



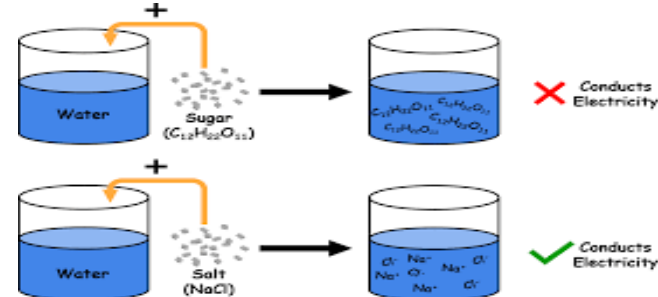
# Eighth Lecture

## Solution of Electrolyte

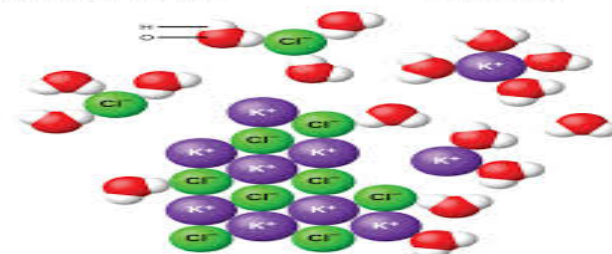
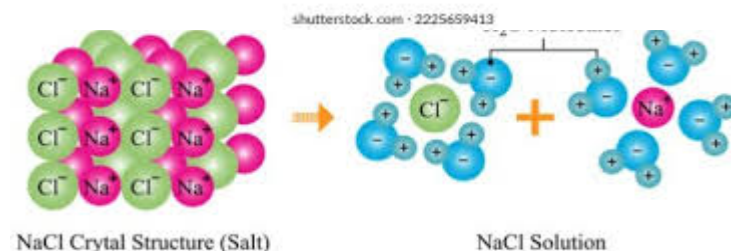
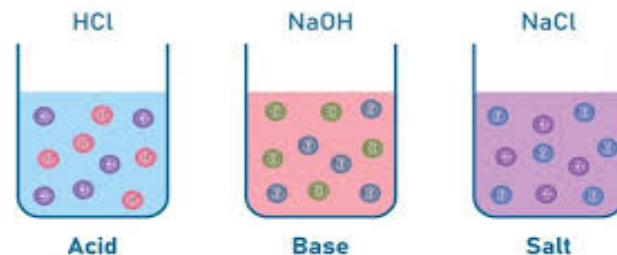
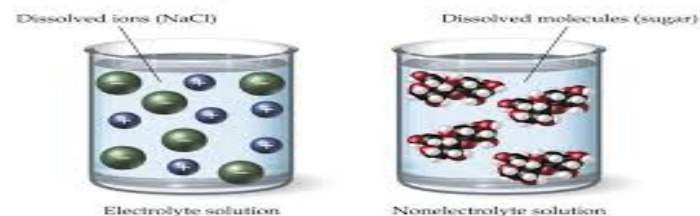
### 2022 - 2023

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester

Dr . Anmar Ghanim Taki Alaaraji

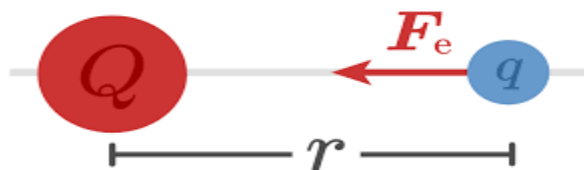


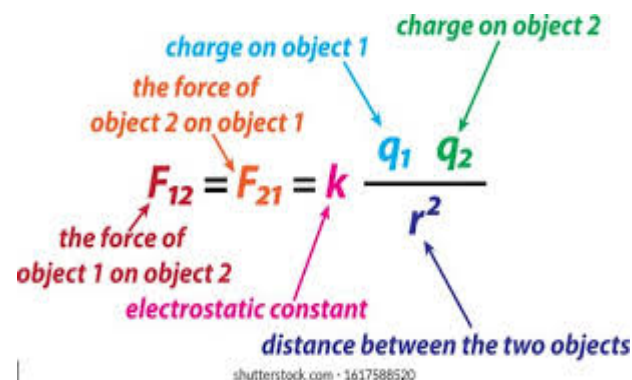
#### electrolyte VS nonelectrolyte



## Colligative Properties of Electrolyte Solutions

An electrolyte solution is a solution that generally contains *ions, atoms or molecules* that have *lost or gained* electrons, and is *electrically conductive*. For this reason they are often called *ionic solutions*, however there are some cases where the *electrolytes are not ions*. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that *opposite charges attract and like charges repel*. It also takes a great deal of force to overcome this electrostatic attraction. The general form of Coulomb's law describes the force of attraction between charges:




$$F_{12} = F_{21} = k \frac{q_1 q_2}{r^2}$$

## Electrolyte Solutions

A simple example of an electrolyte solution is sodium chloride in water. In the presence of water, solid sodium chloride dissociates as it is dissolved, forming an electrolyte solution:



Nonelectrolyte solutions are those in which the solute does not dissociate into ions when dissolved; sugar does not dissociate, for example. The number of moles of dissolved particles is greater for electrolyte solutions, so there will be a greater impact on colligative properties.

In an electrolyte solution, the number of dissolved particles is larger because the solute breaks apart into ions. The greater the number of ions, the larger the impact on colligative properties will be.

**Example**

Which would have the lowest vapor pressure at 25 °C?

- a) 0.1 M solution of NaCl
- b) 0.1 M solution of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (glucose)
- c) 0.1 M solution of Al(NO<sub>3</sub>)<sub>3</sub>**

The correct answer is c. All of the solutions have the same concentration, but when NaCl dissolves, it breaks into 2 particles. Glucose is a non-electrolyte and does not break apart. When Al(NO<sub>3</sub>)<sub>3</sub> dissolves, it produces 4 particles in solution (1 Al<sup>3+</sup> and 3 NO<sub>3</sub><sup>-</sup>), and will have the greatest impact on the vapor pressure.

**Difference between electronic & electrolytic conductors**

Electronic conductors	Electrolytic conductors
(1) Flow of electricity take place without the decomposition of substance.	(1)Flow of electricity takes place by the decomposition of the substance.
(2) Conduction is due to the flow of electron	(2) Flow of electricity is due to the movement of ions
(3) Conduction decreases with increase in temperature	(3) Conduction increases with increase in temperature

## Conductance

is the property of the conductor (metallic as well as electrolytic) which *facilitates* the flow of electricity through it. *It is equal to the reciprocal of resistance*

There are three kinds of conductance that we take into consideration:

1. Specific Conductance or Conductivity
2. Equivalent Conductance
3. Molar Conductance

## Specific conductance

is *an additive* property, if more than one electrolytes are present together *in a dilute solution*, the total specific conductance or conductivity is equal to the sum of specific conductances of individual electrolytes.

Specific conductance is reciprocal of specific resistance. It is denoted by the symbol  $\kappa$  (kappa) or  $L_s$

•The value of specific conductivity depends on two factors : *ionic concentration and speed of ions*.

the formula for specific conductance as shown:

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

where,  $R$ = Resistance,  $l$ = length and  $A$ = cross-sectional area,  $\rho$  is specific resistance

This equation can be modified in terms of cell constant. The ratio of specific conductance to that of conductance is called *the cell constant*.

the unit of specific conductance is  $\text{ohm}^{-1} \text{cm}^{-1}$  or  $\text{mhos cm}^{-1}$  or Siemens  $\text{cm}^{-1}$  or  $\text{S cm}^{-1}$ .



## Equivalent Conductance

The term “equivalent conductance” refers to the conductance (or “conducting power”) of all the ions (of a solution) created by dissolving one gram equivalent of an electrolyte in a specific solution.

We can state that an electrolytic solution’s conductance is influenced by *the ion concentration present in the solution*. It’s represented by the symbol  $\Lambda_e$ .

Equivalent Conductance Formula is as follows:

$$\Lambda_e = K \times V$$

Where,

$\Lambda_e$  = Equivalent Conductance,

K = Specific Conductance (Reciprocal of Specific Resistance),

V = Volume (in ml) of 1 gm-equivalent electrolyte.

Also,

$$\Lambda_e = (K \times 1000) / N$$

Where,

N = Normality

Unit of Equivalent Conductance is  $\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ .

## Molar Conductivity

is another term used to express the conductivities of the electrolytic solution. it is the conductance of an electrolyte measured after dissolving one gram mole in V cc of water.

Molar conductance is defined as the conductance of all ions produced by dissociation of 1 gram mole of an electrolyte dissolved in V cc of the solution when electrodes are 1 cm apart and the area of the electrode is so large that the whole solution is contained between them.

**It is denoted by  $\mu$**  and its value can be obtained by multiplying the specific conductance( $\kappa$ ) and volume(V in cc) containing one mole of the electrolytes as shown below:

$$\mu = \kappa \times V$$

where V= volume in  $\text{cm}^3$  containing 1 gram mole of an electrolyte.

If M be the concentration in gram moles per liter then, a volume containing 1 gram moles of electrolyte becomes  $(1000/M)$ . Therefore, using the value of  $V = 1000/M$ , the above equation becomes,

$$\mu = \kappa \times 1000/M$$

where M= number of moles of the electrolyte present in the 1000 cc of solution.

The unit of molar conductance:  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$

## Effect of dilution on specific conductance

If we *dilute* the solution the *specific conductance decreases*. On diluting the solution the concentration of ions per cc *decreases*. Hence the specific conductance *decreases*. *But the equivalent conductance and molar conductance increases* with *dilution*. This is *because* equivalent conductance and molar conductance *are the product of* specific conductance and the volume of the solution containing one gram-equivalent or one mole of the electrolyte respectively. With dilution specific conductance decreases *while volume increases*. The increase in the second factor is much more than the decrease in the first factor. Also on dilution more and more electrolyte dissociates into ions and hence equivalent conductance and molecular conductance *increases*

## The electrolytic or ionic conductivity depends on the following factors:

- 1 . The properties of the electrolyte which is added in the solution.
- 2 .The size of the ions that are produced in the process and their solvation capacity.
- 3 .The properties of the solvent and its resistance to change shape or mobility (viscosity).
- 4 .The electrolyte's concentration in the solution and temperature at which the solution is being made

## Types of substances based on electrical conductance

Based on electrical conductivity, the materials are divided into two types :

**1) Insulators:** The substances which resist the flow of electric current through them are called insulators. They do not have free electrons or freely moving charged particles.

Such as, Organic polymers (like plastics), glass, diamond, quartz etc.,

**2) Conductors:** The substances which allow the flow of electricity through them with little resistance, they are divided into:

**i) Metallic or electronic conductors:** The conductors which conduct the electricity through the electrons.

Such as, All metals, Graphite etc.

In case of metallic conductors;

\* No chemical reaction occurs during the conduction of electricity.

\* Conductivity *decreases with increase in temperature* due to vibrational disturbances.

**ii) Electrolytes:** The substances which furnish oppositely charged ions for the conduction of electricity.

Such as, NaCl, KCl, CH<sub>3</sub>COOH, HCl. etc.

In case of electrolytes;

- \* There is flow of ions towards the oppositely charged electrodes.
- \* During conduction of electricity through electrolytes, *oxidation occurs at anode* whereas *reduction occurs at cathode* i.e., a *chemical reaction occurs*.
- \* The conductivity *increases with increase in temperature* as the extent of *ionization increases*.

The electrolytes undergo dissociation to provide ions either in *molten state or in aqueous solutions*. Depending on the extent of ionization (or dissociation) in water, the electrolytes are further divided into:

**a) Strong electrolytes:** *Undergo complete ionization in water.*

Such as, NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, NaNO<sub>3</sub> etc.

**b) Weak electrolytes:** *Undergo partial ionization in water.*

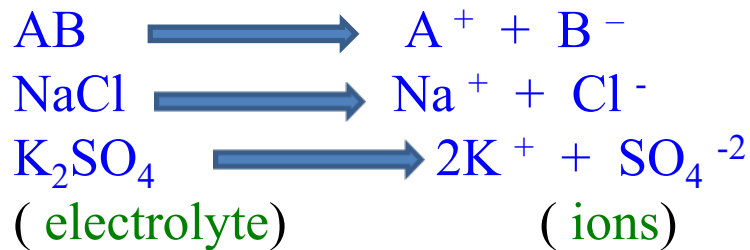
Such as, HF, CH<sub>3</sub>COOH, NH<sub>4</sub>OH, HCOOH etc.

**Non-electrolytes:** The substances which do not provide ions for electrical conduction are called non-electrolytes.

Such as, urea, glucose, sucrose etc.



- An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called *ions*. Positively charged ions are termed *cations* and negatively charged as *anions*.



In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

The process of splitting of the molecules into ions of an electrolyte is called *ionization*. The fraction of the total number of molecules present in solution as ions is known as *degree of ionization* or  $\alpha$ . It is denoted by

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

It has been observed that all electrolytes **do not** ionize *to the same extent*.

Some are almost *completely ionized* while others are *weak ionized*. The degree of ionization depends on a number of factors.

-Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized the ionized and non-ionised molecules, i.e.,  $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$

Applying the law of mass action to above equilibrium  $K = [\text{A}^+][\text{B}^-] / [\text{AB}]$

K is known as ionization constant. *The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes*

When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards **cathode** and the negative ions (anions) move towards **anode** and get discharged, i.e., *electrolysis occurs*.

The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

-The electrolytic solutions is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$	$\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$	(Both ions are equal)
$\text{AB}_2 \rightleftharpoons \text{A}^{2+} + 2\text{B}^-$	$\text{BaCl}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{Cl}^-$	(Anions are double that of cations)
$\text{A}_2\text{B} \rightleftharpoons 2\text{A}^+ + \text{B}^{2-}$	$\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-}$	(Cations are double that of anions)

## Colligative properties are depending on following factors

(1) Colligative properties (\*Number of particles)

\*Number of molecules(*in case of non-electrolytes*)

\*Number of ions(*In case of electrolytes*)

\*Number of moles of solute(*Mole fraction of solute*)

(2) For *different solutes of same molar concentration*, the magnitude of the colligative properties is *more* for that solution which gives more number of particles on ionisation.

(3) For *different solutions* of same molar concentration of different non-electrolyte solutes, the magnitude of the colligative properties will be *same for all*.

(4) For different molar concentrations of the same solute, the magnitude of colligative properties is *more for the more concentrated solution*.

(5) For solutions of different solutes but of same percent strength, the magnitude of colligative property is *more for the solute with least molecular weight*.





# Fifth Lecture

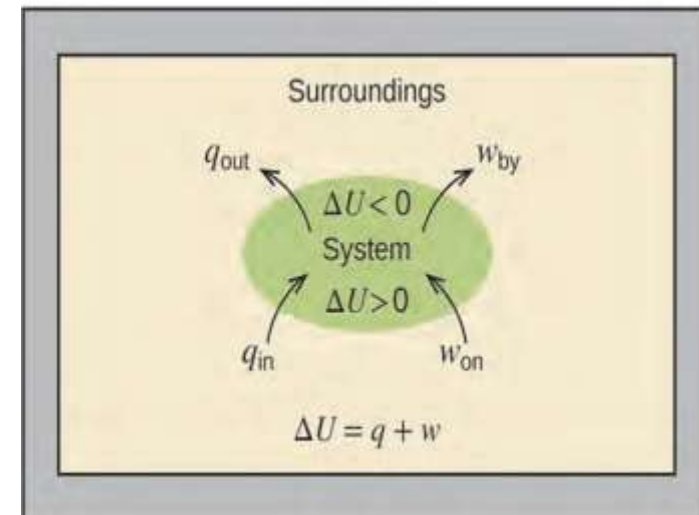
## Thermodynamic II

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester

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	$+\Delta S$	$-\Delta S$
$+\Delta H$	 <b>T</b>	<b>Non</b>
$-\Delta H$	<b>Spon</b>	 <b>T</b>

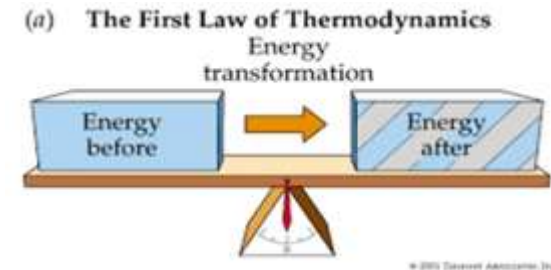
$$\Delta G = \Delta H - T\Delta S$$



# Thermodynamic laws

**First Law:** Energy is Conserved; It cannot be created or destroyed

- the change in internal energy of the gas  
= the heat *absorbed* by the gas *minus* the work done *by* the gas or *plus* the work done *on* the gas



- The *change* in internal energy is  $\Delta U = U_{final} - U_{initial}$
- Then, the 1<sup>st</sup> Law requires:  $\Delta U = Q - W$ , or  $\Delta U = Q + W$   
where Q is the heat absorbed *by* the gas, and W is the work done *by* the gas.
- The 1<sup>st</sup> Law of Thermodynamics is a statement of *conservation of energy*

**TABLE 15–1 Simple Thermodynamic Processes and the First Law**

Process	What is constant:	The first law, $\Delta U = Q - W$ , predicts:
Isothermal	$T = \text{constant}$	$\Delta T = 0$ makes $\Delta U = 0$ , so $Q = W$
Isobaric	$P = \text{constant}$	$Q = \Delta U + W = \Delta U + P \Delta V$
Isovolumetric	$V = \text{constant}$	$\Delta V = 0$ makes $W = 0$ , so $Q = \Delta U$
Adiabatic	$Q = 0$	$\Delta U = -W$



- **Internal Energy ( E or U )** – is the sum of all kinetic and potential energy of all components of the system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- A **positive value** of  $\Delta E$  results when

$E_{\text{final}} > E_{\text{initial}}$ , indicating the system **gained energy**

A **negative value** of  $\Delta E$  results when

$E_{\text{final}} < E_{\text{initial}}$ , indicating the system **lost energy**

- In a chemical reaction, the initial state of the system refers to the *reactants* and the final state to the *products*
- We can analyze the  $\Delta E$  gained or lost in a system by examining the processes that cause the changes to the system

- The internal energy of a system can change in two general ways
  - *As heat or as work*
- When a system undergoes any chemical or physical change, the accompanying change in internal energy is given by:

$$\Delta E = q + w$$

$q > 0$ : Heat is transferred from the surrounding to the system

$q < 0$ : Heat is transferred from the system to the surrounding

$w > 0$ : Work is done by the surroundings on the system

$w < 0$ : Work is done by the system on the surroundings

\*Calculate the change in the internal energy of the system for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings

$$E = q + W = 140\text{J} - 85\text{J} = 55\text{J}$$

**Second Law:** In isolated processes, natural processes are **spontaneous** when they lead to an increase in entropy

**Two statements** of the 2<sup>nd</sup> law which can be shown to be equivalent:

- (**Kelvin**) It is **impossible** to have a heat engine that is 100 % efficient.

→ Not all of the heat taken in by the engine can be converted to work

- (**Clausius**) In a spontaneous process, heat flows from a **hot** to a **cold** substance

→ Work must be done to move heat from a cold to a hot substance.

- **Entropy** is a measure of **disorder/randomness** in a **closed** system

**Disorder increases; entropy increases.**

The change in entropy  $S$  when an amount of heat  $Q$  is added:  $\Delta S = \frac{Q}{T}$ ,

Another statement of the second law of thermodynamics

The total entropy of an isolated system never decreases.

The second law of thermodynamics is a statement about which **processes occur and which do not**. There are many ways to state the second law; here is one:

Heat can flow spontaneously from a *hot* object to a *cold* object; it will not flow spontaneously from a cold object to a hot object.

$$S_f = S_i \text{ (reversible)} \quad . \quad S_f > S_i \text{ (irreversible)}$$

**Third Law:** When the system approaches *absolute zero* temperature, all processes *stop* and the entropy of the system approaches the *lowest possible value* , *No system can reach absolute zero*

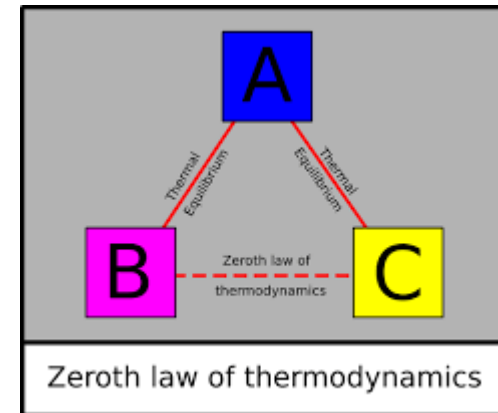
The third law of thermodynamics states that *the entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.*

Entropy, denoted by 'S', ... As per the third law of thermodynamics, the entropy of such a system is exactly zero.

