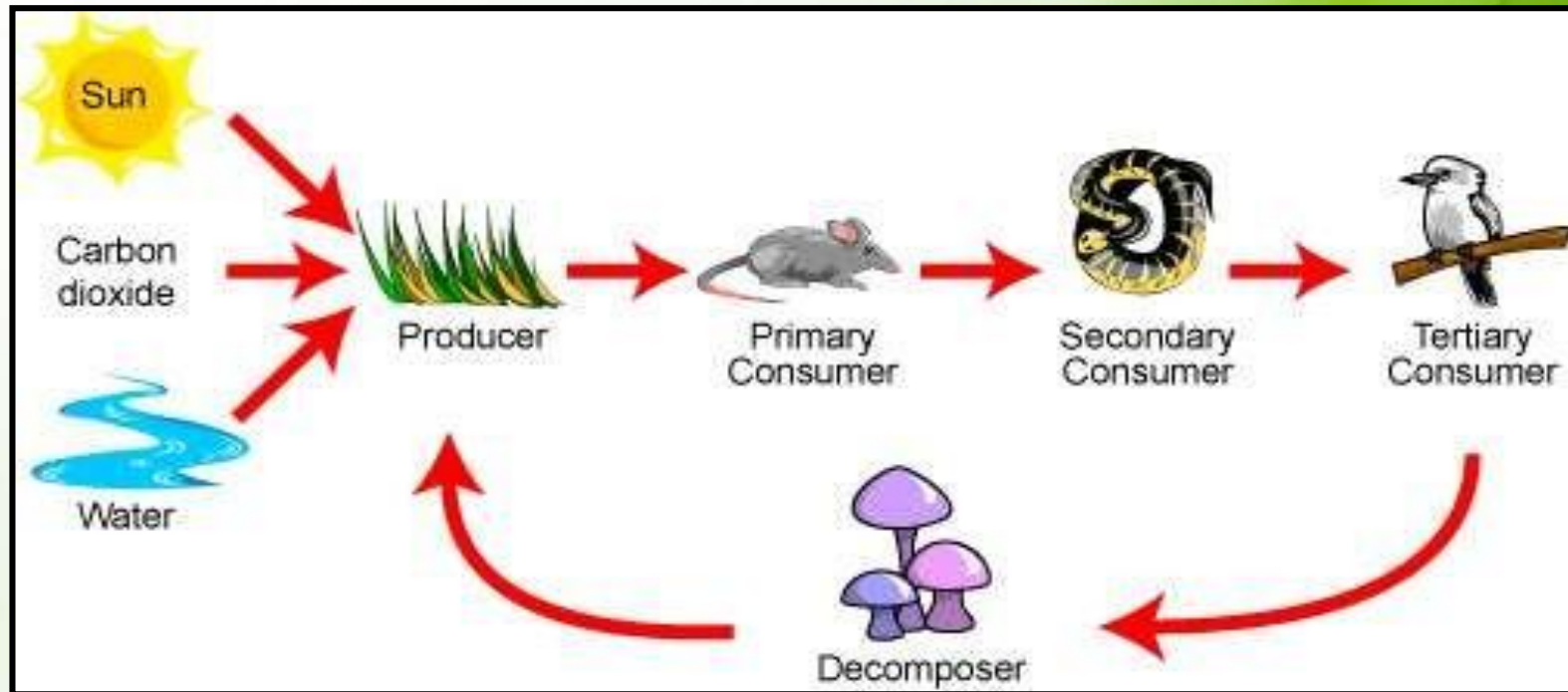
# LAWS GOVERNING ENERGY TRANSFORMATION IN ECOSYSTEM

- Energy transformation in ecosystem can be explained by the laws of thermodynamics.
- Ecosystem follows the first law of thermodynamics, which states that *energy may be transformed from one form to another but it can neither be created nor be destroyed*. This is also true in the case of an ecosystem, when an organism dies its energy is not destroyed but is dissipated in the surrounding through decomposers.
- Further, ecosystem is not exempt from the Second law of thermodynamics which states that *processes involving energy transformation does not occur spontaneously unless there is degradation of energy from a non-random to a random form*. The energy in living organisms is in non-random form i.e. in the form of chemical bonds of biomolecules, but when their decomposition occurs the non-random energy is converted to random form by the decomposers to simpler form.



# INTERCONNECTION AMONG ORGANISMS

- All the organisms in an ecosystem are connected in a very intricate manner and the energy flow occurs through these interconnections.
- These interconnections can be depicted by food chains to understand the basic connection between organisms (In reality they are lot more complexly interconnected).
- There are many types of food chains operating in nature, major one among them are grazing food chain (GFC) and detritus food chain (DFC). A simple GFC is depicted below :-



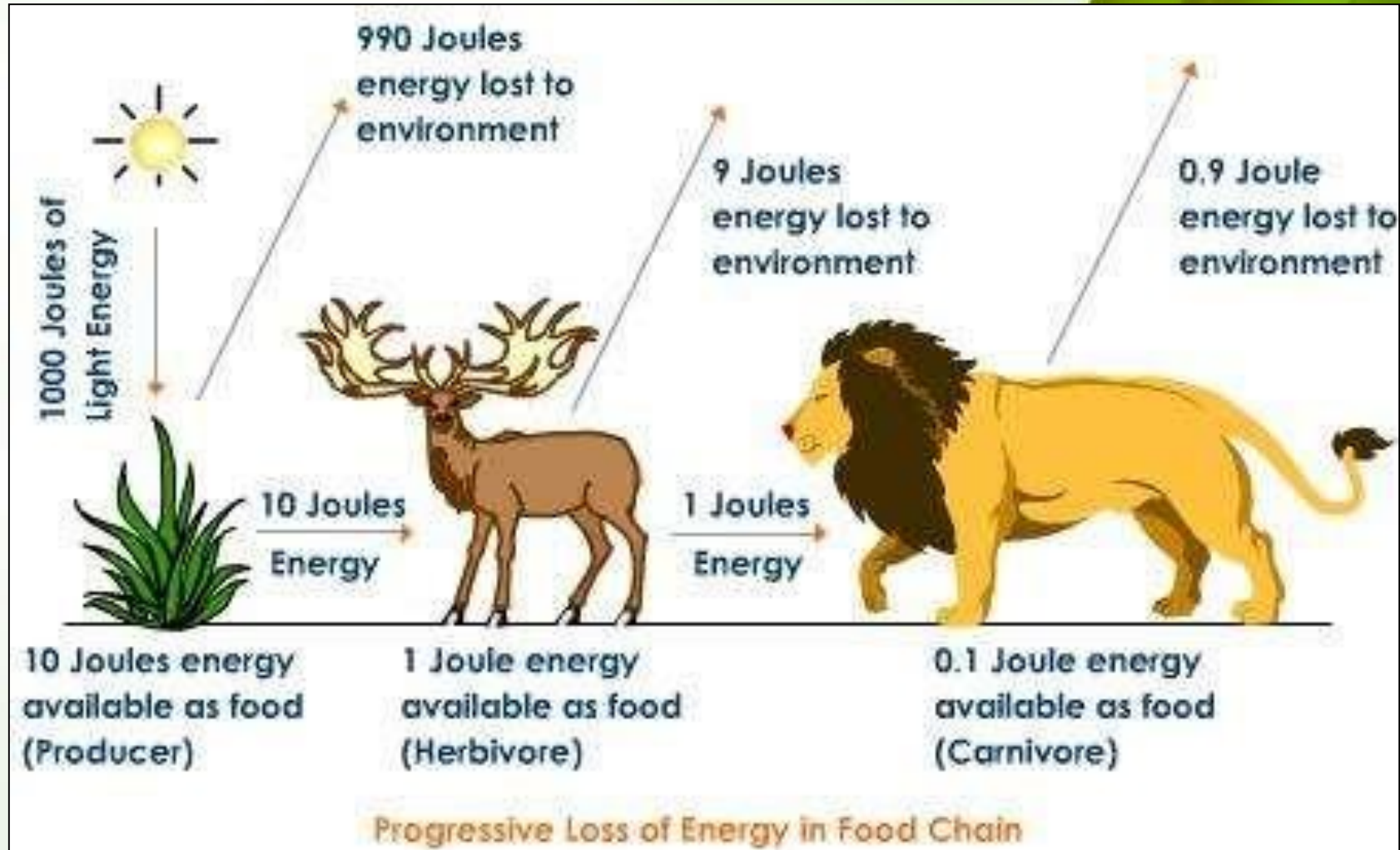
# THE TEN PERCENT LAW



- This law was introduced in context to energy flow in ecosystems by Raymond Lindeman.
- According to this law, during the transfer of energy from organic food from one trophic level to the next, only ten percent of the energy from organic matter is stored as flesh.
- The remaining is lost during transfer, broken down in respiration, or lost to incomplete digestion by higher trophic level.