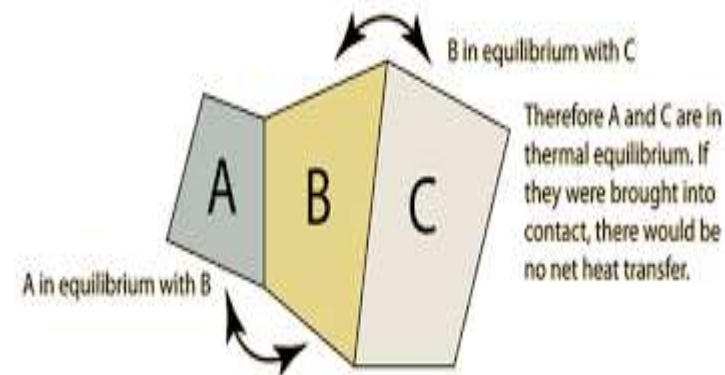
There is no formula associated with the 3rd Law of Thermodynamics

**Example** Steam/vapours of water are the gaseous *forms of water* at high temperature. The molecules within the steam move randomly. Therefore, it has high entropy. If these vapors set for cooling this steam to below 100 degrees Celsius it will get *transformed into water*, where the movement of the molecules will be *restricted* resulting in a *decrease in entropy*.

**Zeroth Law** :The "zeroth law" states that two thermodynamic systems in thermal equilibrium with the same environment are *in thermal equilibrium with each other*.



Zeroth's Law of Thermodynamic states that when body '**A**' is *in thermal equilibrium* with body '**B**' and also separately with body '**C**' then B and C will be in thermal equilibrium with each other. (or) If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.





**Enthalpy** The energy absorbed as heat during a chemical reaction at constant pressure (*very few occur at constant volume*) is represented by  $\Delta H$ .

- $H$  is the symbol for a quantity called *enthalpy*.

$$\Delta H = q_p$$

- Enthalpy (meaning to warm): is the heat
- that is transferred under constant pressure

$$\Delta H = H_{final} - H_{initial} = q_p$$

$Q_p$  = heat *gained* or *lost* by the system when the process occurs under *constant pressure*

The chemical reaction is the system by the value of the enthalpy, we know whether the reaction is endothermic or exothermic

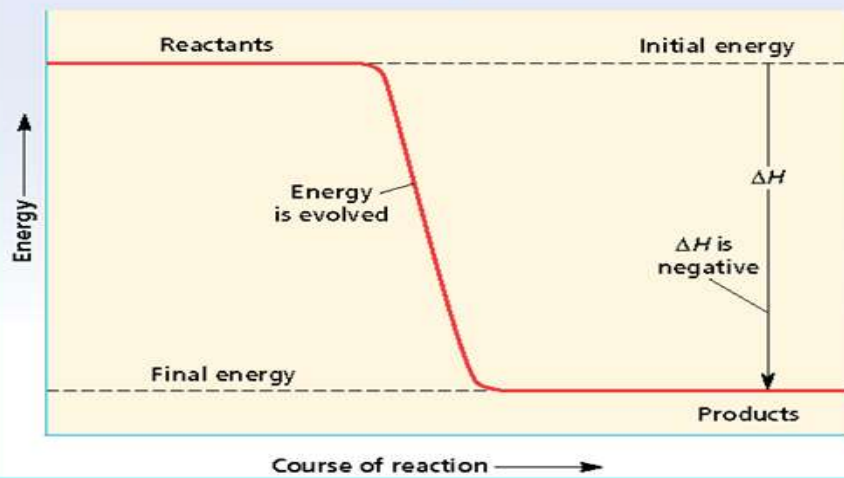
$\Delta H = +ve$                       **endothermic**

$\Delta H = -ve$                       **exothermic**

► Energy is *stored in bonds* between atoms

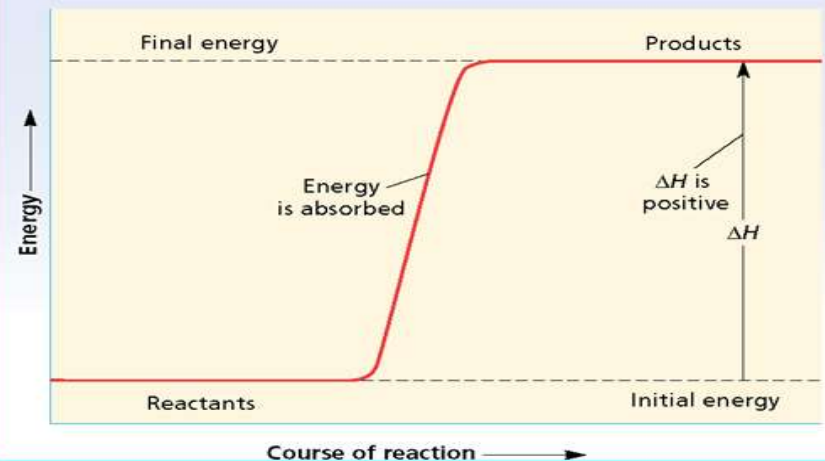


### Exothermic Reaction Pathway



- In an exothermic reaction, energy is **released**, during the reaction;  $\Delta H$  is **negative**.
- ▶ Exothermic - Heat flowing
- ▶ **out of** a system into its surroundings
  - System gets colder but the surroundings get warmer
  - q has a **negative** value  
 $\Delta H < 0$  Exothermic

### Endothermic Reaction Pathway



- In an endothermic reaction, energy is **absorbed**; in this case,  $\Delta H$  is designated as **positive**.
- ▶ Endothermic – Heat flowing **into** a system from its surroundings
  - Surroundings get cooler but the system gets warmer
  - q has a **positive** value  
 $\Delta H > 0$  Endothermic

# Thermochemistry

Studies the relationships between **energy** or **heat** changes(**surroundings**) that occur during chemical reactions and **physical changes** of state(**system**) .

Essentially **all** chemical reactions and changes in physical state involve either: **release** of heat, or **absorption** of heat

## The Flow of Energy

- **Energy** is the capacity to do **work** or supply **heat**.
- Energy has no **mass** or **volume**.
- **Chemical potential energy** is energy stored in **bonds** between atoms .
- The kinds of **atoms** and the **arrangement** of the atoms in a substance determine the amount of **energy** stored in the substance.

## Heat

- **Heat** is a form of **energy** that always **flows** from a **warmer** object to a **cooler** object.
- Heat is represented by **q**.

**Spontaneous process** is any physical or chemical process that can occur on its own without the influence of any external factor. Cold, the melting of a piece of sugar in tea, iron rusting, the reaction of sodium with water

## Entropy

is a thermodynamic function that is a measure of regularity and irregularity

$$\Delta S = S_f - S_i$$

$$\Delta S = +ve$$



Low Entropy



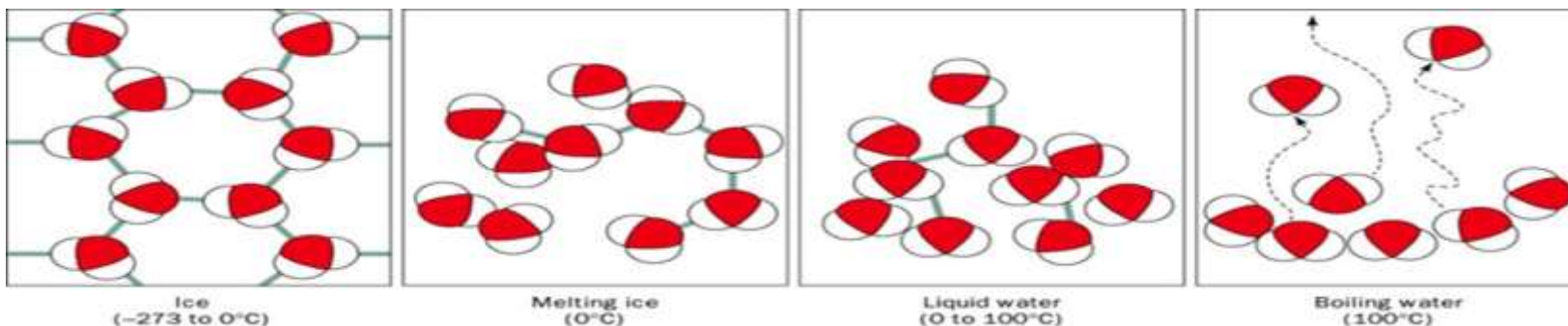
High Entropy

Examples of solid melting, melting, evaporation, heating....

$$\Delta S = -ve$$

Examples of gases dissolving in a solvent, freezing, condensation...

$$\Delta S = +ve$$



# Gibbs Free Energy

Gibbs free energy is a measure of chemical energy . All chemical systems tend naturally toward states of minimum Gibbs free energy

$$G = H - TS$$

Where: G = Gibbs Free Energy , H = Enthalpy (heat content)

T = Temperature in Kelvins , S = Entropy

The Gibbs free energy is a thermodynamic function that gives us a prediction of the spontaneity of physical and chemical processes and represents the maximum energy that can be obtained from measuring the change in enthalpy and entropy

$\Delta G = +ve$  The reaction is not spontaneous

$\Delta G = -ve$  The reaction is spontaneous

$\Delta G = 0$  The reaction is in equilibrium

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

The diagram shows the equation  $\Delta G = \Delta H - T\Delta S$  with three arrows pointing to the  $T\Delta S$  term. The arrows originate from three boxes below:  $T\Delta S_{total}$ ,  $T\Delta S_{surr}$ , and  $T\Delta S_{system}$ .

Applications of the Gibbs Free Energy equation show the direction of chemical reactions , there are two factors that affect the spontaneity of the reaction, according to the relationship:  $\Delta G = \Delta H - T\Delta S$



**First** : the reaction tend to the state in which the energy is the least possible and spontaneity is more likely if  $\Delta H$  is negative.

**Second** : the reaction tend to the state in which the entropy is highest and spontaneity is more likely if  $\Delta S$  is negative

The change in some property, such as G for a reaction of the type:



$$\begin{aligned}\Delta G &= \Sigma (n G)_{\text{products}} - \Sigma (n G)_{\text{reactants}} \\ &= G_C + 4G_D - 2G_A - 3G_B\end{aligned}$$

### *Example*

$\Delta H$  and  $\Delta S$  for transition from liquid water to ice at  $-10^\circ\text{C}$  and 1atm. Pressure are  $-1343$  cal/mole and  $-4.91$  cal/mol.deg. respectively, compute  $\Delta G$  for The phase change at this temperature ?

$$T = (-10 + 273.16) = 263.2 \text{ K}, \Delta G = \Delta H - T\Delta S$$

$$\Delta G = -1343 - (263.2\text{K}) \times (-4.91) = -51 \text{ cal/mole.}$$

The process is spontaneous ( $\Delta G = -Ve$ )

### H . W 13 What are the differences between heat and temperature?

Heat is a form of energy. It is measured in Joules. ... The temperature of an object relates to both the kinetic energy of its particles and the number of particles.

Temperature is the average kinetic energy of the particles in a substance and is measured in Celsius ( $^{\circ}\text{C}$ ), Kelvin(K), Fahrenheit ( $^{\circ}\text{F}$ ),

### H . W 14 : Internal energy of an ideal gas depends on:

- i. the volume of the ideal gas
- ii. the pressure of the ideal gas
- iii. the absolute temperature of the ideal gas

(A) I (B) II (C) III (D) I and II (E) I, II and III

### H . W 15 : Which of the following is a characteristic of an adiabatic process?

(A)  $\Delta U = 0$        $W = 0$        $Q = 0$        $\Delta V = 0$        $\Delta P = 0$

### H W:16 When heat is added to a system, the amount of heat added can

- a. decrease the temperature, decrease internal energy, and do no external work.
- b. increase the temperature, increase internal energy, and do external work.
- c. increase the temperature, decrease internal energy, and do external work.
- d. decrease the temperature, increase internal energy, and do no external work.

**H . W 17 : Circle the correct answer.**

1. When the angle of contact between a solid and a liquid is  $90^\circ$ , then
  - (a) Cohesive force  $>$  Adhesive force
  - (b) Cohesive force  $<$  Adhesive force
  - (c) Cohesive force = Adhesive force**
  - (d) Cohesive force  $\gg$  Adhesive force
  
- 2 . An isolated system is best described by which one of the following statements?
  - (a) Neither matter nor heat can pass into or out of the system**
  - (b) The system has a boundary which allows heat to be transferred but does not allow material to pass into or out of the system
  - (c) The system has a diathermic boundary
  - (d) A system which has reached thermal equilibrium with its surroundings
  
- 3 . Which one of the following statements describes a path function?
  - (a) A property of a system that depends only on the current state of the system, not on the path the system took to reach that state
  - (b) A property of a system that depends on the path taken between the initial and final states**
  - (c) The sum of kinetic and potential energy contained in a substance
  - (d) The heat energy absorbed by a system at constant pressure

4 . Consider the following thermodynamic properties.

- i) work done on a system                      ii) heat absorbed
- iii) entropy                                      iv) enthalpy

Which of these properties are state functions?

- (a) i) and ii) only
- (b) i) and iii) only
- (c) i) only
- (d) iii) and iv) only

5 . Which of the following statements best describes the Second Law of Thermodynamics?

- (a) The internal energy of the universe is constant.
- (b) Energy can be neither created nor destroyed.
- (c) When an isolated system undergoes a spontaneous change, the entropy of the system will increase.
- (d) At absolute zero, the entropy of a perfect crystal is considered to be zero.

6 . Which one of the following equations defines the enthalpy of reaction,  $\Delta H$ , for a reaction occurring at constant pressure that does expansion work? All terms have their usual meanings.

- (a)  $\Delta H = \Delta U$
- (b)  $\Delta H = \Delta U + p\Delta V$
- (c)  $\Delta H = \Delta G - T\Delta S$
- (d)  $\Delta H = q + w$

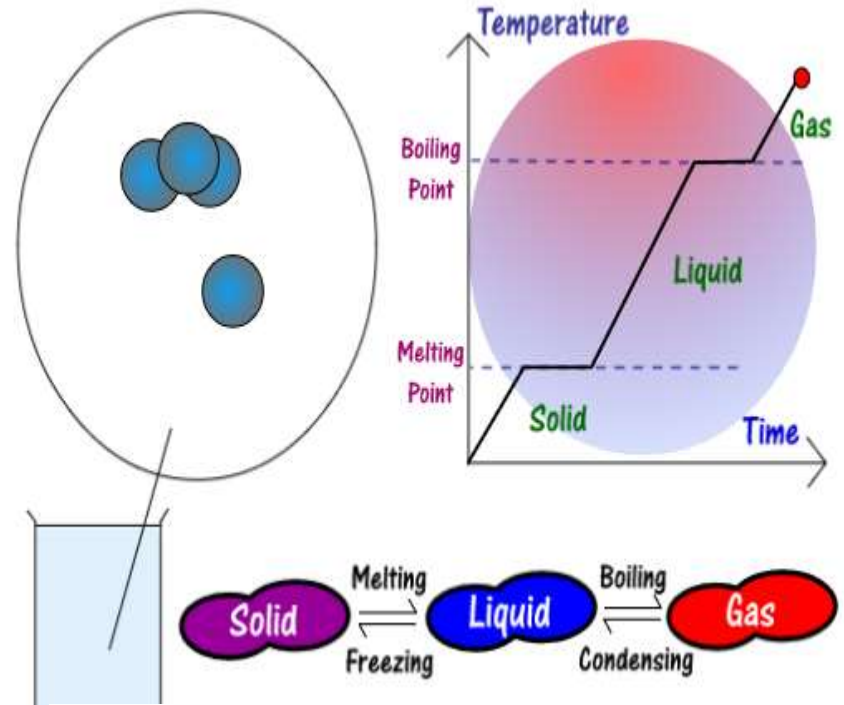


# First Lecture

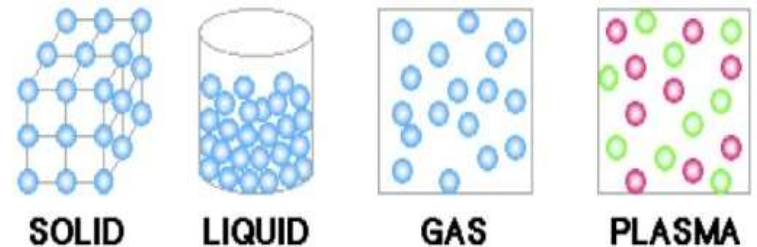
## States of Matter

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester  
2022 - 2023

Dr . Anmar Ghanim Taki Alaaraj



### States of Matter



**Matter** Anything made of particles. It has mass and volume (takes up space).

\*Matter is made up of particles, which called atoms

\*Atoms of a substance are *always moving*, even if only slightly

\*Everything that you interact with every day is made up of atoms

- When you *add* or *subtract* **heat** from a substance, you can change its *state of matter*. The state of matter of a substance is determined by how much energy its particles have.

- Both atoms and molecules are held together by a form of *potential energy* called *chemical energy*

## In chemistry

- **The Study of Matter**

- Structure → what it's made of
- Properties → how it behaves
- Changes → how and why it changes

## States of matter

### State

### Description

Solid

particles vibrate in *a fixed position*, so the solid has a *definite shape and volume*. Volumes of solids do not vary much with changes in temperature. In crystalline solids the particles occupy definite positions in the crystal structure.

Liquid

particles are moving fast enough to have enough energy to *slide past one another*, so the liquid *takes the shape of its container*. They are very hard to compress.

Gas

the particles are moving so quickly that they have enough energy to *move freely away from other particles*. This causes the particles to take up as much space as possible, spreading out *to fill any container*.

Plasma

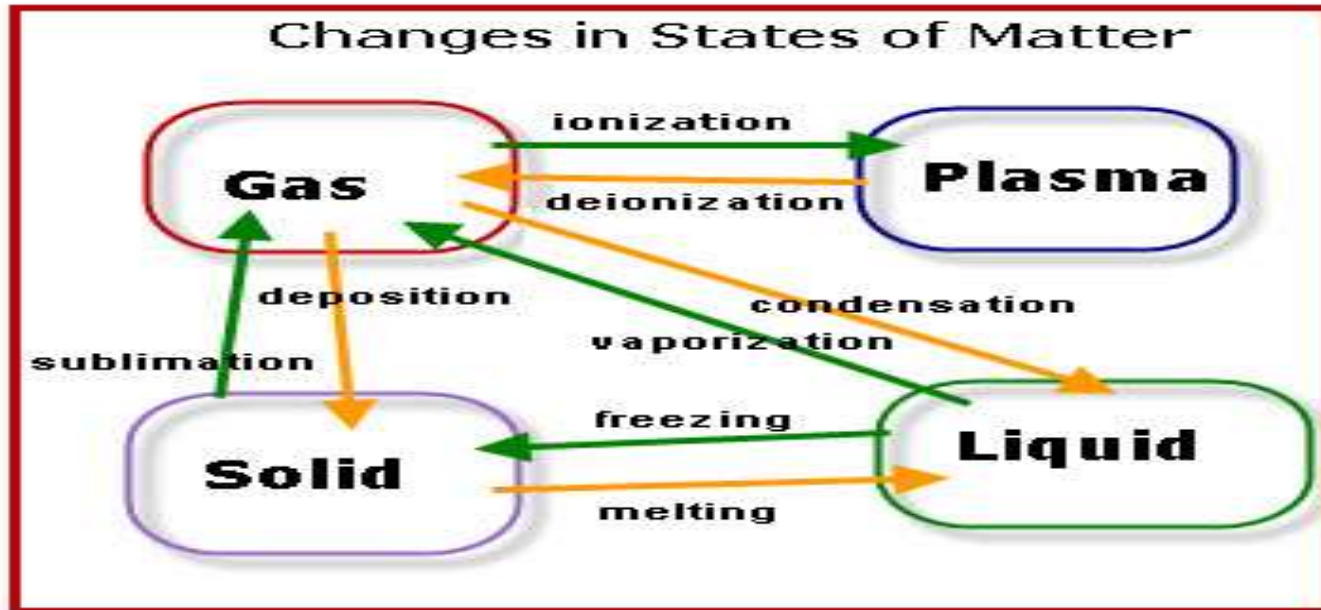
Occurs at very high temperatures and is found in fluorescent light bulbs, the atmosphere, and lightning strikes, like gases *have an indefinite shape and volume*, it is a *mixture of + and – charged particles* and a *very good conductor of electricity*. It is sometimes referred to as the *fourth state of matter*, distinct from the solid, liquid, and gaseous *states*.

# The Four States of Matter

## Basis of Classification of the Four Types :

- Based upon particle arrangement , energy of particles , distance between particles

## Changes in states of matter



- The fundamental difference between states of matter is *the strength of the intermolecular forces of attraction*.
- Stronger forces bring molecules closer together.
- Solids and liquids are referred to as the *condensed phases*.



## Matter Change

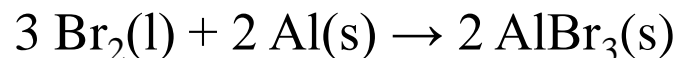
A **physical change** occurs with no change in chemical composition. e.g.: boiling, melting, vaporization. . . Physical properties altered significantly as matter undergoes physical changes.

### Chemical properties

They are exhibited by matter as it undergoes changes in composition:

Acidity , redox properties , reactivity. . .

Chemical changes are transformations in which substances are converted into other substances. e.g.: burning, decomposition , formation



**Extensive properties:** dependent of the quantity of material in the system.

mass, volume, total energy.