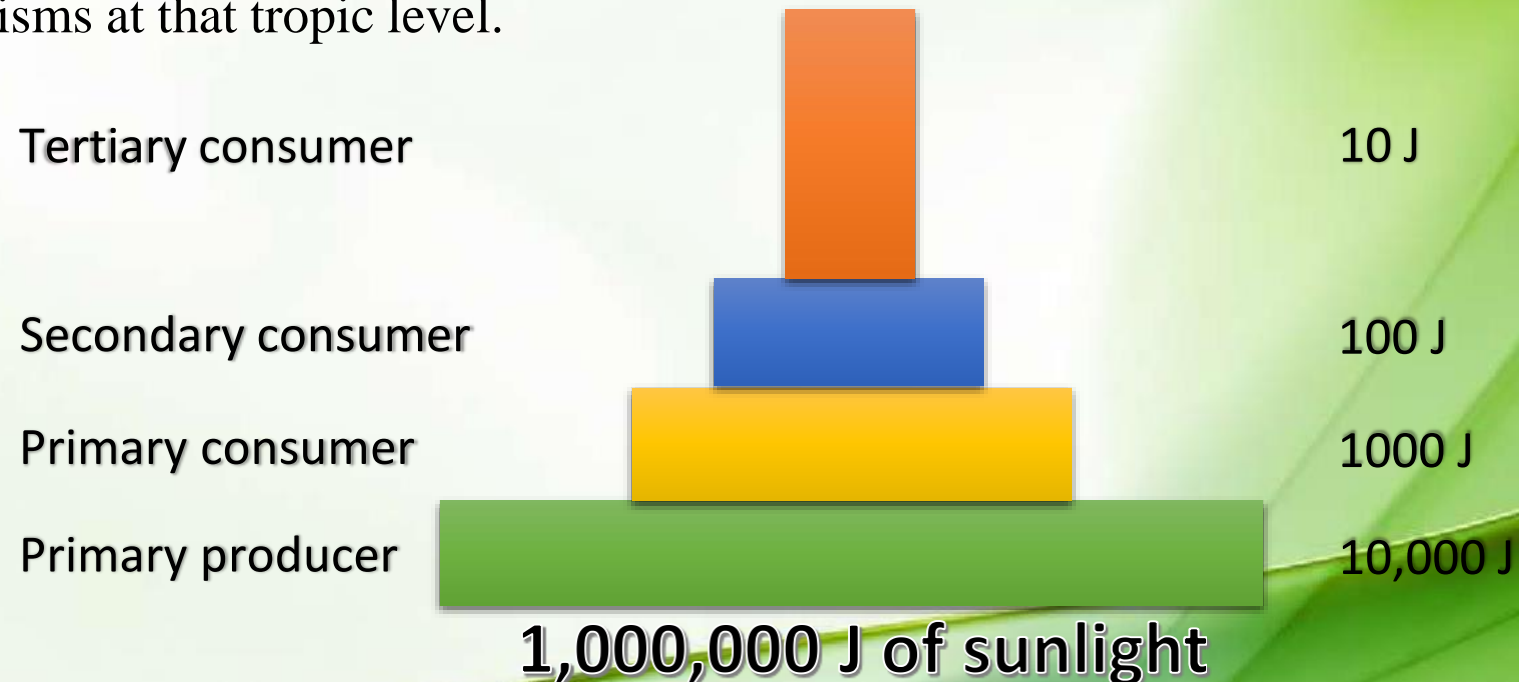


- The ten percent law gives us a basic understanding on the cycling of food chains.
- Furthermore, this law shows the inefficiency of energy capture at each successive trophic level.



# REPRESENTATION OF ENERGY FLOW IN ECOSYSTEM

- Trophic level – Organisms occupy a place in the natural surroundings or in a community according to their feeding relationship with other organisms. Based on the source of their nutrition or food, organisms occupy a specific place in the food chain that is known as their trophic level. A given organism may occupy more than one trophic level simultaneously.
- Organisms at each trophic level depend on those at the lower trophic level for their energy demands.
- Standing crop - Each trophic level has a certain mass of living material at a particular time called as the standing crop. It is measured as the biomass of an organism or their number in a unit area.
- Pyramid of energy - Any calculations of energy content, biomass, or numbers has to include all organisms at that trophic level.





# CONCLUSION

- An ecosystem is a functional unit with energy flowing among its abiotic components very efficiently.
- Energy flow in an ecosystem is always unidirectional.
- Energy in an ecosystem is never destroyed but it is converted from one form to another.
- Only 10 % of energy is passed to the successive trophic level.
- Sun is the ultimate source of energy.
- Plants play a vital role in converting the solar energy to the chemical energy, making the sun's energy available to the organisms at higher trophic levels.
- If any of the link in a food chain or food web (interconnected food chains) is removed efficient energy flow will not occur.

# OXIDATION AND REDUCTION

Oxidation is a process which involves either of the following :

- Addition of oxygen and removal of hydrogen.
- Addition of electronegative element and removal of electropositive element.
- Increase in the valency of an electropositive element.
- Loss of one or more electron by an atom or an ion or molecule.

**Reduction is the reverse process of oxidation.**

# REDOX REACTION

**oxidation-reduction reaction** An oxidizing chemical change, where an element's positive valence is increased (electron loss), accompanied by a simultaneous reduction of an associated element (electron gain)

**oxidation state** The number of electrons to be added (or subtracted) from an atom in a combined state to convert it to elemental form. Also known as oxidation number.

# OXIDATION NUMBER

**Oxidation number (Oxidation state)** is the charge that an atom appears to have in a given species when the bonding electrons are counted using following rules:

**(a).** The oxidation number (O.N.) of an atom in its elemental state is zero, no matter how complicated the molecule is, e.g.,





# OXIDATION NUMBER

- (b). F has oxidation number -1.
- (c). Oxidation number of oxygen is -2 in all compounds except in peroxides, super oxides and oxygen fluoride. The Oxidation Number of
  - Oxygen In  $O_2^{2-}$  is -1
  - Oxygen in  $O^{2-}$  is  $-\frac{1}{2}$
  - Oxygen in  $OF_2$  is +2
  - Oxygen  $O_2F_2$  is +1

# OXIDATION NUMBER

(d) The oxidation number of

- Hydrogen is **+1** in all its compounds
- Hydrogen is **-1** in Metallic Hydrides

(e) The oxidation number of

- Group I elements is **+1**
- Group 2 elements is **+2**.

(f) For complex ion, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

# TYPES OF REDOX REACTIONS :

## Combination reaction :

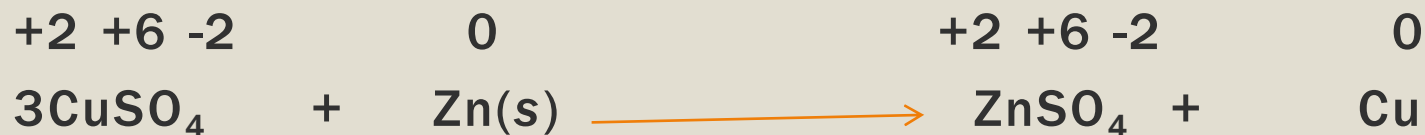


## Decomposition :



# TYPES OF REDOX REACTIONS

## Metal displacement :



## Non-metal displacement :



## Disproportionation :

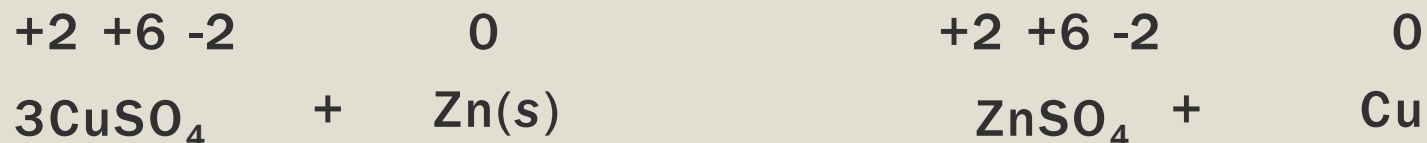


# OXIDIZING AGENT AND REDUCING AGENT

Oxidizing agents are those chemicals, which oxidizes other chemicals but reduces itself.

Reducing agents are those substances, which reduces other but oxidizes itself.

Example:



In this chemical reaction:

- Oxidizing agent:  $3\text{CuSO}_4$
- Reducing agent:  $\text{Zn}$

# OXIDIZING AGENT

Two common oxidizing agents are potassium permanganate ( $\text{KMnO}_4$ ) and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ).



# BALANCING REDOX EQUATIONS

Equations for redox reactions like the preceding one are relatively easy to balance.

However, in the laboratory we often encounter more complex redox reactions involving oxo anions such as

- chromate ( $\text{CrO}_4^{2-}$ ),
- dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ),
- permanganate ( $\text{MnO}_4^-$ ),
  - nitrate ( $\text{NO}_3^-$ ),
  - sulfate ( $\text{SO}_4^{2-}$ ).

# BALANCING REDOX EQUATIONS

In principle, we can balance any redox equation using the procedure, but there are some special techniques for handling redox reactions, techniques that also give us insight into electron transfer processes.

Here we will discuss one such procedure, called the *ion-electron method*.



# BALANCING REDOX EQUATIONS

## *ION-ELECTRON METHOD.*

In this approach, the overall reaction is divided into two half-reactions,

- one for oxidation half reaction
- one for reduction half reaction
- The equations for the two half-reactions are balanced separately
- then added together to give the overall balanced equation.

# ION ELECTRON METHOD

Suppose we are asked to balance the equation showing the oxidation of  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions by dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) in an acidic medium. As a result, the  $\text{Cr}_2\text{O}_7^{2-}$  ions are reduced to  $\text{Cr}^{3+}$  ions. The following steps will help us balance the equation.

**Step 1:** Write the unbalanced equation for the reaction in ionic form.



**Step 2:** Separate the equation into two half-reactions.



# ION ELECTRON METHOD

**Step 3:** Balance each half-reaction for number and type of atoms and charges. For reactions in an acidic medium, add H<sub>2</sub>O to balance the O atoms and H<sup>+</sup> to balance the H atoms.

**Oxidation half-reaction:** The atoms are already balanced. To balance the charge, we add an electron to the right-hand side of the arrow:



# ION ELECTRON METHOD

**Reduction half-reaction:** Because the reaction takes place in an acidic medium, we add  $7\text{H}_2\text{O}$  molecules to the right-hand side of the arrow to balance the O atoms:



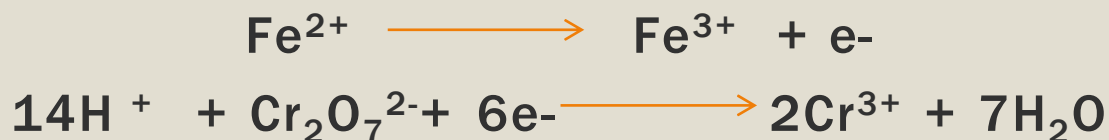
❓ To balance the H atoms, we add  $14\text{H}^+$  ions on the left-hand side:



# ION ELECTRON METHOD

**Step 4:** Add the two half-equations together and balance the final equation by inspection. The electrons on both sides must cancel. If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions to equalize the number of electrons.

Here we have only one electron for the oxidation half -reaction and 6 electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6 and write



# ION ELECTRON METHOD

- ❑ The electrons on both sides cancel, and we are left with the balanced net ionic equation:



- ❑ **Step 5:** Verify that the equation contains the same type and numbers of atoms and the same charges on both sides of the equation.
- ❑ A final check shows that the resulting equation is “atomically” and “electrically” balanced.
- ❑ For reactions in a basic medium, we proceed through step 4 as if the reaction were carried out in an acidic medium. Then, for every  $\text{H}^{+}$  ion we add an equal number of  $\text{OH}^{-}$  ions to both sides of the equation. Where  $\text{H}^{+}$  and  $\text{OH}^{-}$  ions appear on the same side of the equation,

# GALVANIC CELLS

- ❓ When a piece of zinc metal is placed in a  $\text{CuSO}_4$  solution,
- ❓ Zn is oxidized to  $\text{Zn}^{2+}$  ions while  $\text{Cu}^{2+}$  ions are reduced to metallic copper
- ❓ The electrons are transferred directly from the reducing agent (Zn) to the oxidizing agent ( $\text{Cu}^{2+}$ ) in solution. However, if we physically separate the oxidizing agent from the reducing agent, the transfer of electrons can take place via an external conducting medium (a metal wire). As the reaction progresses, it sets up a constant flow of electrons and hence generates electricity (that is, it produces electrical work such as driving an electric motor).