**Intensive properties:** independent of the quantity of material. density, pressure, temperature

#### Independent of amount

- Melting point
- Boiling point
- Color
- Density
- Solubility
- Odor
- Texture

#### Dependent on amount

- Shape
- Length
- Mass
- Volume
- Weight

## Differences between Intensive and Extensive Properties

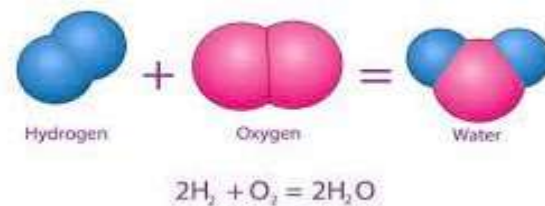
### Difference between Intensive and Extensive properties

INTENSIVE	EXTENSIVE
Independent property	Dependent property
Size does not change	Size changes
It cannot be computed	It can be computed
Can be easily identified	Cannot be easily identified
<i>Example:</i> melting point, colour, ductility, conductivity, pressure, boiling point, luster, freezing point, odour, density, etc	<i>Example:</i> length, mass, weight, volume

## atoms and molecules

A tiny particle of a chemical element is called an **atom**, which may or may not exist independently.

**Molecules** refer to the group of atoms that the bond binds together, representing the smallest unit in a compound.



## Classification of matter

**Solution** is a special type of homogeneous mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent.

**Substance:** is matter which has a specific composition and specific properties. Every pure element is a substance. Every pure compound is a substance.

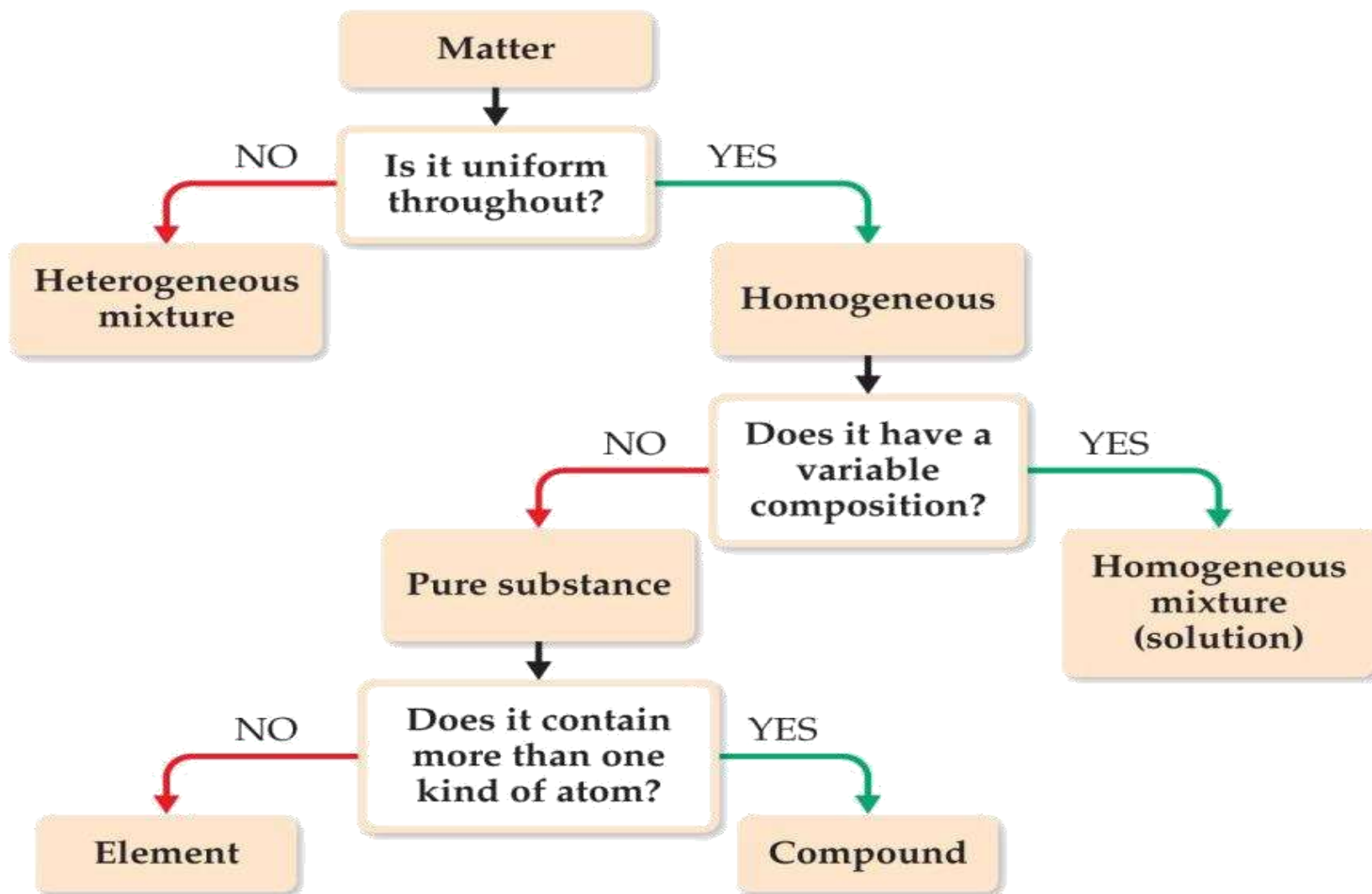
**Elements:** cannot be decomposed into simpler substances by chemical changes.

**Compounds:** can be decomposed into simpler substances by chemical changes, always in a definite ratio.

**Mixtures:** Variable composition. Components retain their characteristic properties. May be separated into pure substances by physical methods (e.g. distillation).

**Homogeneous mixtures:** components are indistinguishable; have same composition (e.g. solutions, alloys).

**Heterogeneous mixtures:** components are distinguishable; do not have same composition (e.g. muddy river water)



## *Changing the state of matter:*

1. freezing point = liquid → solid
2. boiling point = liquid → gas
3. melting point = solid → liquid
4. evaporation (vaporization) = liquid changes to a gas gradually at temperatures below the boiling point
  - a. can occur at any temperature
  - b. much slower than boiling
  - c. considered a cooling process
5. condensation = when a gas changes to a liquid
  - a. gas will condense when cooled to its boiling point or below
  - b. can occur when gas comes in contact with a cool surface
  - c. occurs at the condensation point
  - d. considered a warming process
6. sublimation = solid changes directly into a gas without going through the liquid phase  
Ex: dry ice
7. deposition = gas or vapor changes directly into solid without changing to a liquid  
Ex: frost

## H . W 1 circle only one correct answer .

1. When a thermometer is heated, the red liquid inside the thermometer moves up.

This is mainly because:

- a) The red liquid is thin.
- b) The molecules of the liquid move faster and get a little further apart
- c) Hot liquid is lighter
- d) The glass of the thermometer gets hot

2. Particles of matter have following characteristics:

- a) They constantly move
- b) They attract each other
- c) They are very small
- d) All of the above

3. Which of the following is a property of diffusion?

- a) Slowest in liquids
- b) Fastest in gases
- c) Based on motion of particles
- d) All of the above

## H . W 2 Circle all the correct answers.

1 . To describe a liquid, you could say:

- a) The particles of a liquid are attracted to one another
- b) The particles of a liquid are in motion
- c) The particles of a liquid are able to move past one another
- d) A liquid has mass and takes up space

2. To describe a solid, you could say:

- a) The particles of a solid are attracted to each other
- b) The particles of a solid can move past one another
- c) The particles of a solid vibrate but do not move past one another
- d) A solid has mass and takes up space

3. To describe a gas, you could say:

- a) The particles are very attracted to each other
- b) The particles are not very attracted to each other
- c) The particles are close together like a liquid
- d) The particles of a gas are further apart than the particles in a liquid or solid



## Bonding between atoms

Atoms will position themselves so that the system will achieve the lowest possible energy.

- bond: forces that hold one atom to another in a compound
- To break a bond **requires energy** to be put in to overcome the forces of attraction
- *Bond breaking is **endothermic**.*
- To make bonds **causes a release of energy**.
- *Bond making is **exothermic**.*
- Compounds have less energy (**more stable**) than the substances from which they form.
- Ex: water has less energy than the hydrogen and oxygen from which it formed.
- The energy stored in a bond is **potential**.
- There are four types of bonds (ionic , covalent , coordinate and metallic bond )

## Energy and Changes to Matter

**Exothermic Change:**  $A + B \rightarrow C + D + \text{energy}$

- Energy is released or “ex”its

**Endothermic Change:**  $A + B + \text{energy} \rightarrow C + D$

- Energy is absorbed or “en”ters

## Energy During Phase Changes

**Solid**  **Liquid, Liquid**  **Gas**

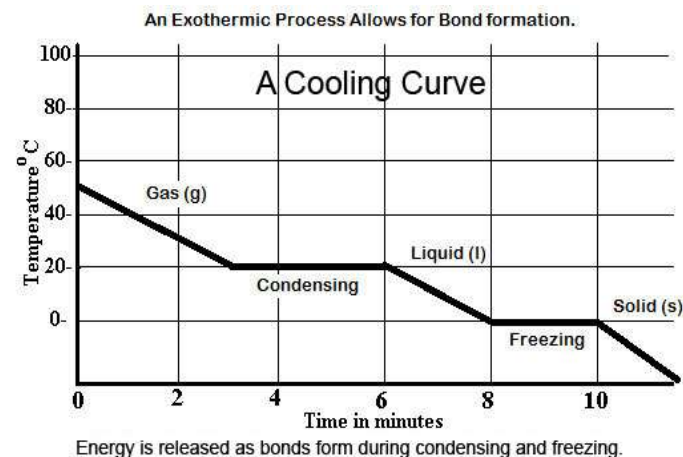
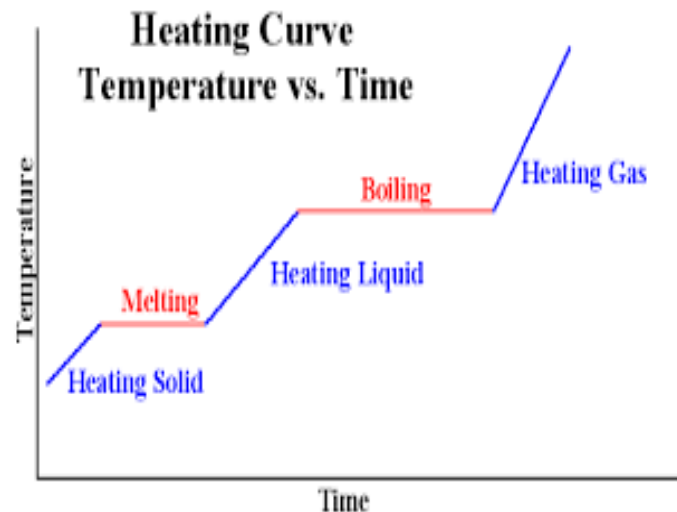
- Endothermic

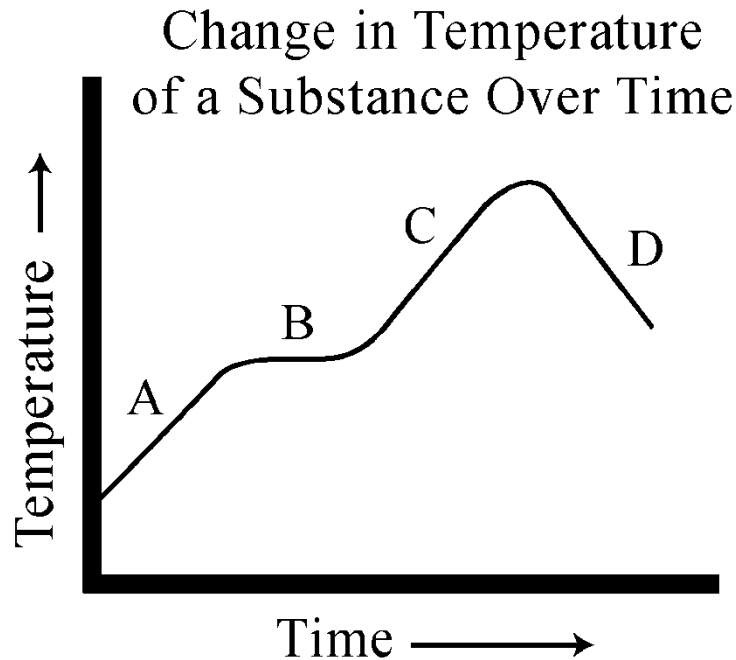
- Energy is absorbed and overcomes attractive forces between particles

**Gas**  **Liquid, Liquid**  **Solid**

- Exothermic

- As particles come closer together energy is released





In the figure above shows how the temperature of a substance changed as it was heated. Which segment of the graph indicates that the substance was undergoing a change of state?

- a) A
- b) B
- c) C
- d) D

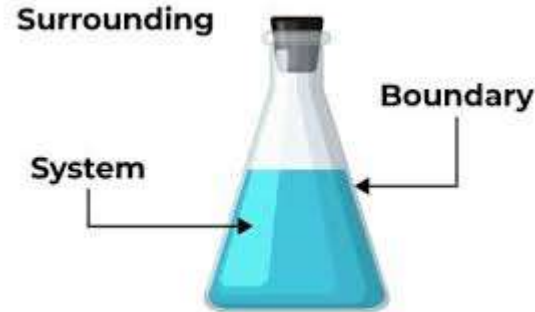


# Forth Lecture

## Thermodynamic 1

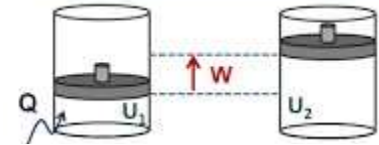
Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester

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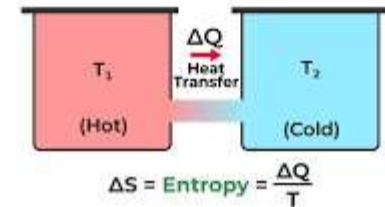


### First Law of Thermodynamics

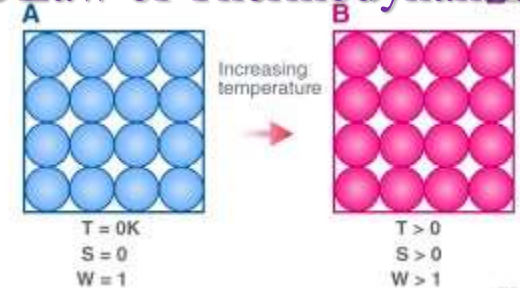
$$Q = (U_1 - U_2) + W$$



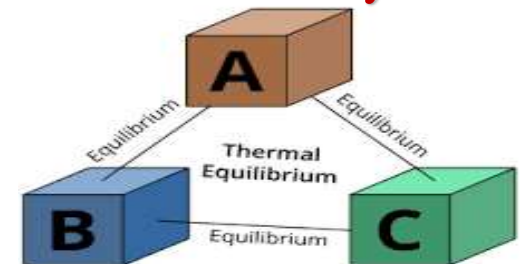
### Second Law of Thermodynamics



### Third Law of Thermodynamic



### Zeroth Law of Thermodynamic



Zeroth law of Thermodynamics

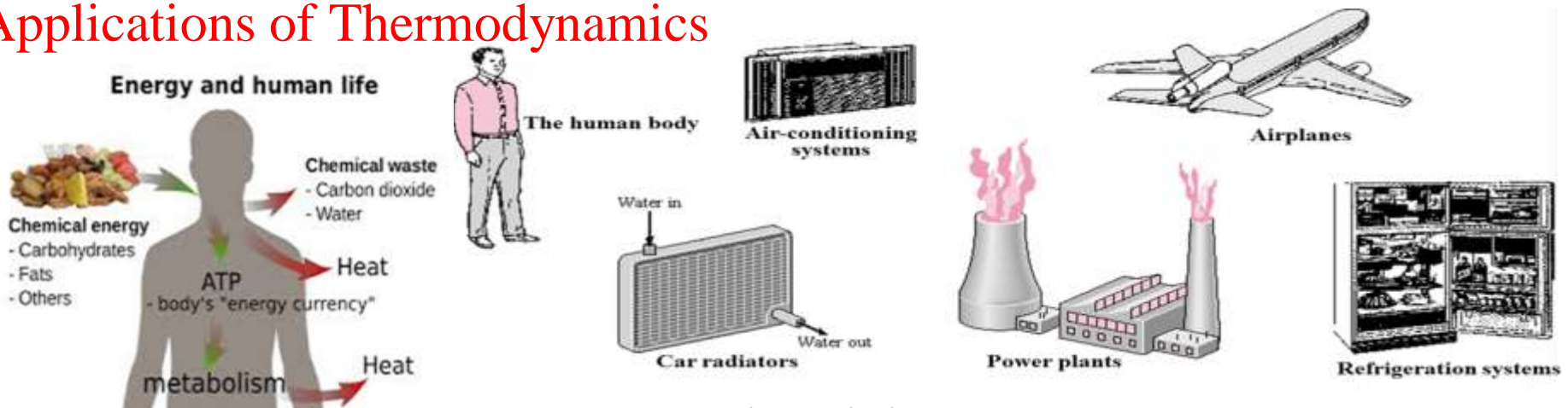
Thermodynamics is an **experimental** science concerned with the study of everything related to temperature and thermal energy.

Thermodynamics is used in many branches of science such as medicine, pharmacy, physics, chemistry and engineering applications in the design of engines, electric power generators, refrigeration and air conditioning devices, and this science enters into various industrial applications, the science dealing with *heat, work and energy*

## Thermodynamics:

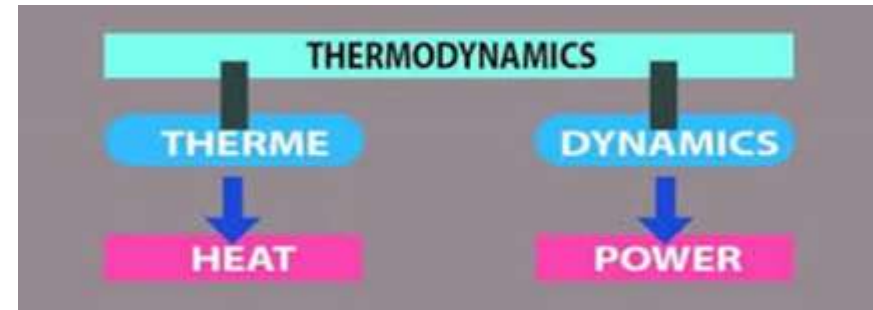
- Describes macroscopic properties of equilibrium systems
- Entirely Empirical
- Built on 4 Laws and “simple” mathematics

## Applications of Thermodynamics



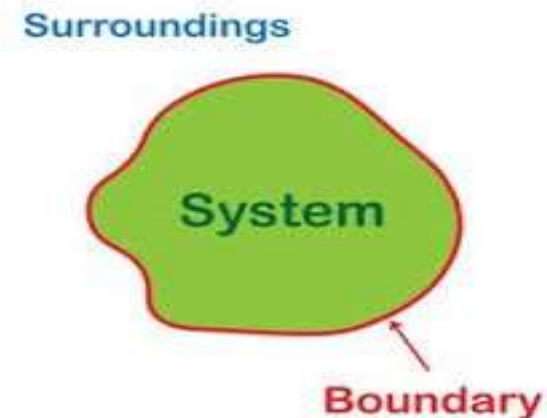
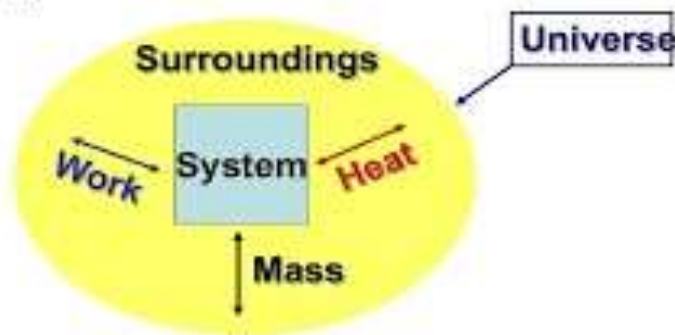
# The laws of thermodynamics

- 0th Law  $\Rightarrow$  Defines Temperature (T)
- 1 st Law  $\Rightarrow$  Defines Energy (U or E)
- 2nd Law  $\Rightarrow$  Defines Entropy (S)
- 3rd Law  $\Rightarrow$  Gives Numerical Value to Entropy



Important terms in the science of thermodynamics that every science and every discipline has its basic concepts, and these concepts are the language that we will use to explain the topics of this science, and these terms include the following:

system	is the specific part of the material to which the study is directed
Surrounding	is the part that surrounds the system and exchanges energy or matter with it
The universe	is both the system and the surrounding



- **The Internal Energy** (U or E) : is *the energy contained within it*. It is the sum of the *kinetic energies* of all of its constituents . It is also includes the energy in all the chemical bonds.

$$\Delta E = q + W$$

Where

- U is the change in internal energy of a system during a process
  - q is the heat
  - W is the mechanical work.
- 
- **Temperature** (T) of a system is a measure of the *average kinetic energy* of its constituents
  - **Heat** (Q) is the energy that is transferred from one system to another because they are initially at *different temperatures*; when the systems reach a common temperature, the flow of heat stops



**Work** In thermodynamics, performed by a system is the energy transferred by the system to its surroundings. *Work is a form of energy*. It is a process done *by or on* a system. In general, work is defined for mechanical systems as the action of a force on an object through a distance.

$$W = F \cdot d$$

where:  $W$  = work (J) ,  $F$  = force (N) ,  $d$  = displacement (m)

### **$p\Delta V$ Work**

Pressure-volume work (or  **$p\Delta V$  Work**) occurs when the volume  $V$  of a system *changes*. The  **$p\Delta V$  Work** is equal to the area under the process curve plotted on the pressure-volume diagram. It is known also as the *boundary work*.

Work must be a *positive* quantity if the system *does it*, and work is a *negative* quantity if work is *done on* the system

## state and path function in thermodynamic

Both path and state functions are often encountered in thermodynamics.

### state functions

A state function is *a property whose value does not depend on the path taken to reach that specific value*. Examples of state functions include density, internal energy, enthalpy, entropy. Such a relation cannot be written for path functions, especially since these cannot be defined for the limiting states. Path functions depend on the route taken between two states. Two examples of path functions are *heat and work*.

### path function

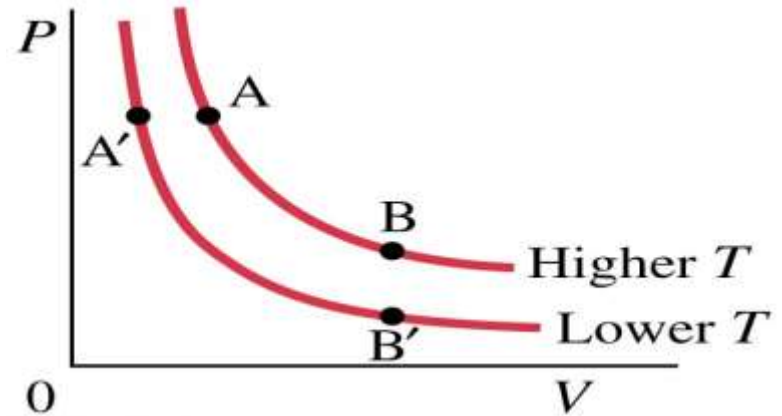
Functions that *depend on the path from two values* are call path functions. Two important examples of a path function are **heat and work**. These two functions are dependent on how the thermodynamic system changes from the *initial state to final state*.

These two functions are introduced by the equation  $\Delta U$  which represents the change in the internal energy of a system.

**Process** : is any change in a system that results in a change in pressure, temperature, or volume (thermodynamic coordinates).

**Isothermal process** : it is the process in which the change is under a *constant temperature*

An isothermal process is one where the temperature *does not change*.

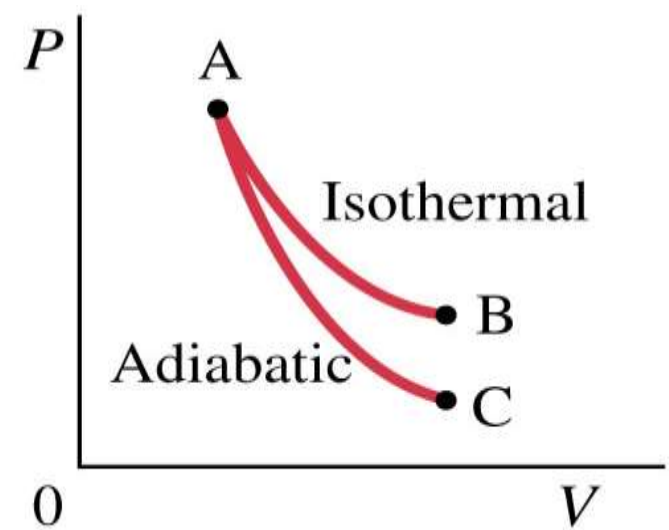


In order for an isothermal process to take place, we assume the system is in contact with a heat reservoir.

In general, we assume that the system remains *in equilibrium* throughout all processes.

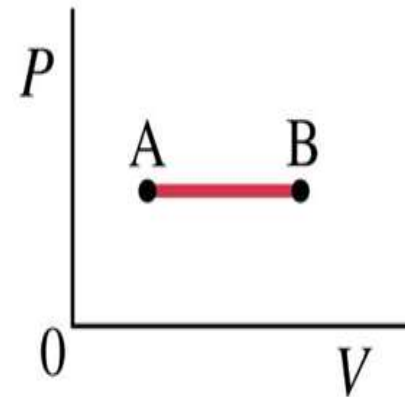
**Adiabatic process** : It is the process in which there is *no change in the amount of heat and takes place in an isolated system*, i.e. there is no *heat transfer to or from* the system.

An adiabatic process is one where there is no heat flow into or out of the system

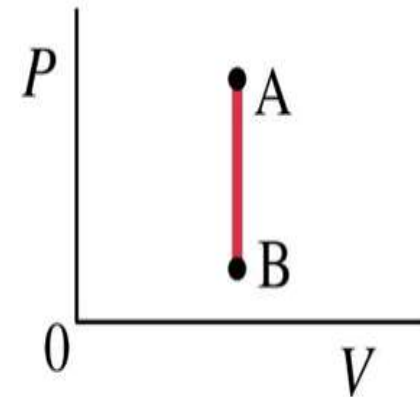


**Isobaric process** : it is the process in which change is under constant pressure

An isobaric process (a) occurs at constant pressure; an isovolumetric one (b) at constant volume.



(a) Isobaric

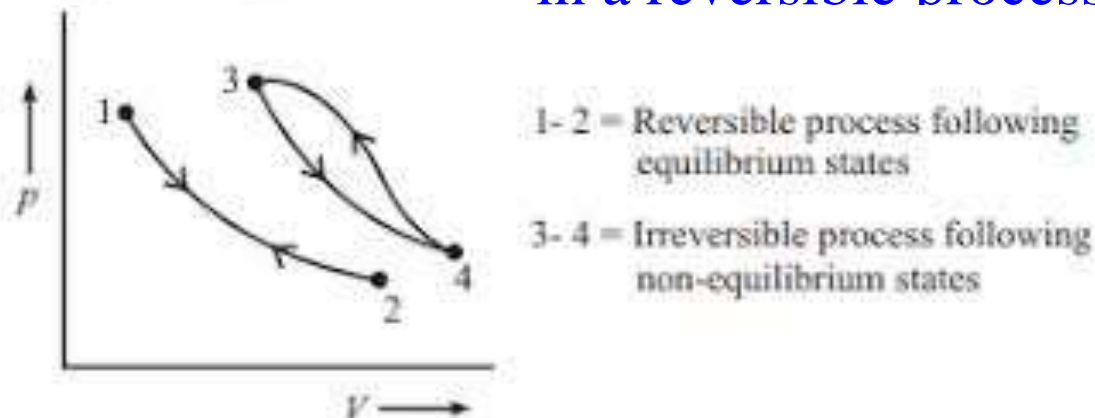
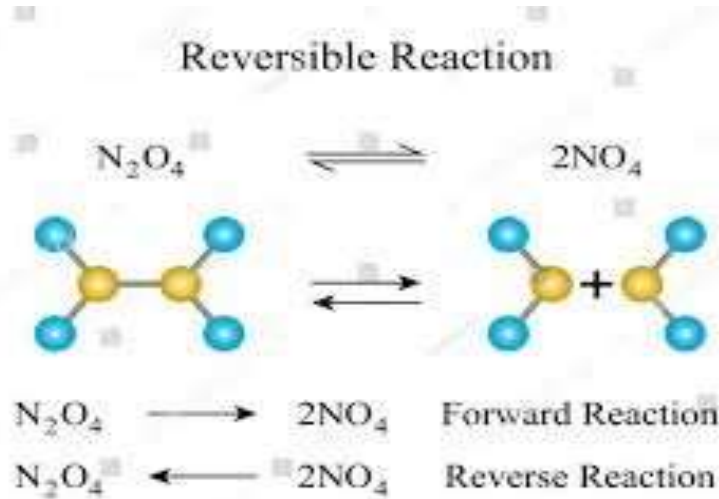


(b) Isovolumetric

**reversible process** :it is the process in which the thermodynamic coordinates are homogeneous when the operation is performed

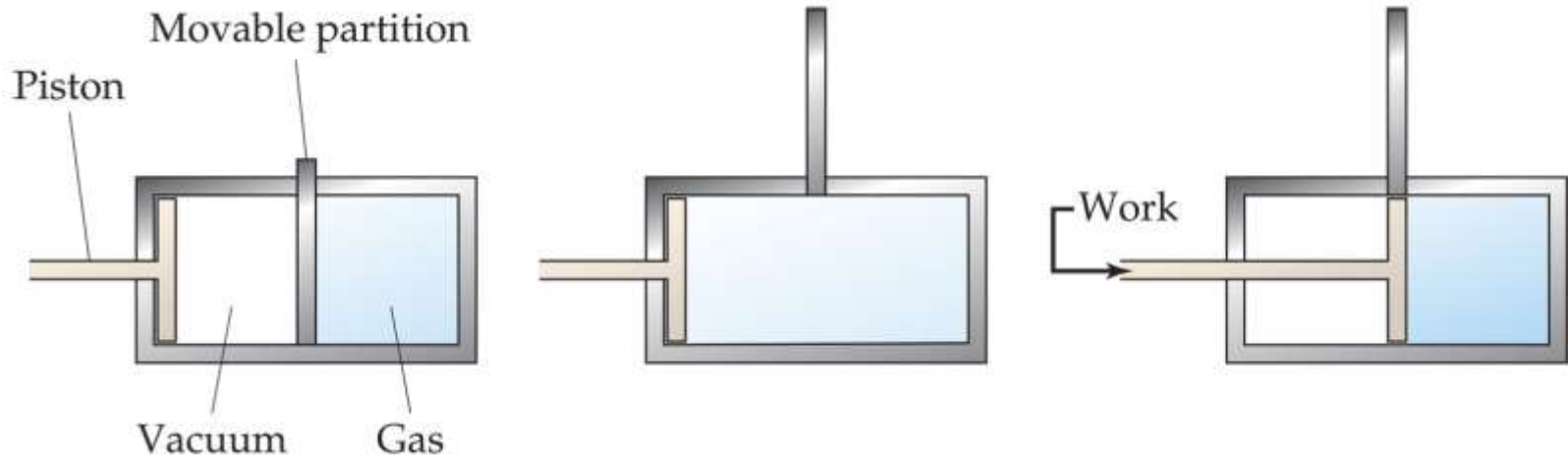
In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

Changes are infinitesimally **small** in a reversible process.



**Fig. Reversible and irreversible processes**

**Irreversible process** : is the process in which the thermodynamic coordinates are not homogeneous when the operation is performed



- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

**State and Equilibrium** A system in equilibrium experiences no changes when it is isolated from its surroundings.

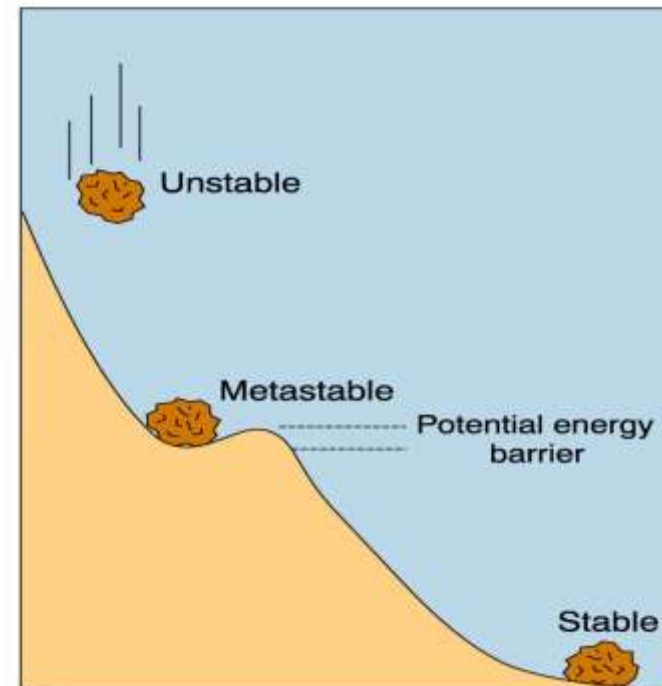
\* **Thermal equilibrium**: when the temperature is the same throughout the entire system.

\* **Mechanical equilibrium**: when there is no change in pressure at any point of the system. However, the pressure may vary within the system due to gravitational effects.

\* **Chemical equilibrium**: when the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

## Energy States

- **Unstable**: falling or rolling
- **Stable**: at rest in lowest energy state
- **Metastable**: generally has a shorter lifetime than the lowest





## Types of Systems :

**Open System:** which is the system that allows the exchange of matter and energy between the system and the surrounding medium.

**Closed system:** which allows the exchange of energy only between the system and the surrounding medium in the form of heat or work.

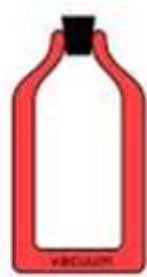
**Isolated system:** which does not allow the transfer of any of the energy and matter between the system and the surrounding medium.



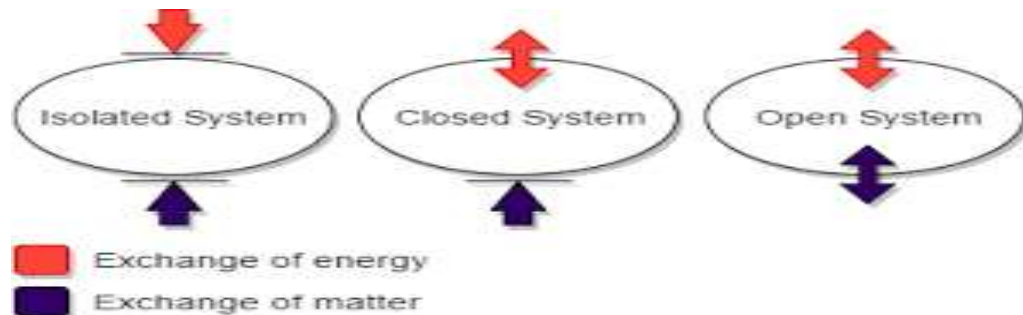
Open System



Closed system



Insulated system



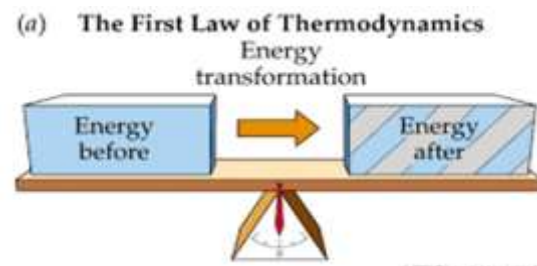
# Thermodynamic laws

**First Law:** Energy is Conserved; It cannot be created or destroyed.

- the change in internal energy of the gas  
= the heat *absorbed* by the gas *minus* the work done *by* the gas or *plus* the work done *on* the gas
- The *change* in internal energy is

$$\Delta U = U_{final} - U_{initial}$$

- Then, the 1<sup>st</sup> Law requires:  $\Delta U = Q - W$ , or  $\Delta U = Q + W$   
where Q is the heat absorbed *by* the gas, and W is the work done *by* the gas.
- The 1<sup>st</sup> Law of Thermodynamics is a statement of *conservation of*



**TABLE 15–1 Simple Thermodynamic Processes and the First Law**

Process	What is constant:	The first law, $\Delta U = Q - W$ , predicts:
Isothermal	$T = \text{constant}$	$\Delta T = 0$ makes $\Delta U = 0$ , so $Q = W$
Isobaric	$P = \text{constant}$	$Q = \Delta U + W = \Delta U + P \Delta V$
Isovolumetric	$V = \text{constant}$	$\Delta V = 0$ makes $W = 0$ , so $Q = \Delta U$
Adiabatic	$Q = 0$	$\Delta U = -W$

- **Internal Energy ( E or U )** – is the sum of all kinetic and potential energy of all components of the system.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- A **positive value** of  $\Delta E$  results when  $E_{\text{final}} > E_{\text{initial}}$ , indicating the system **gained energy**

A **negative value** of  $\Delta E$  results when

$E_{\text{final}} < E_{\text{initial}}$ , indicating the system **lost energy**

- In a chemical reaction, the initial state of the system refers to the reactants and the final state to the products
- We can analyze the  $\Delta E$  gained or lost in a system by examining the processes that cause the changes to the system

- The internal energy of a system can change in two general ways
  - *As heat or as work*
- When a system undergoes any chemical or physical change, the accompanying change in internal energy is given by:

$$\Delta E = q + w$$

$q > 0$ : Heat is transferred from the surrounding to the system

$q < 0$ : Heat is transferred from the system to the surrounding

$w > 0$ : Work is done by the surroundings on the system

$w < 0$ : Work is done by the system on the surroundings

- Calculate the change in the internal energy of the system for a process in which the system **absorbs** 140 J of heat from the surroundings and **does** 85 J of work **on** the surroundings

$$E = q + W = 140\text{J} - 85\text{J} = 55\text{J}$$

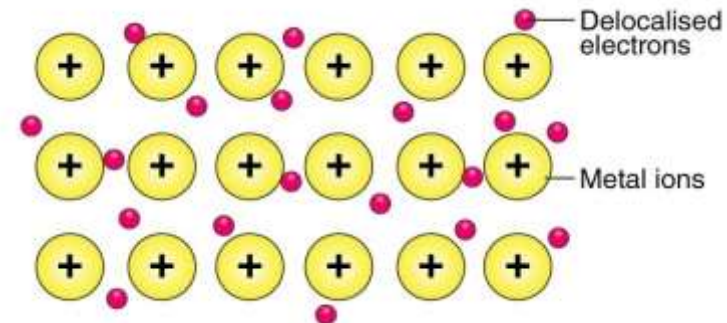
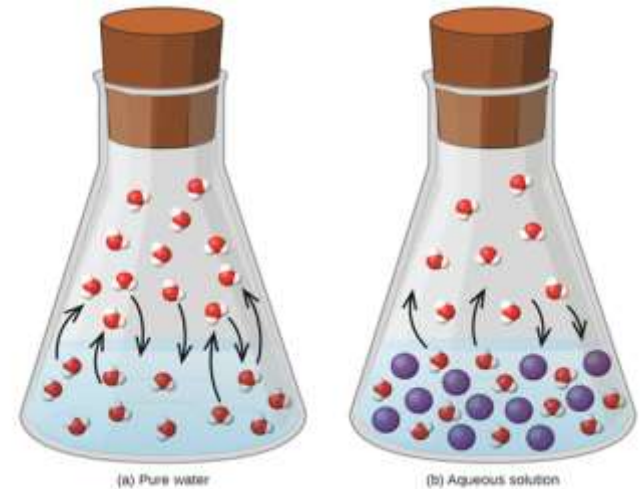
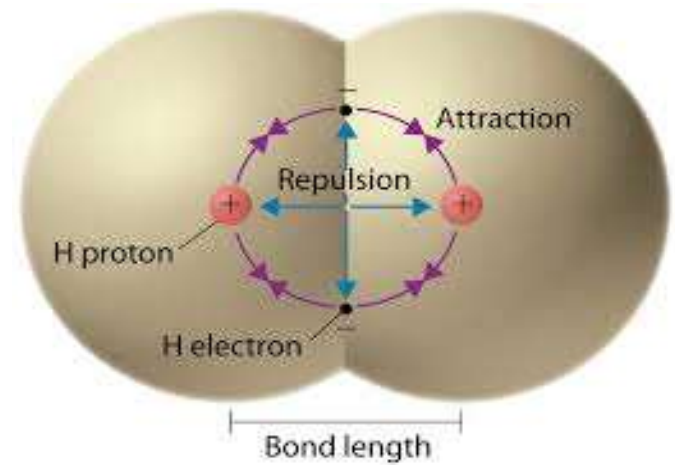


# Second Lecture

## Binding Forces

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester  
2023 - 2022

Dr . Anmar Ghanim Taki Alaaraji



## binding forces

**Intramolecular forces** are forces *that hold atoms together within a molecule*.

**Intermolecular forces** are *forces that exist between molecules*.

An intramolecular force (or primary forces) is **any force that binds together the atoms making up a molecule or compound**, ... Chemical bonds are considered to be intramolecular forces, these forces are often stronger than **intermolecular forces**.

## Types

### Ionic Bonds

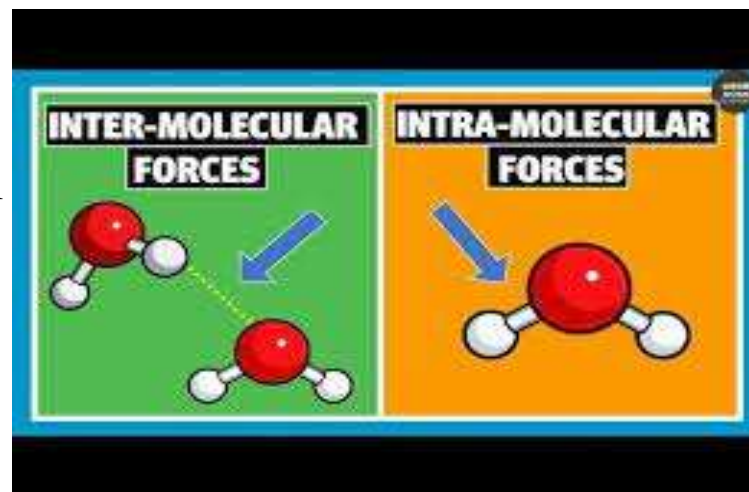
- Transfer of electrons between a non metal & a metal
- Observed in formation of salts, example NaCl

### Covalent Bond

- Sharing of electrons between two non metals
- Observed in organic compounds , example CH<sub>4</sub>

### Metallic bond

Metallic electrons are generally **delocalized** ; the result is a large number of free electrons around positive **nuclei** , sometimes called an electron sea.