# GALVANIC CELLS

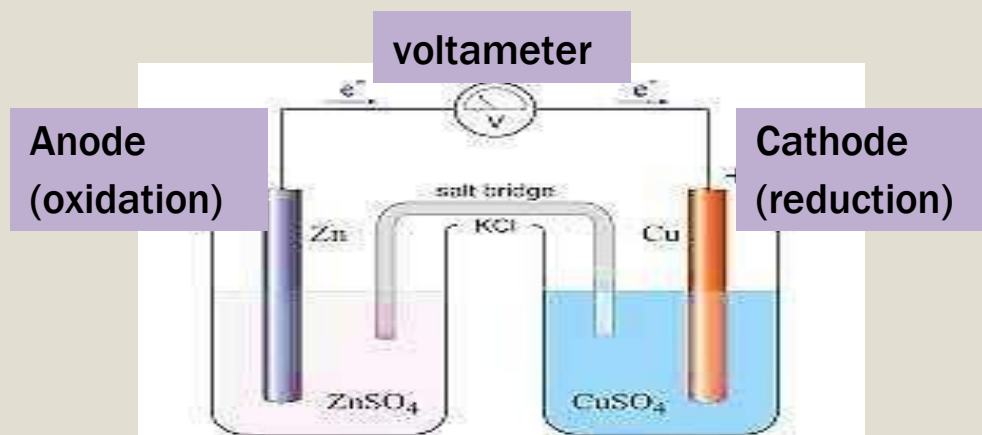
❓ The experimental apparatus for generating electricity through the use of a spontaneous reaction is called a *galvanic cell* or *voltaic cell*, after the Italian scientists Luigi Galvani and Alessandro Volta, who constructed early versions of the device.



# GALVANIC CELL

- ❓ In Galvanic cell, a zinc bar is immersed in a  $\text{ZnSO}_4$  solution, and a copper bar is immersed in a  $\text{CuSO}_4$  solution. The cell operates on the principle that the oxidation of Zn to  $\text{Zn}^{2+}$  and the reduction of  $\text{Cu}^{2+}$  to Cu can be made to take place simultaneously in separate locations with the transfer of electrons between them occurring through an external wire. The zinc and copper bars are called *electrodes*. This particular arrangement of electrodes (Zn and Cu) and solutions ( $\text{ZnSO}_4$  and  $\text{CuSO}_4$ ) is called the Daniel cell.
- ❓ By definition, the ***anode*** in a galvanic cell is *the electrode at which oxidation occurs* and the ***cathode*** is *the electrode at which reduction occurs*.

# GALVANIC CELL



Anode



Cathode

# GLAVANIC CELLS

? Zn is oxidized to  $\text{Zn}^{2+}$  at anode.



?  $\text{Cu}^{2+}$  is reduced to Cu at cathode.



? The net reaction:



# SIGNIFICANCE OF SALT BRIDGE

## Salt bridge and its significance :

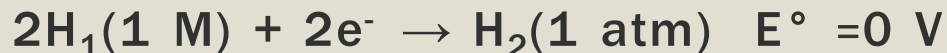
- ❑ An inverted U-tube filled with concentrated solution of inert electrolyte like  $\text{NH}_4\text{NO}_3$ ,  $\text{KCl}$ .
- ❑ (a) It connects the solution of two half-cells.
- ❑ (b) It prevents the accumulation of charges in anodic as well as cathodic half-cells.

# ELECTRODE POTENTIAL

- When the concentrations of the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions are both  $1.0\text{ M}$ , we find that the voltage or emf of the Daniel cell is  $1.10\text{ V}$  at  $25^\circ\text{C}$ . This voltage must be related directly to the redox reactions, but how?
- The overall cell reaction can be thought of as the sum of two half-cell reactions, the measured emf of the cell can be treated as the sum of the electrical potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction (from  $1.10\text{ V}$ ). It is impossible to measure the potential of just a single electrode, but, if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, serves as the reference for this purpose. Hydrogen gas is bubbled into a hydrochloric acid solution at  $25^\circ\text{C}$ .

# STANDARD HYDROGEN ELECTRODE (SHE)

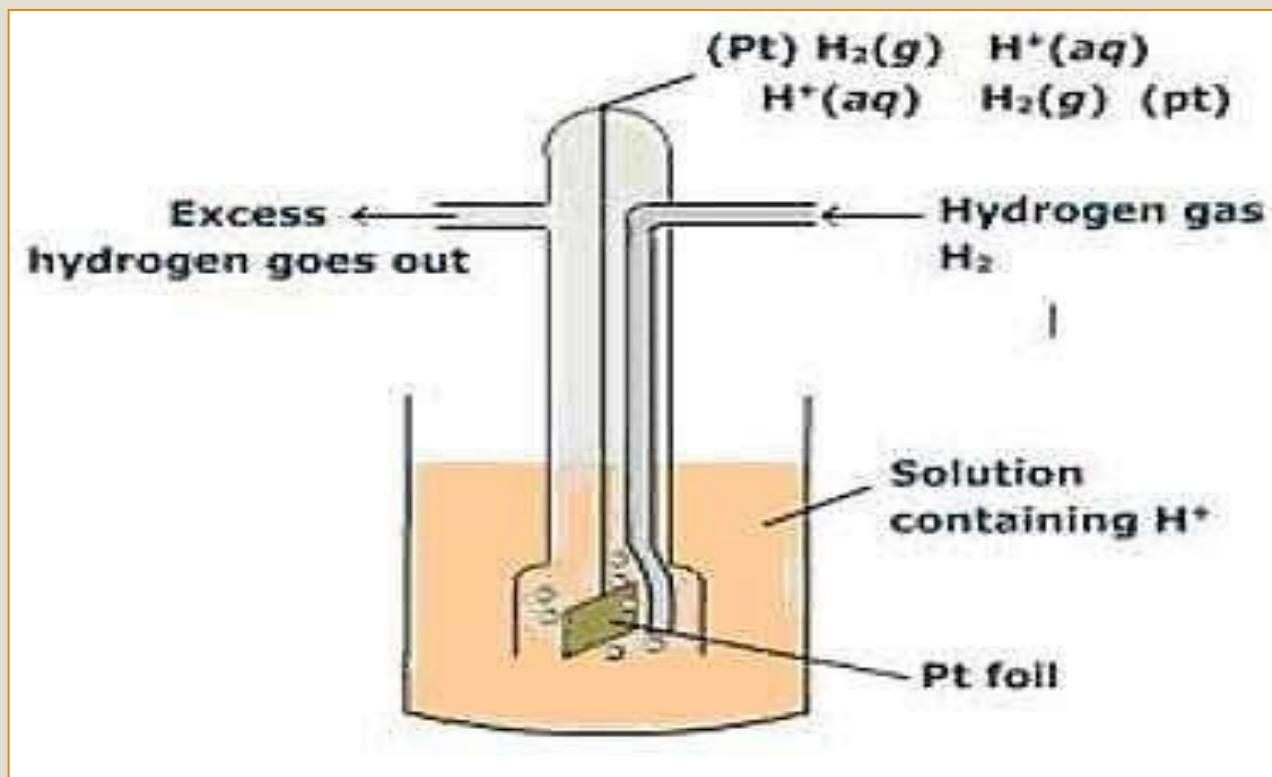
- ❓ The platinum electrode has two functions:
- ❓ First, it provides a surface on which the dissociation of hydrogen molecules can take place:
- ❓ Second, it serves as an electrical conductor to the external circuit.
- ❓ Under standard-state conditions (when the pressure of H<sub>2</sub> is 1 atm and the concentration of the HCl solution is 1 M; the potential for the reduction of H<sup>+</sup> at 25°C is taken to be exactly zero:



- ❓ E° is the standard reduction potential, or the voltage associated with a reduction reaction at an electrode, when all solutes are 1 M and all gases are at 1 atm. Thus, the standard reduction potential of the hydrogen electrode is defined as zero.

The hydrogen electrode is called the standard hydrogen electrode (SHE).

# STANDARD HYDROGEN ELECTRODE (SHE)



# USE OF STANDARD HYDROGEN ELECTRODE (SHE)

When all the reactants are in their standard states (that is,  $H_2$  at 1 atm,  $H_1$  and  $Zn^{+2}$  ions at 1 M), the emf of the cell is 0.76 V at 25°C, We can write the half-cell reactions as follows:

**Anode (oxidation):**  $Zn_{(s)} \rightarrow Zn^{+2} (1 \text{ atm}) + 2e^-$   $E^\circ = ? \text{ V}$

**Cathode (reduction):**  $2H_1(1 \text{ M}) + 2e^- \rightarrow H_2(1 \text{ atm})$   $E^\circ = 0 \text{ V}$

**Overall:**  $Zn_{(s)} + 2H_1(1 \text{ M}) \rightarrow Zn^{+2} (1 \text{ atm}) + H_2(1 \text{ atm})$

$$E^\circ \text{ cell} = E^\circ \text{ cathode} - E^\circ \text{ anode}$$

$$E^\circ \text{ cell} = E^\circ_{H_1/H_2} - E^\circ_{Zn^{+2}/Zn}$$

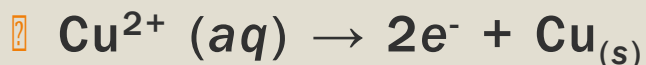
$$0.76 \text{ V} = 0 \text{ V} - E^\circ_{Zn^{+2}/Zn}$$

$$E^\circ_{Zn^{+2}/Zn} = 0.76 \text{ V}$$

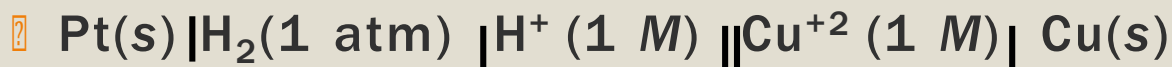


# STANDARD REDUCTION POTENTIAL OF COPPER

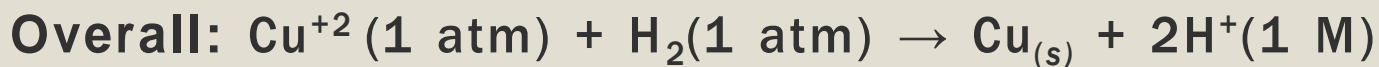
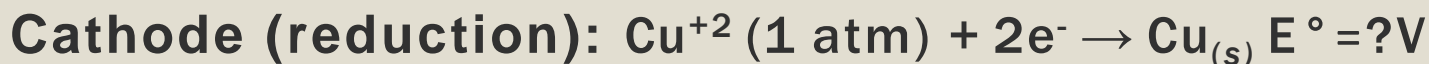
❓ The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a SHE. In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as is consistent with the reduction reaction:



❓ The cell diagram is



the half-cell reactions are



# STANDARD REDUCTION POTENTIAL OF COPPER

the half-cell reactions are

**Anode (oxidation):**  $\text{H}_2(1 \text{ atm}) \rightarrow 2\text{H}^+(1 \text{ M}) + 2\text{e}^-$   $E^\circ = 0\text{V}$

**Cathode (reduction):**  $\text{Cu}^{+2}(1 \text{ atm}) + 2\text{e}^- \rightarrow \text{Cu}_{(s)}$   $E^\circ = ?\text{V}$

**Overall:**  $\text{Cu}^{+2}(1 \text{ atm}) + \text{H}_2(1 \text{ atm}) \rightarrow \text{Cu}_{(s)} + 2\text{H}^+(1 \text{ M})$