# Intermolecular Forces

## Forces of attraction between molecules

- The attractions between molecules *are not nearly as strong as* the intramolecular attractions (bonds) that hold compounds together.
- Many physical properties reflect intermolecular forces, like boiling points, melting points, viscosity, surface tension, and capillary action.

## Types

### Binding & Attractive Forces

#### \* Binding Forces

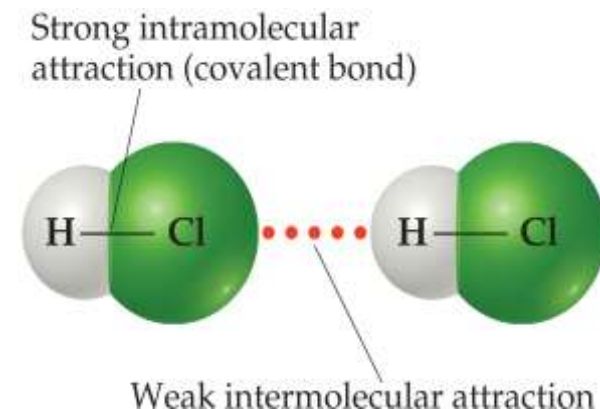
**Cohesion** – similar molecules

**Adhesion** – different molecules

**Repulsive** – prevent molecules from annihilating each other

#### \* Attractive Forces

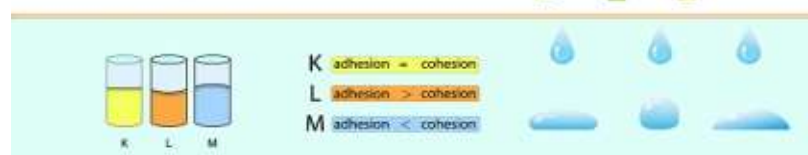
Van der Waals , Hydrogen bond



### Adhesion



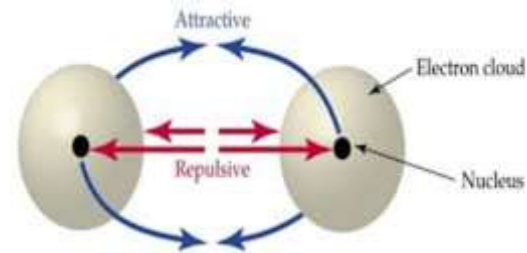
### Cohesion





## Repulsive and Attractive Forces

- When molecules interact, both repulsive and attractive forces operate.
- When the molecules are brought so close that the outer charge clouds touch, they repel each.
- Thus, attractive forces are necessary for molecules to cohere, whereas repulsive forces act to prevent the molecules from interpenetrating and annihilating each other.

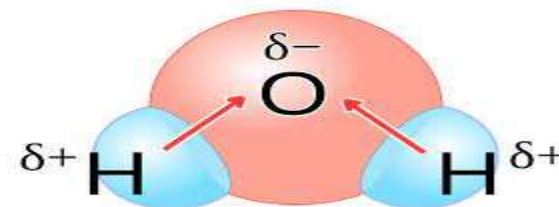
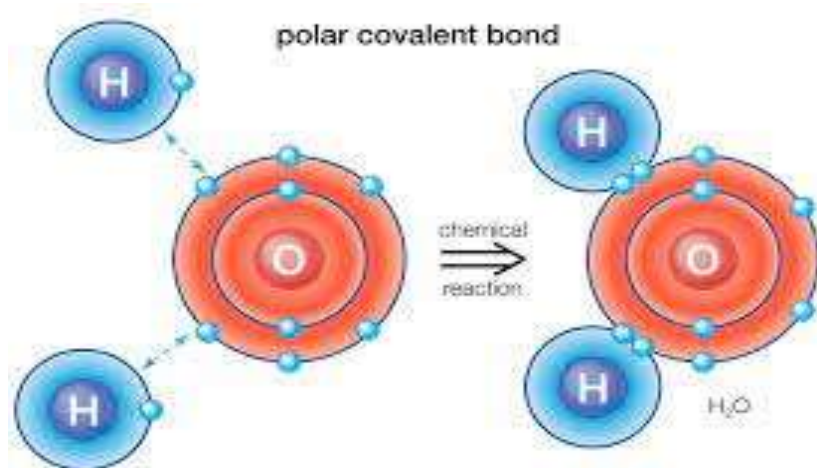


## Types of Intermolecular Force (Attractive Forces)

- Weakest to strongest forces:
  - dispersion forces (or London dispersion forces)
  - dipole–dipole forces
  - hydrogen bonding (a special dipole–dipole force)
  - ion–dipole forces
- **Note:** The first two types are also referred to collectively as *van der Waals forces*.

## polar bond

A polar covalent bond is a covalent bond in which the atoms have an unequal attraction for electrons, and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical



H W 4 : Which molecule has no polar bond ?

A.  $\text{CCl}_4$

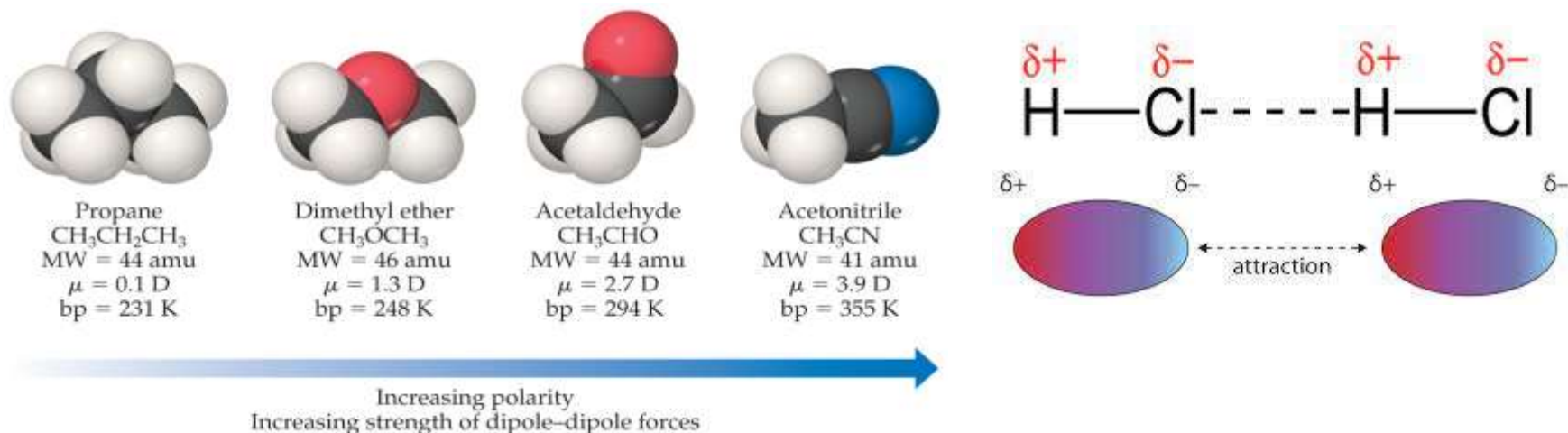
B.  $\text{H}_2\text{CO}$

C.  $\text{OF}_2$

D. None

## Dipole–Dipole Interactions

- Polar molecules have a more positive and a more negative end—a dipole (two poles,  $\delta^+$  and  $\delta^-$ ).
- The oppositely charged ends attract each other.



Dipole–Dipole interactions result when two dipolar molecules interact with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule. For molecules of approximately equal mass and size, the more polar the molecule, the higher its boiling point.

**H W 5 :** Which of these is a polar molecule?

A.  $\text{XeF}_4$

B.  $\text{BF}_3$

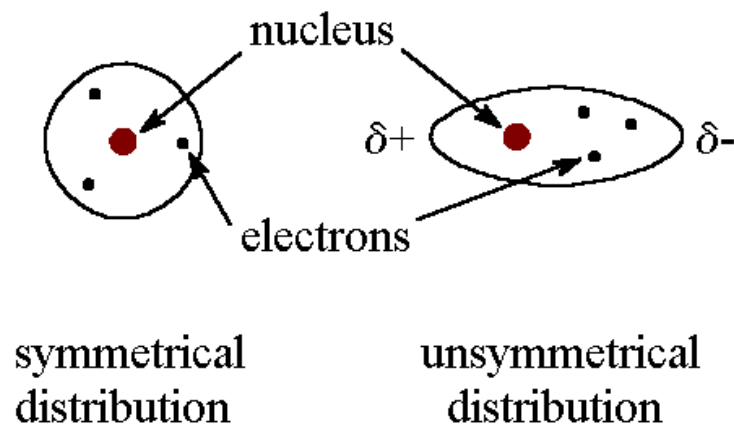
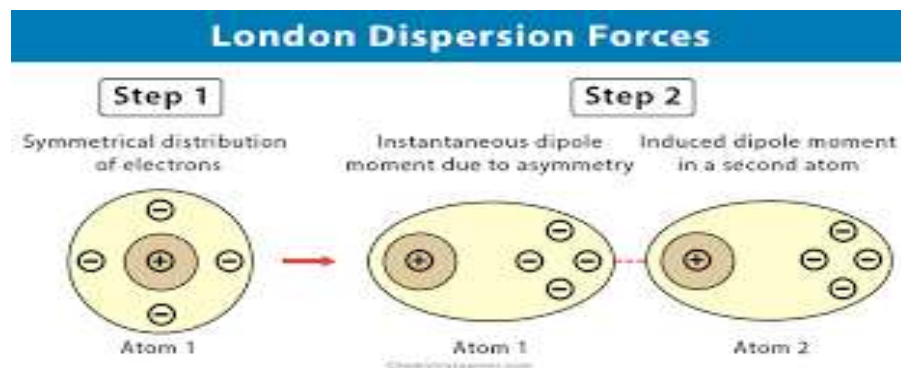
C.  $\text{I}_2\text{Cl}_6$

D.  $\text{PCl}_2\text{F}_3$

# Dispersion Forces

The London dispersion force is the weakest intermolecular force. It is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This force is sometimes called an induced dipole-induced dipole attraction. London forces are the attractive forces that cause nonpolar substances to condense to liquids and to freeze into solids when the temperature is lowered sufficiently.

The tendency of an electron cloud to distort is called its *polarizability*.



**H W 6** :in which of the following molecule is covalent bond must be polar?

A. HI

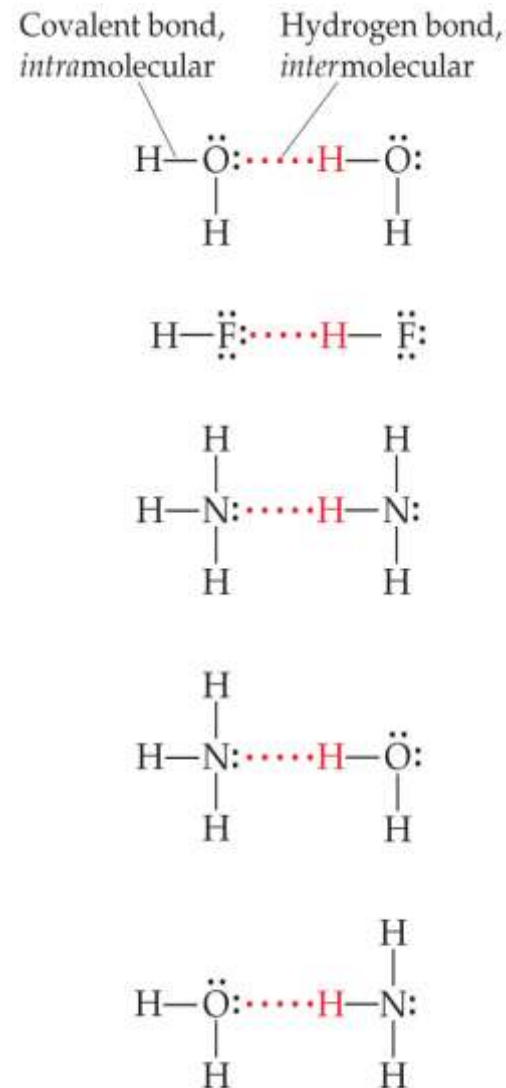
B. HBr

C. HCl

D. H<sub>2</sub>

# Hydrogen Bonding

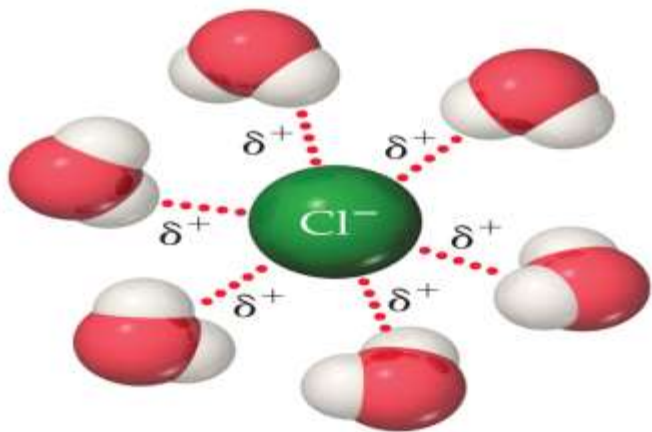
- The dipole–dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.
- A hydrogen bond is an attraction between a hydrogen atom attached to a highly electronegative atom and a nearby small electronegative atom in another molecule or chemical group
- These atoms interact with a nearly bare nucleus (which contains one proton).



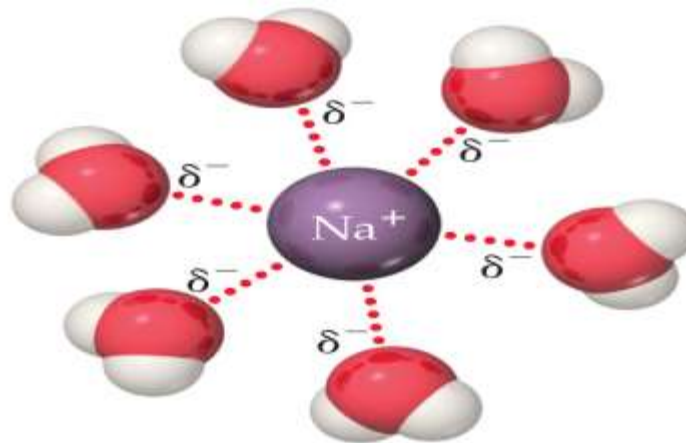
## Ion–Dipole Interactions

An ion-dipole interaction is the result of an electrostatic interaction between a charged ion and a molecule that has a dipole. It is an attractive force that is commonly found in solutions, especially ionic compounds dissolved in polar liquids.

The strength of these forces is what makes it possible for ionic substances to dissolve in polar solvents.



Positive ends of polar molecules are oriented toward negatively charged anion

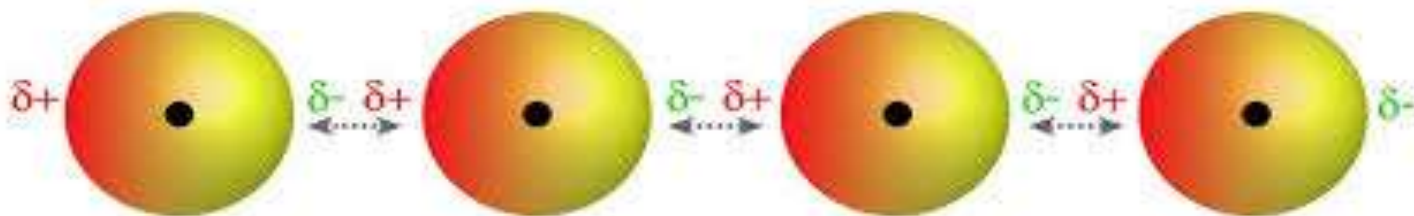
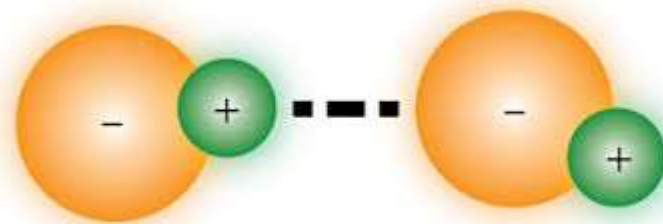


Negative ends of polar molecules are oriented toward positively charged cation

## Van der Waal forces

Van der Waals forces are the sum of the attractive and repulsive electrical forces between atoms and molecules. ... Examples of van der Waals forces include *dispersion forces, and dipole-dipole interactions*.

These bonds can occur between nonpolar or polar molecules. van der Waals bonds are extremely dependent on the distance of separation between molecules, and are significant only when the electron clouds of the molecules are just touching.

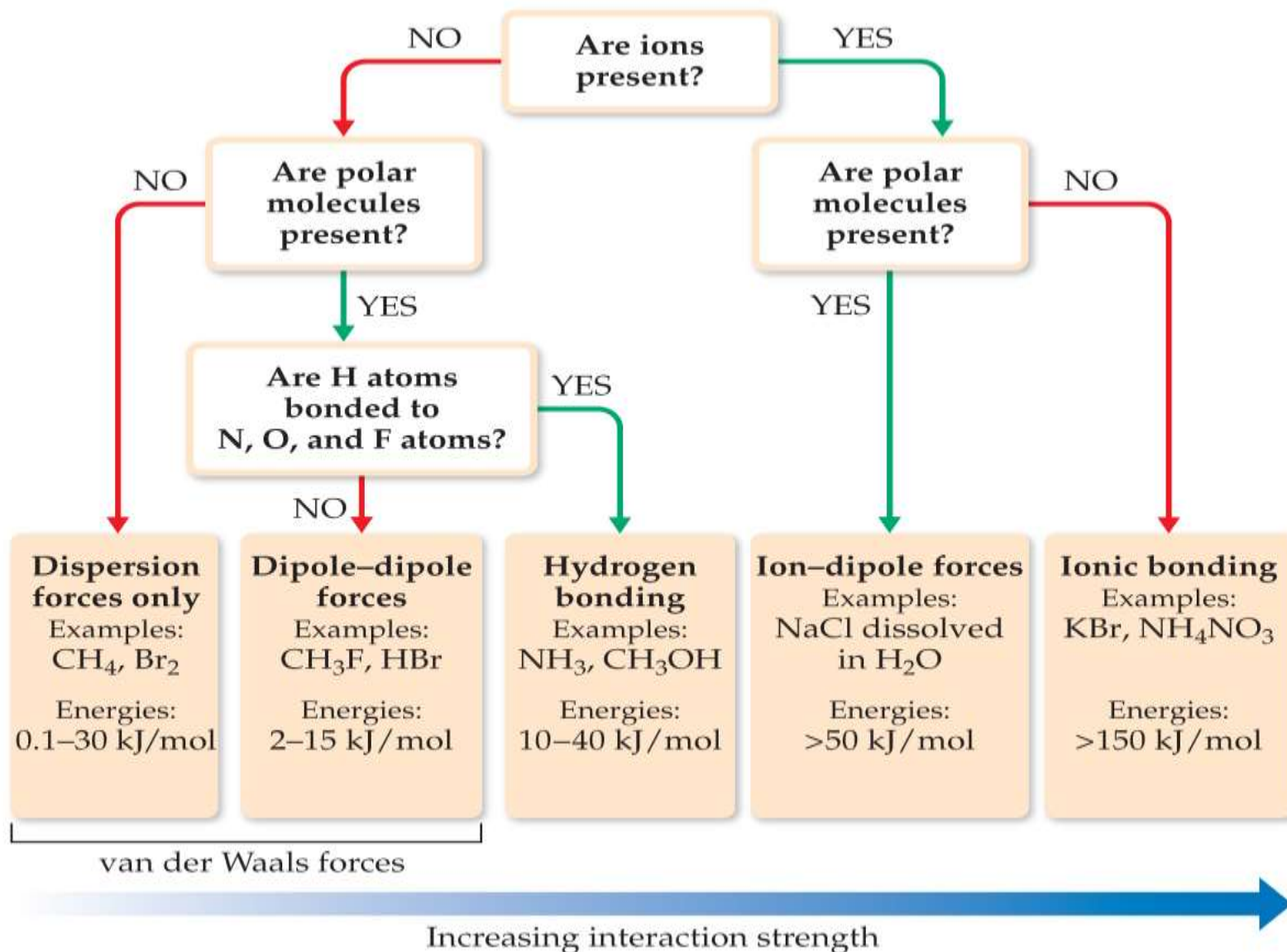


**van der Waals interaction:** induced dipoles caused by charge fluctuations

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# Summarizing Intermolecular Forces





## H . W 7 Circle the correct answers.

1. The Atoms of solid Ar are held together by

- (a) Van der Waals forces
- (b ) Hydrogen bonds
- (c) Ionic bonds
- (d ) Hydrophobic forces

2. Which of the following has the weakest bond?

- (a) Ice
- (b) Diamond
- (c) KCl
- (d) Neon

3. Which of the following is the weakest bond?

- (a) Ionic bonds
- (b) Metallic bonds
- (c) Covalent bonds
- (d) Van der Waals forces

4. Which of the following has both covalent and ionic bonds?

- (a) NaOH
- (b) KCl
- (c) CH<sub>4</sub>
- (d) SO<sub>2</sub>

5 . Non-polar molecules can contain polar bonds.

- (a) True
- (b) False

## The gaseous state of matter

Gases have lower density than other states of matter, such as solids and liquids. There is a great deal of empty space between particles, which have a lot of kinetic energy

An ideal gas is defined as **one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces**. It is a theoretical gas composed of a set of randomly-moving point particles. In such a gas, all the internal energy is in the form of kinetic energy and any change in internal energy is accompanied by a change in temperature.

Specifically, an ideal gas ...

- Obeys all of the gas laws under all conditions.
- Does not condense into a liquid when cooled.
- Shows perfectly straight lines when its  $V$  and  $T$  &  $P$  and  $T$  relationships are plotted on a graph.

We assume that gases are ideal to simplify our calculations.

$$V \propto 1/P \text{ (Boyle's law)}$$

$$V \propto T \text{ (Charles' law)}$$

$$V \propto n \text{ (Avogadro's law)}$$

## Physical Characteristics of Gases

Physical Characteristics	Typical Units
Volume, <b>V</b>	liters ( <b>L</b> )
Pressure, <b>P</b>	atmosphere (1 <b>atm</b> = $1.015 \times 10^5 \text{ N/m}^2$ )
Temperature, <b>T</b>	Kelvin ( <b>K</b> )
Number of atoms or molecules, <b>n</b>	<b>mole</b> (1 mol = $6.022 \times 10^{23}$ atoms or molecules)

The gas laws formulated by Boyle ,Charles and Gay-Lussac refer to an ideal situation where no interactions exist and collisions are perfectly elastic, and thus no energy is exchanged upon collision.

- **Boyle' s law** :  $P \propto 1/V$  ----- ( at constant **T**)

Or  $PV=k$  -----(1), (k-constant)

- **Gay-Lussac and Charles**

$V \propto T$ ----- (at constant **P**)  $V =k T$  .....(2) , and

$P \propto T$  ----- ( at constant **V**)

$P=k T$ .....(2)

- **Avogadro's law**

$V \propto n$  .....(at constant **P** & **T**.)

$V= k n$  .....(3)

So combined (1, 2, 3) give :-

$PV \propto n T$

$PV= n RT$  .....(4)

\* also combined eq.1 ,2 and 3 give:  $PV/T =k$

*and for two gases state*.  $P_1V_1/T_1 =k$  and  $P_2V_2/T_2 =k$

### Example-1

What is the volume of 2 mole of an ideal gas at 25C° and 780 mmHg ?

$$P = 780 \text{ mm-Hg.} / 760 \text{ mm-Hg. atm}^{-1} = 1.0263 \text{ atm} \quad T = 25\text{C}^{\circ} + 273.16\text{K} = 298.16\text{K}$$

$$R = 0.08205 \text{ liter.atm/ mole.deg}$$

$$P V = nRT$$

$$1.0263 \text{ atm} \times V = 2 \text{ mole} \times (0.08205 \text{ liter.atm /mole.deg.} \times 298.16\text{K})$$

$$V = 47.65 \text{ liter.}$$

### Example-2

The volume of an ideal gas 30 ml at 20C° and a pressure of 740 mm.Hg. What is the volume at 0C° and 760 mm.Hg ?

$$P_1 = 740 \text{ mm.Hg} , V_1 = 30 \text{ ml} \text{ and } T_1 = 273 + 20 = 293\text{K} \text{ And } P_2 = 760\text{mm.Hg} , V_2 = ? \text{ and } T_2 = 0 + 273 = 273 \text{ K}$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 , 740 \times 30 / 293 = 760 \times V_2 / 273 \quad V_2 = 27.2 \text{ ml.}$$

**H W 8** What is the pressure of 2000 mmole of an ideal gas at 0C° and 4500ml?

## Real gases

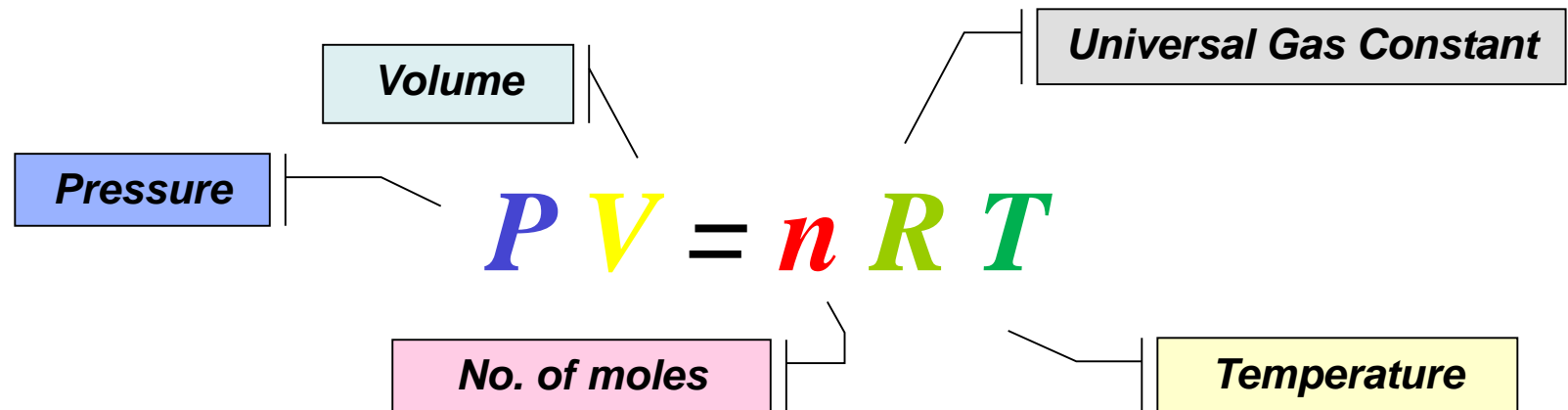
are non ideal gases whose molecules occupy space and have interactions; consequently, they do not adhere to the [ideal gas law](#). To understand the behavior of real gases, the following must be taken into account:

- [compressibility](#) effects;
- variable [specific heat capacity](#);
- [van der Waals forces](#);
- non-equilibrium thermodynamic effects;
- issues with molecular dissociation and elementary reactions with variable composition

A real gas is defined as a gas that at all standard pressure and temperature conditions does not obey gas laws. It deviates from its ideal behavior. True gases have velocity, mass, and volume. They liquefy when cooled to their boiling point. The space filled by gas is not small when compared to the total volume of gas.

# Ideal Gas Equation

The Ideal gas law is the equation of state of a hypothetical ideal gas. It is a good approximation to the behavior of many gases under many conditions, although it has several limitations. The ideal gas equation can be written as



The diagram shows the Ideal Gas Equation  $PV = nRT$  with color-coded variables and labels in boxes connected by lines:

- P** (blue) is labeled **Pressure** (blue box).
- V** (yellow) is labeled **Volume** (light blue box).
- n** (red) is labeled **No. of moles** (pink box).
- R** (green) is labeled **Universal Gas Constant** (grey box).
- T** (green) is labeled **Temperature** (yellow box).

According to the Ideal Gas equation-

The product of Pressure & Volume of a gas bears a constant relation with the product of Universal gas constant and the temperature.

When the molecular mass of any gas is multiplied by its specific gas constant (R), it is observed that the product R is always the same for all gases. This product is called universal gas constant and it is denoted as R.

$$R = 0.0821 \text{ atm L / mol K}$$

$$R = 8.314 \text{ kPa L / mol K}$$

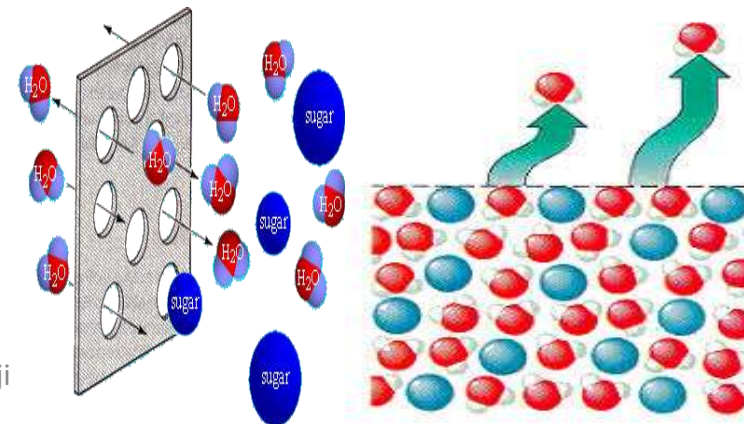
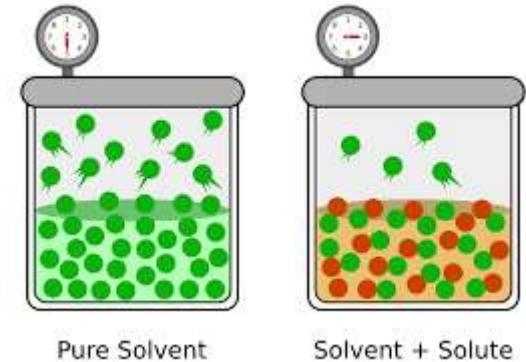
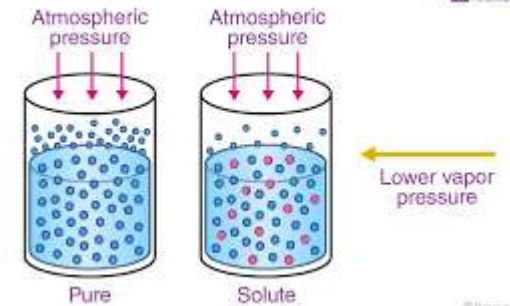
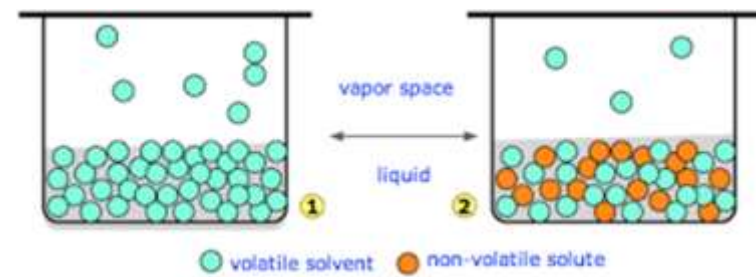


# Seventh Lecture

## Colligative Properties

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester  
2022 - 2023

Dr . Anmar Ghanim Taki Alaaraji





## Colligative Properties

Dissolving solute in pure liquid will change all physical properties of liquid, Density, Vapor Pressure, Boiling Point, Freezing Point, and Osmotic Pressure.

Colligative Properties are properties of a liquid that *change* when a solute *is added*.

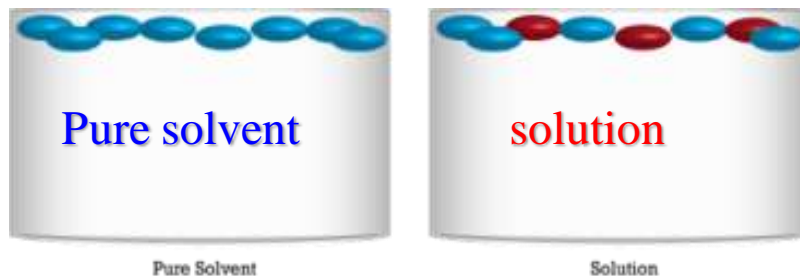
The magnitude of the change depends on the *number of solute particles* in the solution, **NOT** on the *identity of the solute particles*.

Four important colligative properties of solutions are:

- vapor-pressure lowering
- boiling-point elevation
- freezing-point depression
- osmotic pressure

- *Lowering of the Vapor Pressure*

A *colligative property* is a property of a solution that *depends only on the number of solute particles* dissolved in the solution and *not on their identity*. The vapor pressure of a liquid is determined by *how easily its molecules are able to escape the surface of the liquid* and *enter the gaseous phase*. When a liquid evaporates easily, it will have a relatively large number of its molecules in the gas phase and thus will *have a high vapor pressure*. Liquids that *do not evaporate easily* have a lower vapor pressure.

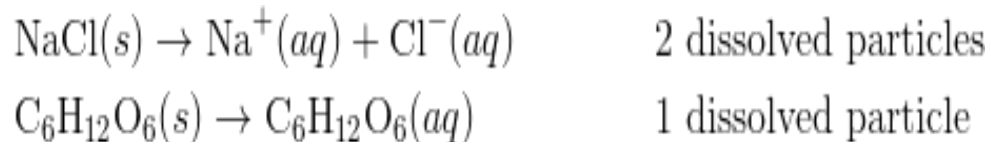


The Figure shows the surface of a pure solvent compared to a solution. In pure solvent, the surface is entirely occupied by liquid molecules, some of which will evaporate and form a vapor pressure. In a solution, a nonvolatile solute has been dissolved into the solvent. Nonvolatile means that the solute itself has little tendency to evaporate. Because some of the surface is now occupied by solute particles, there is less area for solvent. This results in less solvent being able to evaporate. The addition of a nonvolatile solute results in a lowering of the vapor pressure of the solvent.

The lowering of the vapor pressure depends on the number of solute particles that have been dissolved. The chemical nature of the solute is not important because the vapor pressure is merely a physical property of the solvent. The only requirement is that the solute only dissolved and does not undergo a chemical reaction with the solvent.

While the chemical nature of the solute is not a factor, it is necessary to take into account whether the solute is an electrolyte or a nonelectrolyte. Remember that ionic compounds are strong electrolytes and thus dissociate into ions when they dissolve. This results in a larger number of dissolved particles.

For example, consider two different solutions of *equal concentration*. One is made from the ionic compound sodium chloride, while the other is made from the molecular compound glucose. The following equations show what happens when these solutes dissolve.



The sodium chloride dissociates into **two ions**, while the glucose **does not dissociate**. Therefore, equal concentrations of each solution will result in twice as many dissolved particles in the case of the sodium chloride. The vapor pressure of the sodium chloride solution will be *lowered twice the amount as the glucose solution*.

- **Addition of a nonvolatile solute to a solution lowers the vapor pressure of the solution.**

### **Non-Volatile Solutes**

Experimentally, we know that the vapor pressure of the solvent above a solution containing a non-volatile solute (i.e., a solute that does not have a vapor pressure of its own) is directly proportional to the mole fraction of solvent in the solution. This behavior is summed up in ***Raoult's Law***:

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

where:

$P_{\text{solvent}}$  is the vapor pressure of the solvent above the solution,

$X_{\text{solvent}}$  is the mole fraction of the solvent in the solution, and

$P^{\circ}_{\text{solvent}}$  is the vapor pressure of the pure solvent.

Note that

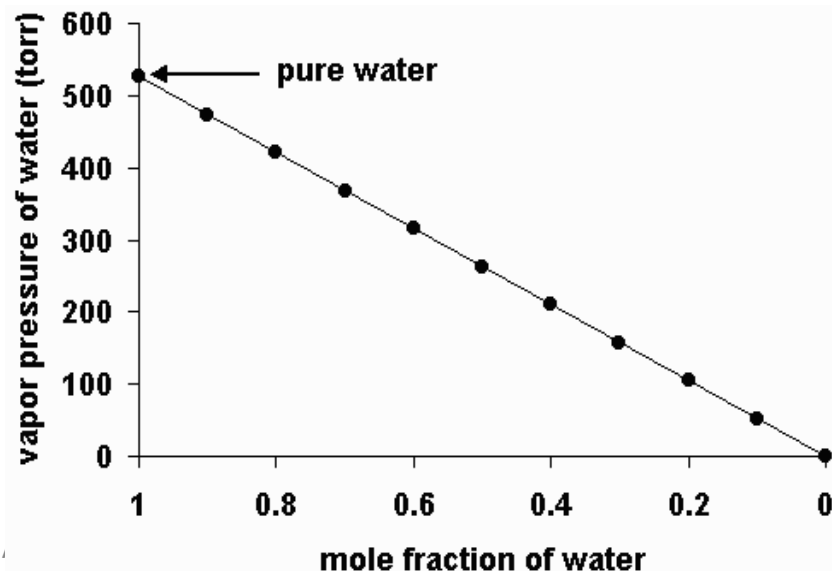
•when  $X_{\text{solvent}} = 1$  (pure solvent),  $P_{\text{solvent}} = P^{\circ}_{\text{solvent}}$ , and

•when  $X_{\text{solvent}} < 1$  (solute(s) present),  $P_{\text{solvent}} < P^{\circ}_{\text{solvent}}$  (*i.e., the vapor pressure of the solvent above the solution is lower than the vapor pressure above the pure solvent*).

The following graph shows the vapor pressure for water (solvent) at 90°C as a function of mole fraction of water in several solutions containing sucrose (a non-volatile solute). Note that the vapor pressure of water **decreases** as the concentration of sucrose increases.

**Vapour-Pressure Lowering**

$$P_1 = X P_0$$

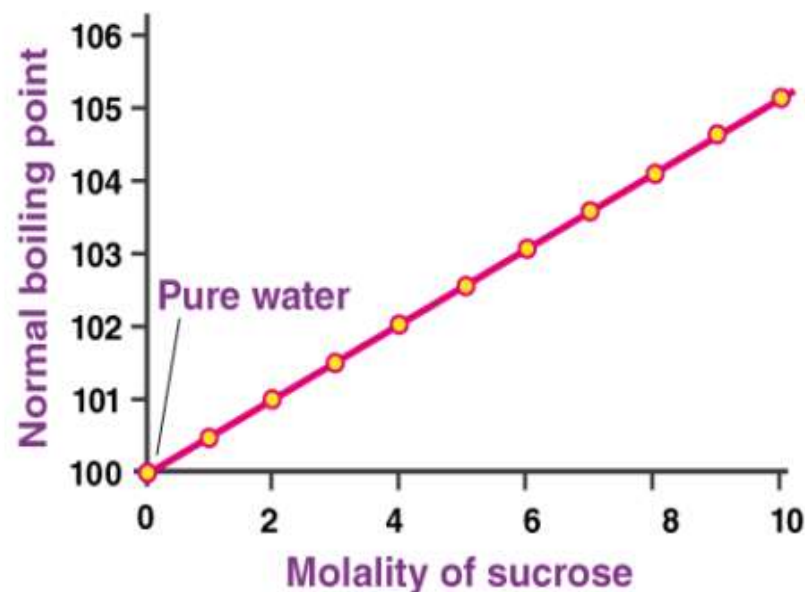


## Boiling Point Elevation

refers to the increase in the boiling point of a *solvent* upon the *addition of a solute*. When a non-volatile solute is added to a solvent, the resulting solution has a higher boiling point than that of the pure solvent. For example, the boiling point of a solution of sodium chloride (salt) and water is greater than that of *pure water*.

Boiling point elevation is a *colligative property* of matter, i.e. it is dependent *on the solute-to-solvent ratio* but *not on the solute's identity*. This means that the elevation in the boiling point of a solution depends *on the amount of solute added to it*. The greater the concentration of solute in the solution, the greater the boiling point elevation.

A graph detailing the elevation in the boiling point of water upon the addition of sucrose is provided above. At 1 atm of pressure, pure water boils at 100°C. However, a 10 molal solution of sucrose in water boils at approximately 105°C.

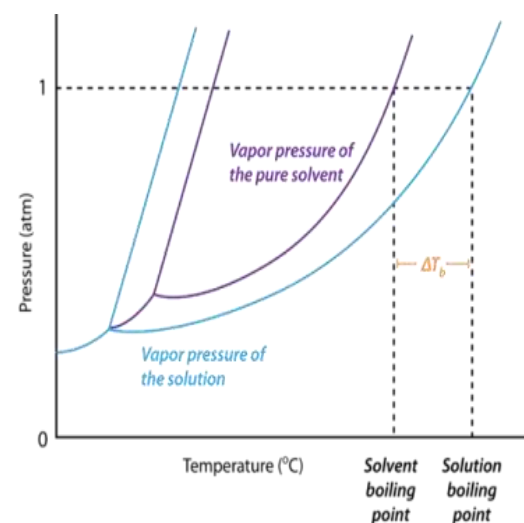


## How Boiling Point Elevation Occur?

The boiling point of a liquid is the temperature at which its vapour pressure **is equal** to the pressure of its *surrounding environment*. Non-volatile substances do not readily undergo evaporation and have **very low** vapour pressures (assumed to be zero). When a non-volatile solute is added to a solvent, the vapour pressure of the resulting solution is *lower than that of the pure solvent*.

Therefore, a greater amount of heat must be supplied to the solution for it to **boil**. This increase in the boiling point of the solution is *the boiling point elevation*. An increase in the concentration of added solute is accompanied by a *further decrease in the vapour pressure of the solution* **and** *further elevation in the boiling point of the solution*.