Under standard-state conditions and at  $25^\circ\text{C}$ , the emf of the cell is  $0.34 \text{ V}$ , so we write

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{+2}/\text{Cu}} - E^\circ_{\text{H}^+/\text{H}_2}$$

$$0.34 \text{ V} = E^\circ_{\text{Cu}^{+2}/\text{Cu}} - 0 \text{ V}$$

$$E^\circ_{\text{Cu}^{+2}/\text{Cu}} = 0.34 \text{ V}$$

In this case, the standard reduction potential of copper,  $E^\circ_{\text{Cu}^{+2}/\text{Cu}}$  is  $0.34 \text{ V}$ ,

# ELECTRODE POTENTIAL OF ELECTROCHEMICAL CELL

By convention, the standard emf of the cell,  $E^\circ_{\text{cell}}$ , which is composed of a contribution from the anode and a contribution from the cathode, is given by

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

where both  $E^\circ_{\text{cathode}}$  and  $E^\circ_{\text{anode}}$  are the standard reduction potentials of the electrodes.

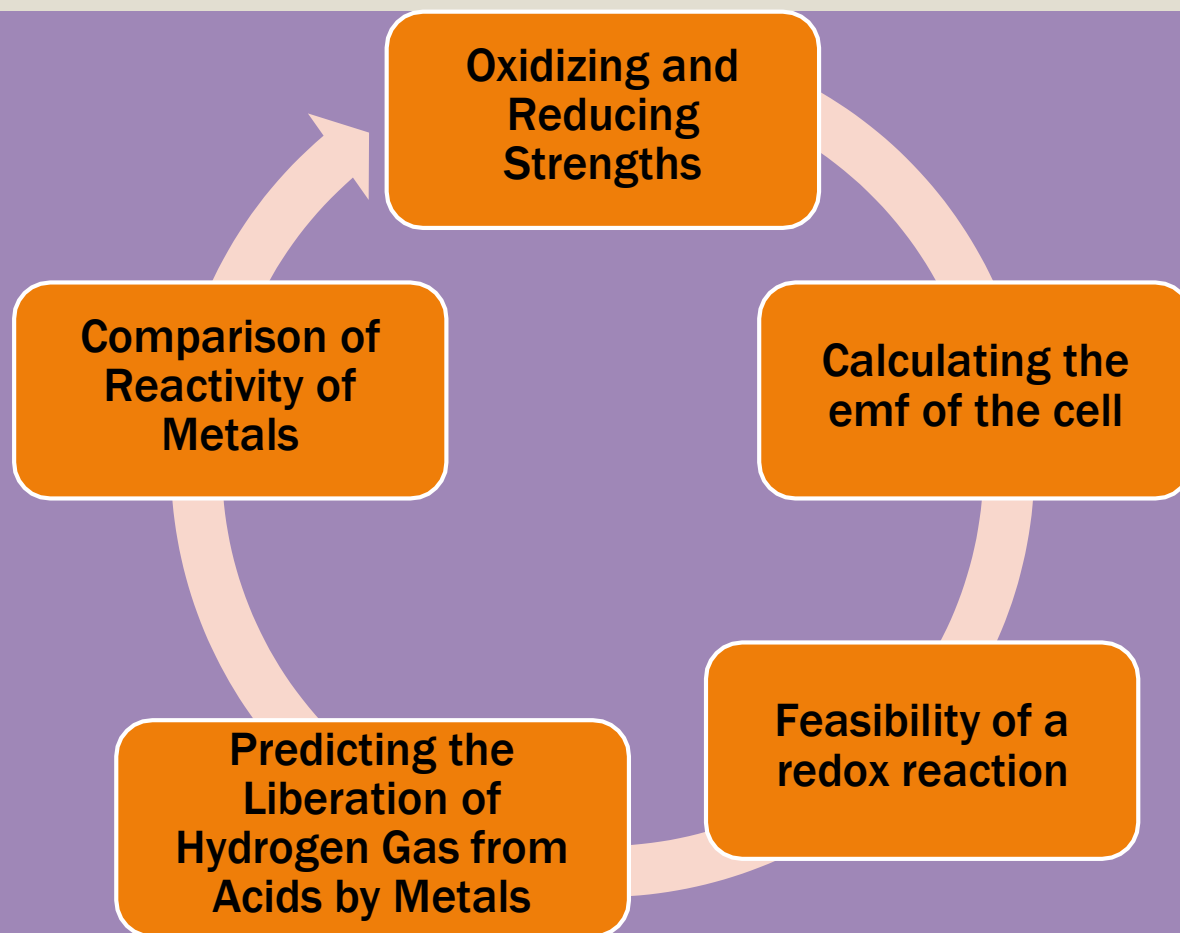
For a cell

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.34 \text{ V} - 0.76 \text{ V} \\ &= 1.10 \text{ V} \end{aligned}$$

# STANDARD OXIDATION-REDUCTION POTENTIALS AT 25°C

MORE ACTIVE	Reaction	$E_0$ (volts)	
↑	$\text{Na} \rightarrow \text{Na}^+ + e^-$	-2.71	
	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	-2.38	
	$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$	-1.66	
	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	-0.763	
	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	-0.409	
	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$	-0.250	
	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$	-0.126	
	$\text{H} \rightarrow 2\text{H}^+ + 2e^-$	0.00 Reference	
	↓	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$	+0.34
		$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$	+0.401
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$		+0.771	
$2\text{H}^+ \rightarrow \text{Hg}_2^{2+} + 2e^-$		+0.905	
$\text{Ag} \rightarrow \text{Ag}^+ + e^-$		+0.799	
$2\text{Br}^- \rightarrow \text{Br}_2 + 2e^-$		+1.06	
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$		+1.23	
$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$		+1.36	
$\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$		+1.2	
$\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$		+1.498	
MORE NOBLE			