The figure shows the phase diagram of a solution and the effect that the lowered vapor pressure has on the boiling point of the solution *compared to the solvent*. In this case, the solution has a higher boiling point *than the pure solvent*. Since the vapor pressure of the solution is lower, more heat must be supplied to the solution to bring its vapor pressure up to the pressure of the external atmosphere. The **boiling point elevation** is the difference in temperature between the boiling point of the **pure** solvent and that of **the solution**.



## Boiling Point Elevation Formula

The boiling point of a solution containing a *non-volatile solute* can be expressed as follows:

Boiling point of solution = boiling point of pure solvent + boiling point elevation ( $\Delta T_b$ )

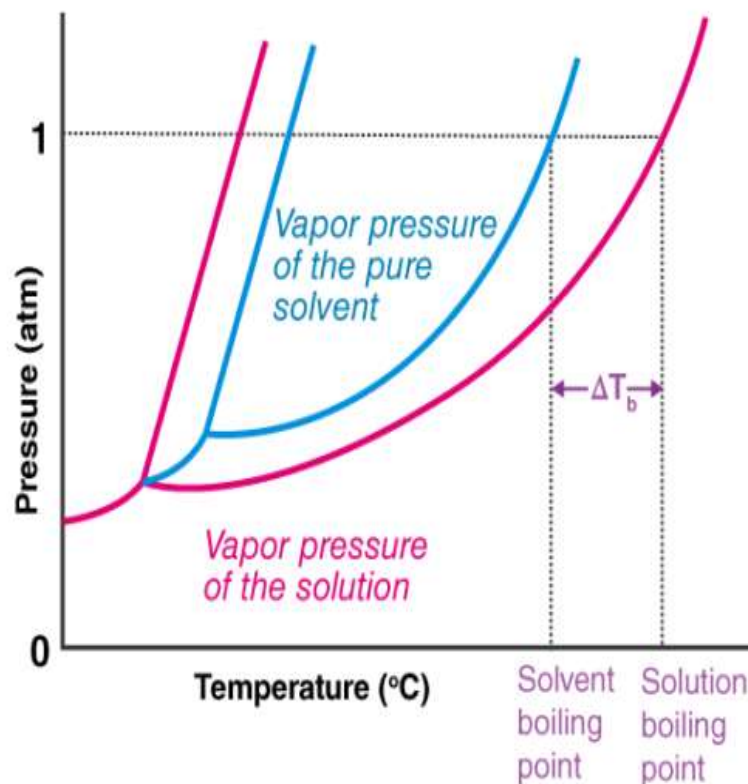
The elevation in boiling point ( $\Delta T_b$ ) is proportional to the concentration of the solute in the solution. It can be calculated via the following equation.

**Boiling-Point Elevation**  $\Delta T_b = i K_b m$

Where,

- $i$  is the Van't Hoff factor
- $K_b$  is the molal boiling-point elevation constant
- $m$  is the *molality* of the solute

It is important to note that this formula becomes *less precise* when the concentration of the solute is *very high*. Also, this formula doesn't hold true for volatile solvents.





## Freezing point depression

is the phenomena that describes why **adding a solute** to a solvent results in the **lowering of the freezing point** of the solvent. When a substance starts to freeze, the molecules *slow down due to the decreases in temperature*, and the intermolecular forces start to **take over**. The molecules will then arrange themselves in a pattern, and thus turn **into a solid**. *For example*, as water is cooled to the freezing point, its molecules become slower and hydrogen bonds begin to “**stick**” more, eventually creating a solid. If salt is added to the water, the  $\text{Na}^+$  and  $\text{Cl}^-$  ions attract to the water molecules and interfere with the formation of the large network solid known as **ice**. In order to achieve a solid, the solution must be cooled to an even **lower temperature**. The freezing point depression can also be explained in terms of vapor pressure. Adding solute to a solvent will essentially dilute the solvent molecules, and according to Raoult’s law, this leads to a *decrease in vapor pressure*. Considering the fact that the vapor pressure of the solid and liquid forms must be the same at freezing point, because *otherwise the system would not be at equilibrium*, the lowering of the vapor pressure leads to the **lowering** of the temperature at which the vapor pressures of the liquid and frozen forms of the solution **will be equal**.



## Effect of solutes on physical properties

A triple phase diagram which shows the pressure and temperature of the normal boiling and freezing points of a solvent (green lines) and the boiling and freezing points of a solution (purple lines). Notice that at 1 atm of pressure, the freezing point has been lowered (represented by numbers 2 and 4).

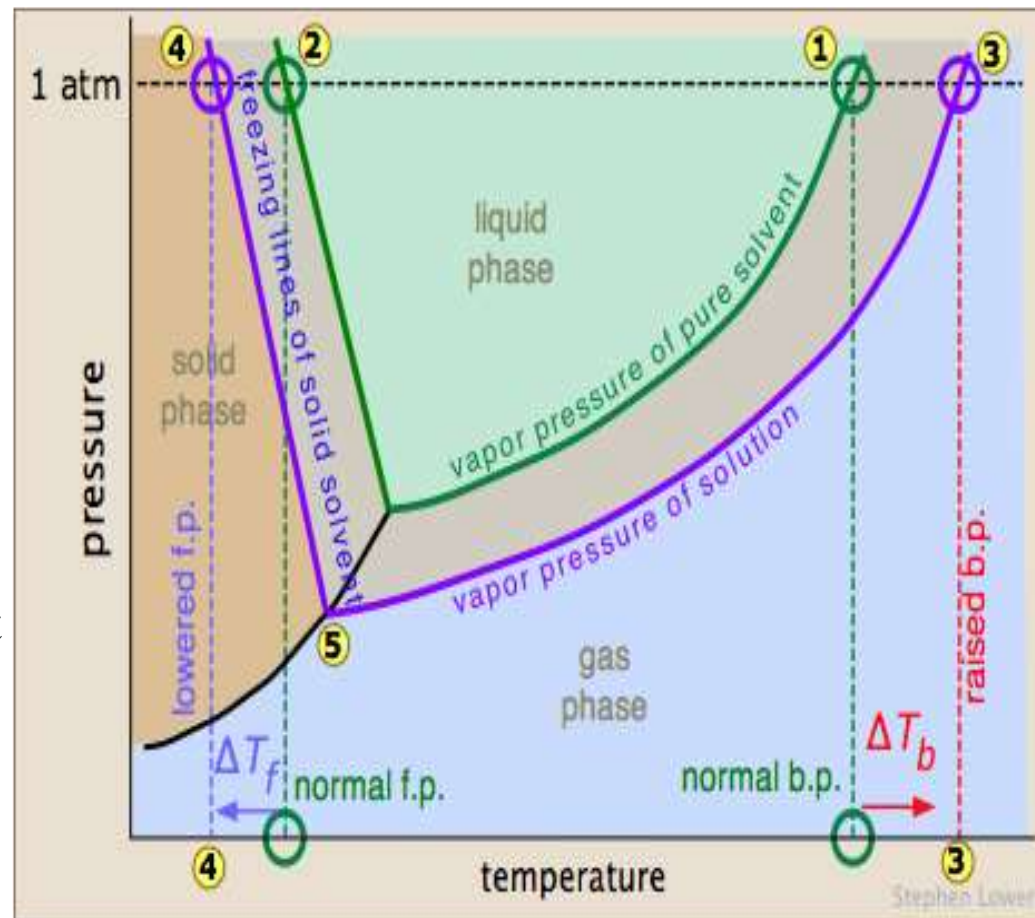
The freezing point depression can be calculated by the formula:

### Freezing-Point Depression

$$\Delta T_f = iK_f m$$

In this equation,  $\Delta T_f$  is the freezing point depression,  $K_f$  is the freezing point depression constant, and  $i$  is the van't Hoff factor. The freezing point depression constant changes

*depending on the solvent*, and the van't Hoff factor accounts for **the number of particles that a dissolving solute creates in solution**,  $m$  the molality concentration.



## osmotic pressure

The term ‘osmosis’ refers to the movement of solvent molecules through a *semipermeable membrane* from a region where the solute concentration is *low* to a region where the solute concentration is *high*. Eventually, an equilibrium is established between the two sides of the semipermeable membrane (equal solute concentration on both sides of the semipermeable membrane).

*Important note:* The semipermeable membrane only allows the movement of solvent molecules through it – solute particles cannot pass through it.

If *sufficient pressure* is applied to the solution side of the semipermeable membrane, the process of osmosis is *stopped*. The minimum amount of pressure required to nullify the process of osmosis is called *osmotic pressure*.

Osmotic pressure can be calculated with the help of the following formula:

$$\text{Osmotic Pressure (p)} \quad p = i MRT \text{ or } \pi = iCRT \text{ Where,}$$

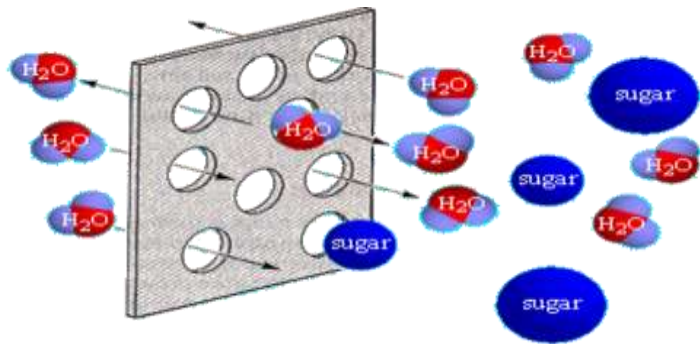
- $\pi$  is the osmotic pressure , or  $p$
- $i$  is the van't Hoff factor
- $C$  is the molar concentration of the solute in the solution , or  $M$
- $R$  is the universal gas constant
- $T$  is the temperature

This relationship between the osmotic pressure of a solution and the molar concentration of its solute was put forward by the Dutch chemist Jacobus van't Hoff. It is important to note that this equation only holds true for solutions *that behave like ideal solutions*.

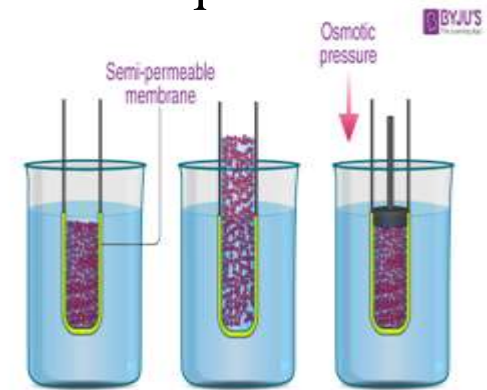
**Osmotic pressure** Is the minimum pressure that must be applied to a solution *to stop the flow* of solvent molecules through a semipermeable membrane (osmosis). It is a colligative property and is *dependent on the concentration of solute particles in the solution*.

### Van't Hoff and Morse Equations for Osmotic Pressure

Van't Hoff concluded that there was an *apparent analogy between solutions and gases* and that the osmotic *pressure in a dilute solution was equal to* the pressure that the solute would exert if it were a gas occupying the same volume. The equation is



$$\pi V = nRT$$



As a conclusion

### **Colligative Properties of Non-electrolyte Solutions**

*Colligative properties* are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.

*Vapour-Pressure Lowering*  
*Boiling-Point Elevation*  
*Freezing-Point Depression*  
*Osmotic Pressure (p)*

$$P_1 = X P_0$$

$$\Delta T_b = i K_b m$$

$$\Delta T_f = i K_f m$$

$$p = iMRT$$

In the illustration provided above, it can be observed that the solvent molecules tend to pass through the semipermeable membrane into the solution side until the osmotic pressure (of the solution) is applied to the solution side.

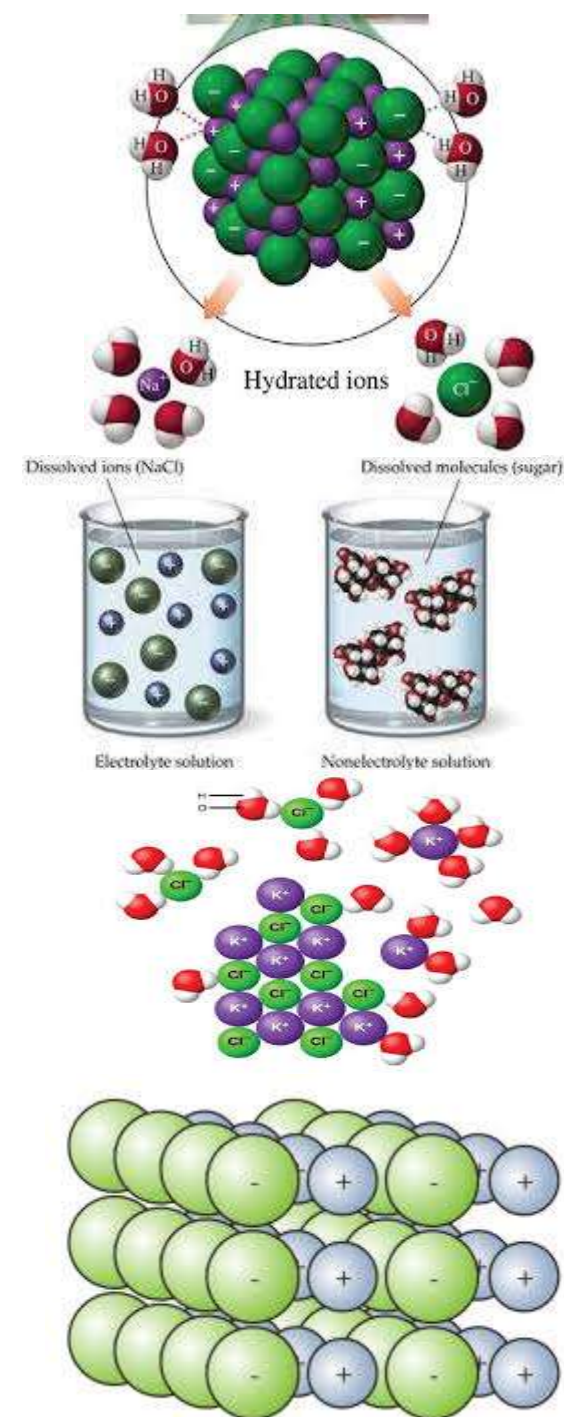


# Sixth Lecture

## solution of Nonelectrolytes

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester  
2022 - 2023

Dr . Anmar Ghanim Taki Alaaraji





**Solute** : *a dissolved substance* especially a component of a solution present in smaller amount than the solvent.

The solutes (whether gases, liquids, or solids) are divided *into two main classes*; *non-electrolytes* and *electrolytes*.

### **Nonelectrolytes**

are substances that *do not yield ions* when dissolved in water and therefore *do not conduct an electric current* through the solution, i.e. *sucrose, glycerin, naphthalene, and urea*.

Material substances can be mixed together to form a variety of pharmaceutical mixtures (or dispersions) such as *true solutions*, *colloidal dispersions*, and *coarse dispersions*.

**true solution** - mixture of two or more components that form a homogenous molecular dispersion, the particles are smaller than 1 nanometer. e.g. *sugar or salt solution in water*.

**colloidal dispersion** - represents a system having a particle size intermediate between that of a true solution and a coarse dispersion, roughly 1 to 500 nm.

**coarse dispersion** -the diameter of the particles in emulsions and suspensions for the most part being larger than  $\sim 500$  nm ( $0.5\ \mu\text{m}$ ).

In a binary (two component) solution, the component present in the greatest concentration is referred to as *the solvent*. The compound present in the lesser amount is referred to as *the solute*.

When a *solid* is dissolved in a liquid, the liquid is referred to as the solvent regardless of concentration.

In a *solution* of liquids, water if present is considered to be the solvent.

In *mixture* of liquids which are miscible in all proportions, the terms solute and solvent have little relevance.

### **Electrolytes:**

are substances that form *ions* in solution, *conduct the electric current* and show apparent **irregular** colligative properties, i.e. produce a considerably greater freezing point depression and boiling point elevation than do nonelectrolytes of the same concentration, i.e. hydrochloric acid, sodium sulfate, ephedrine, and phenobarbital.

Electrolytes may be subdivided into *strong electrolytes* and *weak electrolytes* depending on whether the substance is *completely or only partially ionized in water*.

## Physical Properties of Substances

The physical properties of substances can be classified as *colligative*, *additive*, and *constitutive*.

**Colligative properties** depend mainly on the *number of particles* in a solution.

The colligative properties of solutions are *osmotic pressure*, *vapor pressure lowering*, *freezing point depression*, and *boiling point elevation*.

**Additive properties** depend on *the total contribution of the atoms in the molecule* **or** *on the sum of the properties of the constituents in a solution*.

e.g. the molecular weight, that is, the sum of the masses of the constituent atoms.

**Constitutive properties** Any physical or chemical property that depends *on the constitution or structure of the molecule*.. i.e., the arrangements of atoms within the molecule.



Familiar examples of physical properties include *density, color, hardness, melting and boiling points, and electrical conductivity*. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed.

## Types of Solutions

Solute	Solvent	Example
Gas	Gas	Air
Liquid	Gas	Water in oxygen
Solid	Gas	Iodine vapor in air
Gas	Liquid	Carbonated water
Liquid	Liquid	Alcohol in water
Solid	Liquid	Aqueous sodium chloride solution
Gas	Solid	Hydrogen in palladium
Liquid	Solid	Mineral oil in paraffin
Solid	Solid	Gold—silver mixture, mixture of alums

**Strong electrolytes:** Dissociate completely in water. eg, Sodium chloride, hydrochloric acid, sodium sulfate;

**Weak electrolytes:** partially dissociate and is an equilibrium process.  
eg, ephedrine, phenobarbital.

Expression	Symbol	Definition
Molarity	M	Moles (gram molecular weights) of solute in 1 liter of solution
Normality	N	Gram equivalent weights of solute in 1 liter of solution
Molality	<i>m</i>	Moles of solute in 1000 g of solvent
Mole fraction	<i>X</i>	Ratio of the moles of one constituent (e.g., the solute) of a solution to the total moles of all constituents (solute and solvent)
Mole percent	mol %	Moles of one constituent in 100 moles of the solution; mole percent is obtained by multiplying mole fraction by 100
Percent by weight	% w/w	Grams of solute in 100 g of solution
Percent by volume	% v/v	Milliliters of solute in 100 mL of solution
Percent weight-in-volume	% w/v	Grams of solute in 100 mL of solution
Milligram percent	—	Milligrams of solute in 100 mL of solution

Both *molarity* and *normality* have the disadvantage of changing value with temperature because of the *expansion or contraction of liquids* and should not be used when one wishes to study the properties of solutions at *various temperatures*.

Another difficulty arises in the use of molar and normal solutions for the study of properties such as *vapor pressure and osmotic pressure, which are related to the concentration of the solvent*. The volume of the solvent in a molar or a normal solution is not usually known, and it varies for different solutions of the same concentration, depending upon the solute and solvent involved.

### **Mole Fraction**

$$X_1 = n_1 / n_1 + n_2 \quad , \quad X_2 = n_2 / n_1 + n_2$$

For a system of two constituents. Here  $X_1$  is the mole fraction of constituent 1 (solvent),  $X_2$  is the mole fraction of constituent 2 (solute), and  $n_1$  and  $n_2$  are the numbers of moles of the respective constituents in the solution. The sum of the mole fractions of solute and solvent must equal unity.

## Ideal Solutions

In an *ideal solution* there is *no* change in the properties of the components, other than dilution, when they are mixed to form the solution.

*No* heat is *evolved* or *absorbed* during the mixing process, and the final volume of the solution represents an additive property of the individual constituents. In an *ideal solution* the interaction between molecules of the components *does not differ* from the interactions between the molecules of each component

When 100 mL of methanol is mixed with 100 mL of ethanol, the final volume of the solution is 200 mL, and no heat is evolved or absorbed. The solution is nearly *ideal*.

*An ideal solution* or ideal mixture is a solution in which the enthalpy of solution ( $\Delta H_{\text{solution}}=0$ ) is zero; with the *closer to zero* the enthalpy of solution, the more "ideal" the behavior of the solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ( $\Delta S_{\text{solution}}$ ). *Why ?*

**Ideal Solutions** , are the solutions which obey Raoult's Law ( $P_{\text{solution}} = X_{\text{solvent}} P^0_{\text{solvent}}$ ) at every range of concentration and at all temperatures.

We can obtain ideal solutions by mixing two ideal components that are, solute and a solvent having similar molecular size and structure.

For Example, consider two liquids A and B, and mix them. The formed solution will experience several intermolecular forces of attractions inside it, which will be:

- A – A intermolecular forces of attraction
- B – B intermolecular forces of attraction
- A – B intermolecular forces of attraction

The solution is said to be an ideal solution, only when the intermolecular forces of attraction between A – A, B – B and A – B *are nearly equal*.

## Ideal Solutions and Raoult's Law

In an ideal solution, the partial vapor pressure of each volatile constituent is equal to the vapor pressure of the pure constituent multiplied by its mole fraction in the solution. Thus, for two constituents A and B,

$$P_A = P_A^\circ X_A \quad , \quad P_B = P_B^\circ X_B$$

where  $p_A$  and  $p_B$  are the partial vapor pressures of the constituents over the solution when the mole fraction concentrations are  $X_A$  and  $X_B$ , respectively

### Example /Partial Vapor Pressure

What is the partial vapor pressure of benzene and of ethylene chloride in a solution at a mole fraction of benzene of 0.6? The vapor pressure of pure benzene at 50°C is 268 mm, and the corresponding  $p_A^\circ$  for ethylene chloride is 236 mm.

$$P_B = 268 \times 0.6 = 160.8 \text{ mm}$$

$$P_A = 236 \times 0.4 = 94.4 \text{ mm}$$

$$P = P_A + P_B = 160.8 + 94.4 = 255.2 \text{ mm}$$

# Real Solution

In chemistry, a real solution is a homogeneous mixture of at least two chemical substances. A “real” solution differs from a colloidal solution (colloid). According to the concentration of the solute

True Solution	Colloidal Solution
1. True solutions are the mixtures in which the solute and the solvent mix properly in the liquid phase.	1. Colloidal solutions are the mixtures in which the solute is uniformly distributed in the solvent.
2. It is a homogenous solution.	2. It is a heterogeneous solution.
3. The size of the particles is less than 1nm.	3. The size of the particles is 1-1000nm.
4. The diffusion of the particle in this solution is smooth and simple through parchment and filter paper as well.	4. The particles of the colloidal solutions do not diffuse through the parchment paper but it does pass through filter paper.
5. The particles of true solution does not sediment.	5. The particles of a colloid might sediments sometimes.
6. The particle of the true solution are invisible to naked eye.	6. The particles of the colloidal solution are visible through an electron microscope, but not through naked eye.
7. It is a transparent solution.	7. It is a translucent solution.
8. Example: Sugar solution in water	9. Example: Starch dissolved in water.



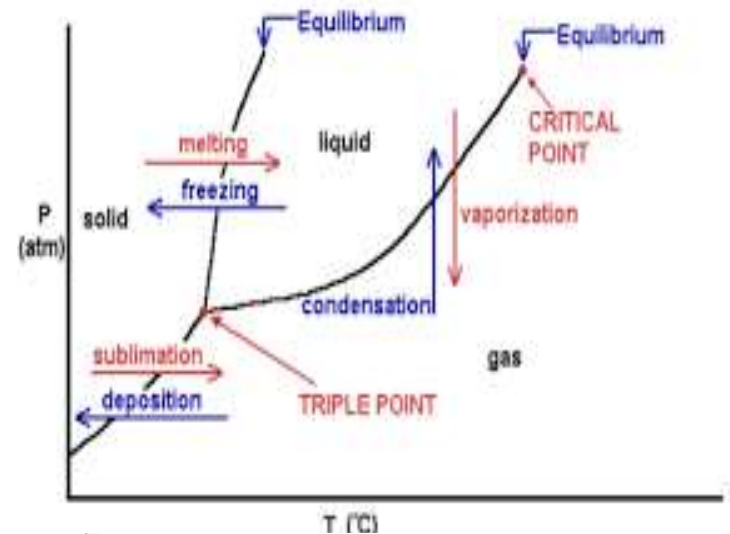
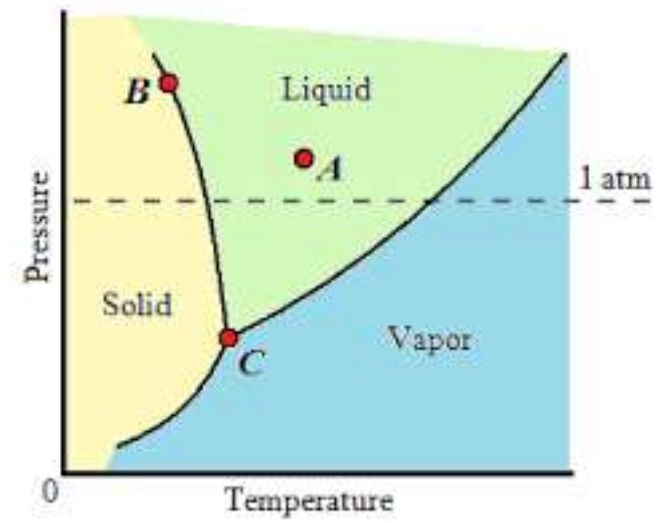


# Third Lecture

## Phase Equilibria & Phase Rule

Physical Pharmacy – I  
2<sup>nd</sup> Class 1<sup>st</sup> Semester  
2022 - 2023

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$$F = C - P + 2$$

# Equilibrium

They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C).

## physical and chemical equilibrium

a physical equilibrium is an equilibrium in which the physical state of the system *does not change* whereas chemical equilibrium is the equilibrium state in which the concentrations of reactants and products is not changed with time.

## types of physical equilibrium

### 1.Solid-Liquid Equilibrium

For example, the equilibrium between ice and water is a physical equilibrium because there are no chemical reactions taking place

### 2.Liquid-Vapour Equilibrium

The equilibrium between water and steam is a physical equilibrium in which no chemical reactions are taking place.

### 3.Solid-Vapour Equilibrium

This type of physical equilibrium can be observed in substances that undergo sublimation.

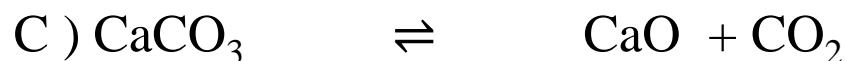
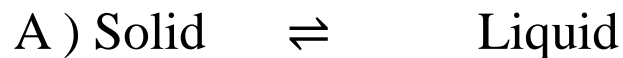
## Phase

*is physically distinct portion of a system having its own boundary*

- ✓ Every pure material is considered to be a phase
- ✓ If more than one phase is present in a given system, each will have its own distinct properties, and a boundary separating the phases will exist across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics
- ✓ Sometimes, a single-phase system is termed *homogeneous*
  - 1) The mixture of ice and water = *have two* phase which is solid and liquid
  - 2) The mixture of oxygen gas and nitrogen gas = have *one phase* which is gas phase (the system is homogeny)
  - 3) The mixture of oil and water = have *2 same phase(liquid)*. Oil and water are not homogeny and have the boundaries to separate both phase
  - 4)  $\text{CaCO}_{3(s)} \longrightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)} = 3 \text{ phase (2 solid, 1 gas)}$

**H . W 8** Circle the correct answers.

1 . The following one is example to physical equilibrium



2 . Increase in the pressure of the following equilibrium  $\text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_2\text{O} (\text{g})$  ,  
result in :

A ) Formation of more  $\text{H}_2\text{O} (\text{l})$

B ) Formation of more  $\text{H}_2\text{O} (\text{g})$

C ) Increase in b.p of  $\text{H}_2\text{O} (\text{l})$

D ) Decrease in b.p of  $\text{H}_2\text{O} (\text{l})$

## Component

A component is a chemically independent constituent of a system . The number of components ( $C$ ) in a system is the minimum number of independent species necessary to define the composition of all the phases present in the system

### \* Gases

- Gaseous state always a single phase → mixed at atomic or molecular level

### \* Liquids

► Liquid solution is a single phase → e.g. **NaCl in H<sub>2</sub>O**

► Liquid mixture consists of two or more phases

→ e.g. **Oil in water** (*no mixing at the atomic/molecular level*)

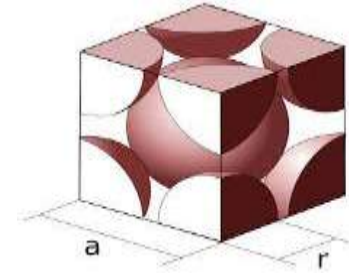
### \* Solids

• In general due to several compositions and crystals structures many phases are possible

• For the same composition different crystal structures represent different phases. *E.g. Fe (BCC) and Fe (FCC) are different phases*

The terms BCC and FCC are used to name two different arrangements of crystalline structures.

*BCC stands for body-centered cubic structure whereas FCC stands for face-centered cubic structure*



- For the same crystal structure different compositions represent different phases.

*e.g. in Au-Cu alloy 70%Au-30%Cu & 30%Au-70%Cu are different phases*

## phase equilibrium

the heterogeneous equilibrium composed of one or more substances capable of moving from one phase to another, without a chemical reaction, such as the transition of water from a liquid state to a gaseous state and visa versa:



A phase equilibrium occurs between a liquid and its vapor, or between a solid and a liquid, or between a solid and a vapor, or between vapor and liquid and a solid together.

Under certain conditions of *pressure and temperature*, and any change in these conditions leads to a *shift in the equilibrium* from one phase to the other.

The phase rule is an important relationship in physical chemistry and depends on the second law of thermodynamics (*hot things always cool unless you do something to stop them*). that disorder, characterized as a quantity known as *entropy* .

## Degree of Freedom or Variance

■ *In physics & chemistry* , a **degree of freedom** is an independent *physical parameter* in the formal description of the state of a *physical system* . The set of all states of a system is known as the system's *phase space* , and the degrees of freedom of the system are the *dimensions* of the phase space.

properties of the phase in a particular system

- 1 . do not depend on the amount of matter present (**Intensive properties**), such as temperature, pressure, and density
  - 2 .It depends on the amount of matter (**Extensive properties**) such as weight and size.
- The **degrees of freedom for a particular system** are known as **independent and dependent variables** , degrees of freedom have the freedom to vary,. The number of degrees of freedom is denoted by the symbol (**F**).

The rule of systems in equilibrium expresses the relationship between the number of phases, the number of independent components, and the number of degrees of freedom.

Mathematically with the following equation:

$$\mathbf{F} = \mathbf{C} - \mathbf{P} + 2 \text{ or } \mathbf{F} - \mathbf{C} + \mathbf{P} = 2 \text{ or } \mathbf{F} + \mathbf{P} = \mathbf{C} + 2$$



where **F** represents the number of degrees of freedom **or** (Gibbs phase rule ).

**P** The number of phases.

**C** The number of *independent* components.

This rule does not include any limitations on the nature of the substance and is effective provided that it is affected by *only heat, pressure, and concentration*

If we assume that we have a system that contains one component in gas phase (water vapor) and by apply phase rule ,the degrees of freedom for such a system are:

$$F = C - P + 2 = 1 - 1 + 2 \quad \therefore F = 2$$

This system has two degrees of freedom or it is a system with two variables, that is, to define the state of this system completely, we need to specify each of pressure and temperature

When an equilibrium occurs between two phases, for example, ice and water:

$$F = 1 - 2 + 2 \quad \therefore F = 1$$

That is, we need *temperature or pressure* in order to define this system, so the system has one degree of freedom or has a variable one.

# PHASE RULES

Also known as Gibbs phase rule

$$F = C - P + 2$$

Degree of freedom or the number of independent variables

Number of component

The number of phase

2 variables (temperature and pressure)

For a system in equilibrium

The phase rule

$$F = C - P + 2$$

$$F - C + P = 2$$

## Phase rule uses:

### One component system

In order to clarify the phase rule, we study in the following some systems and start with the simplest one, which is the system composed of one pure body. And by applying Phase rule for this type of system we get

$$F = C - P + 2 = 1 - P + 2 \quad \therefore F = 3 - p$$

\*\*\*\* Since the number of degrees of freedom cannot be negative

In mono component, it is not possible to obtain more than three types of mono-systems, which are a single-phase system (such as steam water), a two-phase system (such as ice and water), and a three-phase system (such as ice, water and steam).

**A - Single phase system**  $1 = P, 1 = C$

$$F = C - P + 2 \longrightarrow F = 1 - 1 + 2 = 2$$

That is, there are **two** independent variables whose value must be determined in order to determine the state of the system. For example, a pure water vapor system where its state is determined referring to the pressure and temperature of the system, where the temperature can be changed within certain limits without changing the pressure and vice versa, because the pressure and temperature are variable

## B - Two-phase system $2 = P, 1 = C$

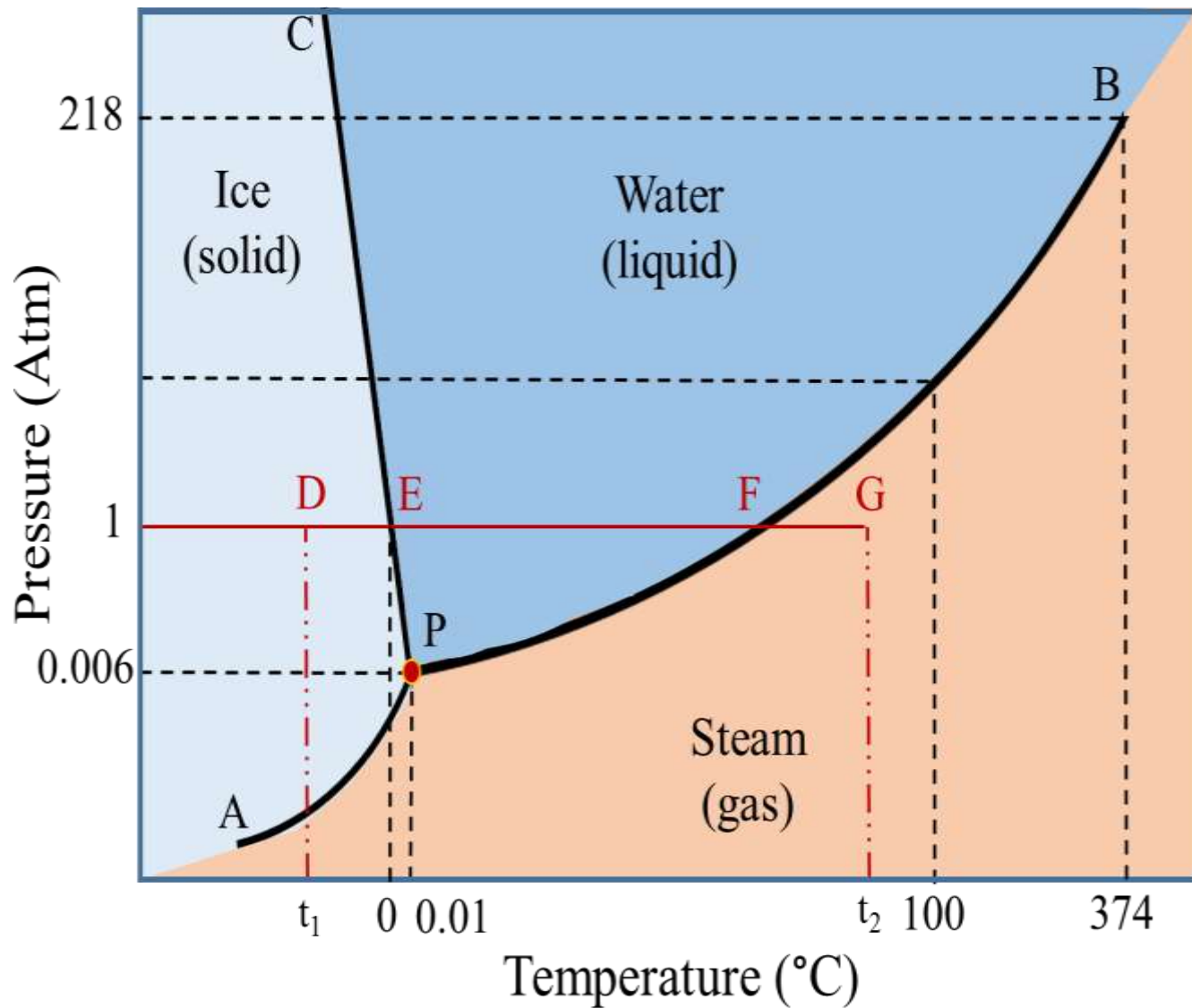
$$F = C - P + 2 \longrightarrow F = 1 - 2 + 2 = 1$$

An example is a system consisting of a fluid balanced with steam in this system, determining the temperature is sufficient to determine the value of the saturated vapor pressure, **because** *each temperature has a specific saturated vapor pressure* thus, when the temperature changes slightly, the equilibrium shifts so that part of one of the phases moves to the other to get the state of equilibrium again

## C- Three-phase system $3 = P, 1 = C$

$$F = C - P + 2 \longrightarrow F = 1 - 3 + 2 = 0$$

There are **no** degrees of freedom, so the equilibrium of the system does not occur except at a certain *temperature and pressure*, and any change in temperature or pressure, it leads to the demise of one of the phases. For example, the presence of the three phases of water (ice, liquid and vapor) in a state of heat or pressure equilibrium at a constant temperature of  $0.01^\circ \text{C}$  ... and a constant pressure of  $610.6 \text{ N/m}^2$



The diagram divided into *three regions*, APB, CPB, and APC, which show the vapor, liquid, and snow regions, respectively. where there is only a single phase within each of these regions, and using the phase rule:  $F = 1 - 1 + 2 = 2$

We find that these areas have *two degrees of freedom*, and this means that to fully define any point in these areas, it is necessary to specify temperature and pressure.

*The curve PA* in the above figure shows the values of pressures and temperatures at which the solid and vapor phases exist together in equilibrium, (curve of the vapor pressure of solid ).

*The curve PB* represents the temperatures and pressures at which both liquid and vapor phases exist in equilibrium, (*vapor pressure curve of a liquid*). At higher temperatures, no equilibrium occurs between liquid and vapor, where the equilibrium curve between liquid and vapor ends at point **B**, so the temperature corresponding to point **B** is known as the critical temperature of vapor and is equal to  $473^{\circ}\text{C}$ .

*The curve PC* also gives the values of pressures and temperatures at which the solid and liquid phases exist in a state of equilibrium (indicate the melting point and pressure function)

Thus, it appears from the three curves that *each temperature degree corresponds to a certain pressure* and vice versa. When the phase is in the state in equilibrium, we need the *temperature or pressure* to locate any point on the three curves (i.e. for the system one degree of freedom). This is consistent with the phase rule where:

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 2 + 2 = 1 \end{aligned}$$

The graph shows that the three curves intersect at point P only, where this point is known as the *triple point*. It is the only point where the three phases are *in equilibrium*. It should be noted that the three phases can be present in equilibrium only under certain conditions, which if any of them changes (temperature and pressure) even if the change is small, it will deviate Equilibrium and the three phases will not exist together. Thus, the degree of freedom of the system *at point P. is equal to zero* and can obtaining the same result when applying the phase rule

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 = 0 \end{aligned}$$



## H . W 9 Circle the correct answers.

1. Gibbs phase rule for general system:

- (a)  $P+F=C-1$
- (b)  $P+F=C+1$
- (c)  $P+F=C-2$
- (d)  $P+F=C+2$

2. In a single-component condensed system, if degree of freedom is zero, maximum number of phases that can co-exist \_\_\_\_\_.

- (a) 0
- (b) 1
- (c) 2
- (d) 3

3. The degree of freedom at triple point in unary diagram for water \_\_\_\_\_.

- (a) 0
- (b) 1
- (c) 2
- (d) 3

4. What is the point at which all the three phases of a system exist?

- a) Triple point
- b) Sublimation point
- c) Vapor point
- d) Eutectic point

5. Select a non-homogeneous system from the following.

- a) Salt solution
- b) Sugar solution
- c) Glucose in water
- d) Saturated solution of NaCl

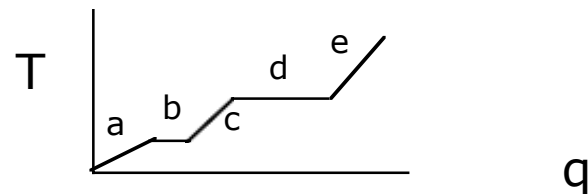
6. The part whose physical and chemical properties are completely equal and homogenous is called

- a) Phase
- b) interface
- c) Surface
- d) all of the above

## H . W 10 :

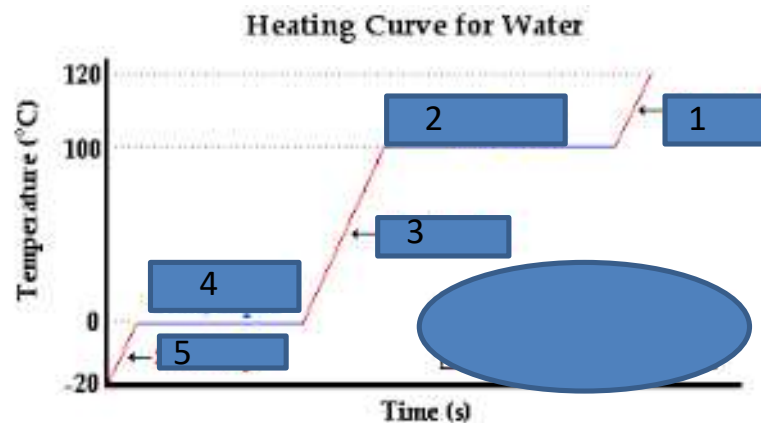
Region “e” on the heating curve shown (Temperature versus heat, “q”) corresponds to:

- a) pure gas increasing in temperature
- b) liquid increasing in temperature
- c) solid increasing in temperature
- d) solid melting
- e) liquid boiling



H . W 11 : what are the numbers 1 , 2 , 3 , 4 , 5 represent to

- 1 . .....
- 2 . .....
- 3 . .....
- 4 . .....
- 5 . .....



## H . W 12 :

In which phase does the substance whose phase diagram is shown below exist at 0°C and 1.0 atm pressure?

- a. gas      b. liquid
- c. solid    d. supercritical fluid