# SIGNIFICANCE OF STANDARD OXIDATION-REDUCTION POTENTIALS



# OXIDIZING AND REDUCING STRENGTHS

- ❓ The electrochemical series helps to pick out substances that are good oxidizing agents and those which are good reducing agents. For example, a very high negative reduction potential of lithium electrode indicates that it is very difficult to reduce  $\text{Li}^+$  ions to Li atoms. Therefore,  $\text{Li}^+$  cannot accept electrons easily and so loses electrons to behave as a reducing agent. As the reduction potential increases (negative value decreases), the tendency of the electrode to behave as reducing agent decreases. Thus, all the substances appearing on the top of the series behave as good reducing agents. For example Li and K are good reducing agents while  $\text{F}^-$  and Au are the poorest reducing agents.
- ❓ Similarly, substances at the bottom of the table have high reduction potential and they can be easily reduced. Therefore, they act as strong oxidizing agents. From the table we can conclude that  $\text{H}^+$  is a better oxidizing agent than  $\text{Zn}^{2+}$  while  $\text{Cu}^{2+}$  is a better oxidizing agent than  $\text{H}^+$ ; Fe is a better oxidizing agent than  $\text{Cl}_2$  and so on. All the substances appearing at the bottom of the table are good oxidizing agents.

# COMPARISON OF REACTIVITY OF METALS

- ② The relative ease with which the various species of metals and ions may be oxidized or reduced is indicated by the reduction potential values. The metals with lower reduction potential are not reduced easily but are easily oxidized to their ions losing electrons. These electrons would reduce the other metals having higher reduction potentials. In other words, a metal having smaller reduction potential can displace metals having larger reduction potentials from the solution of their salt.
- ② For example, copper lies above silver in the electrochemical series, therefore, if copper metal is added to  $\text{AgNO}_3$  solution, silver is displaced from the solution. In general a metal occupying higher position in the series can displace the metals lying below it from the solutions of their salts and so are more reactive in displacing the other metals. Thus, Li is the most electropositive element in solutions and fluorine is the most electronegative element.

# CALCULATION OF THE EMF OF THE CELL

The following steps determine the reduction potential of the cathode and anode:

**Step I :** The two half- cell reactions are written in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right electrode is written as reduction reaction.

**Step II:** The number of electrons in the two equations are made equal by multiplying one of the equations if necessary by a suitable number. However, electrode potential values ( $E^\circ$ ) are not multiplied.

**Step III:** The electrode potentials of both the electrodes are taken to be reduction potentials and so the EMF of the cell is equal to the difference between the standard potential of the right hand side and the left hand side electrode.

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

**Step IV:** If the EMF of the cell is +ve, the reaction is feasible in the given direction and the cell is correctly represented, i . e., oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). If it is - ve, the cell reaction is not feasible in the given direction and the cell is wrongly represented. Thus, to get positive value for the EMF the electrodes must be reversed.



# PREDICTING THE LIBERATION OF HYDROGEN GAS FROM ACIDS BY METALS

- ❓ All metals having negative electrode potentials (negative  $E^\circ$  values) show greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized, and  $H^+$  (hydrogen) ions get reduced to form hydrogen gas. Thus, the metals having negative  $E^\circ$  values liberate hydrogen from acids.
- ❓ metal having negative  $E^\circ$  value
- ❓ For example, metals such as Mg ( $E (Mg^{2+} / Mg) = - 2.37 \text{ V}$ ),
- ❓ Zn ( $E (Zn^{2+} / Zn) = - 0.76 \text{ V}$ ), Iron ( $E (Fe^{2+} / Fe) = - 0.44 \text{ V}$ ) etc., can displace hydrogen from acids such as HCl and  $H_2SO_4$ .
- ❓ But metals such as Copper, ( $E (Cu^{2+} / Cu) = + 0.34\text{V}$ ), silver ( $E (Ag^+ / Ag) = + 0.80\text{V}$ ) and gold ( $E (Au^{3+} / Au) = +1.42 \text{ V}$ ) cannot displace hydrogen from acids because of their positive reduction potential value.

# FEASIBILITY OF A REDOX REACTION

- From the  $E^\circ$  values of the two electrodes one can find out whether a given redox reaction is feasible or not. A redox reaction is feasible only if the species which has higher potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidized i.e., loses electrons.
- The electrochemical series gives the increasing order of electrode potentials (reduction) of different electrodes on moving down the table. This means that the species, which accept the electrons (reduced) must be lower in the electrochemical series as compared to the other which is to lose electrons. (oxidized). For example,

# FEASIBILITY OF A REDOX REACTION

- From the electrochemical series  $E^\circ$  value of Cu = +0.34 V and that of Ag = +0.80 V since the reduction potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction occurs more readily than the reaction
- The reduction potential of copper is less than that of Ag, this means that copper will be oxidized or will go into solution as ions in comparison to Ag. Thus, the reaction, occurs more readily than Therefore, silver will be reduced and copper will be oxidized and the above reaction is not feasible. Rather the reverse reaction, can occur. Thus a metal will displace, any other metal, which occurs below it in the electrochemical series from its salt solution. When a metal having lower  $E^\circ$  value is placed in a solution, containing ions of another metal having higher  $E^\circ$  value, then the metal having lower  $E^\circ$  value gets dissolved and the ions of the metal having higher  $E^\circ$  value get precipitated.