Thermodynamic

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Lec 1

<u>Thermodynamic :</u>

is the study which is concerned with the ways in which energy stored in body and how energy transformation which involve heat and work take place.

It deals with the quantitative relationships of interconversion of the various forms of energy, including mechanical, chemical, electric, and radiant energy.

Thermodynamic properties include Temperature, pressure, mass, and volume

Q/ what is heat and what is temperature ?

Temperature : is a measure of hotness or coldness , its considered as a thermodynamic property , that is the measure of energy contained in amass

Heat : the form of energy that is transferred from one place to another as a consequence of the temperature difference between the two places

Numerically it can be expressed by (**Joule**) or (**Calorie**)

If two bodies are in thermal equilibrium with a third body , they are in thermal equilibrium with each other , this simple fact is known as (Zeroth law)

<u>Note :</u> the work of thermometer depends upon this law

A thermodynamic system is simply defined as a quantity of matter or a region in space chosen for study

The region outside the system is called (**surrounding**)

The physical (or virtual) barriers that separate the system from its surrounding is called (**Boundary**)

It is useful at this point to distinguish the attributes of the three types of systems that are frequently used to describe thermodynamic properties:

1/ **open system :** can exchange both energy and matter with its surrounding

2/ **closed system :** can exchange energy but not matter with its surrounding

3/ **isolated system :** that cant exchange neither matter nor energy .

For instance, if two immiscible solvents, water and carbon tetrachloride, are confined in a closed container and iodine is distributed between the two phases, each phase is an open system, yet the total system made up of the two phases is closed because it does not exchange matter with its surroundings.

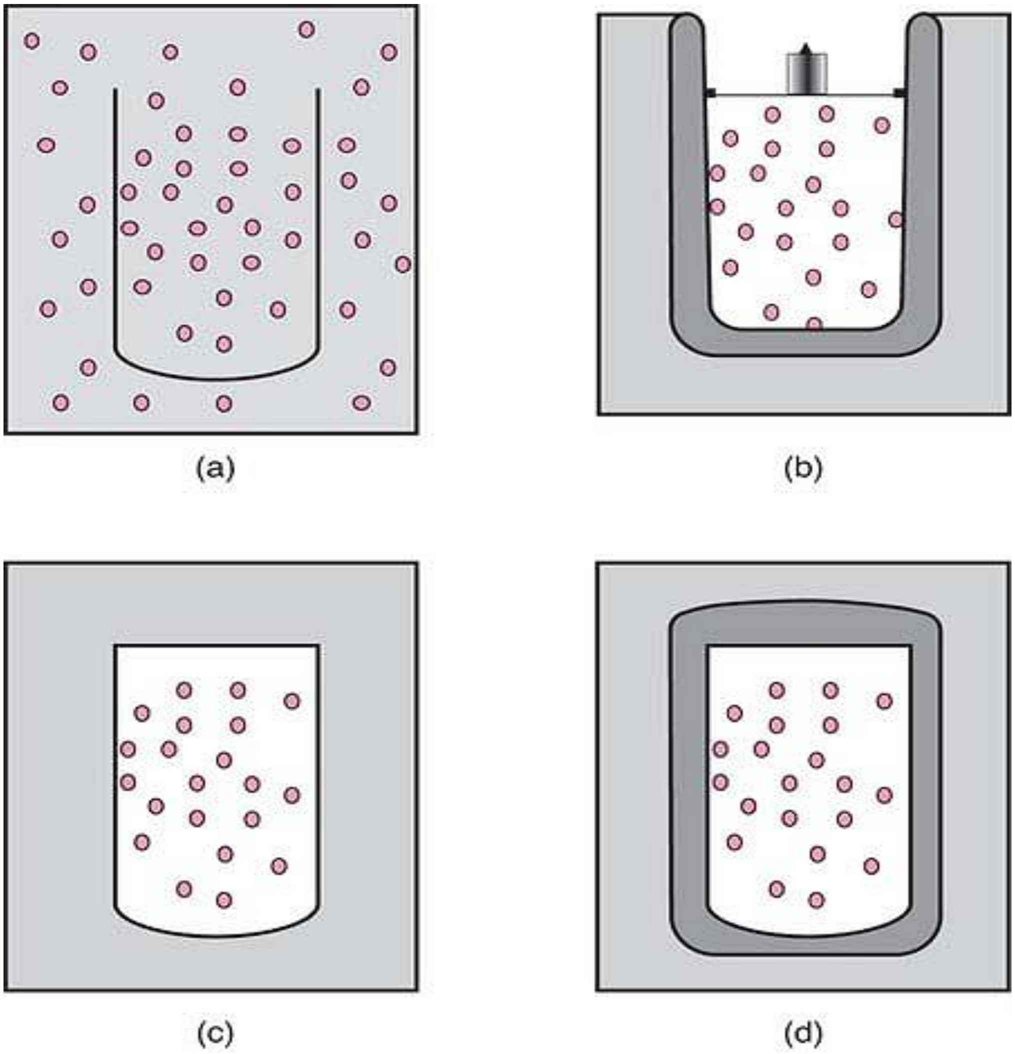


Fig. Examples of thermodynamic systems. (a) An open system exchanging mass with its surroundings; (b) a closed system exchanging work with its surroundings; (c) a closed system exchanging heat with its surroundings; (d) an isolated system, in which neither work nor heat can be exchanged through boundaries.

There are many kinds of processes that can be carried out in thermodynamic system

1- *Isothermal process:* are those processes in which the system is maintained at a constant temperature , the isothermal system requires either open or closed system
   An isothermal reaction may be carried out by placing the system in a large constant-temperature bath so that heat is drawn from or returned to it without affecting the temperature significantly.
2- *Adiabatic process :* is the one in which no heat enter or leave the system , this process require an isolated system and the temperature of the system may be changed
   A reaction carried on inside a sealed Dewar flask or “vacuum bottle” is adiabatic because the system is thermally insulated from its surroundings.
3- *Spontaneous process :* is the one that occur naturally and take place with out intervention (ex. If a filled balloon is punctured , much of the contained gas is transferred to the atmosphere)

Thermodynamics is based on three “laws” or facts of experience that have never been proven in a direct way, in part due to the ideal conditions for which they were derived. Various conclusions, usually expressed in the form of mathematical equations, however, may be deduced from these three principles, and the results consistently agree with observations.

First Law of Thermodynamics

The first law is a statement of the conservation of energy. It states that, **although energy can be transformed from one kind into another, it cannot be created or destroyed**. Put in another way, **the total energy of a system and its immediate surroundings remains constant during any operation**.

This statement follows from the fact that the various forms of energy are equivalent, and when one kind is formed, an equal amount of another kind must disappear. The relativistic picture of the universe expressed by Einstein's equation

$$\textbf{Energy = (mass change) * (velocity of light)}^2$$

suggests that matter can be considered as another form of energy, 1 g being equivalent to 9 × 1013 joules. These enormous quantities of energy are involved in nuclear transformations but are not important in ordinary chemical reactions.

According to the first law, the effects of Q (heat absorbed) and W (work) in a given system during a transformation from an initial thermodynamic state to a final thermodynamic state are related to an intrinsic property of the system called the **internal energy**, defined as

$$\Delta E = E2 - E1 = Q + W$$

where E_2 is the internal energy of the system in its final state and E_1 is the internal energy of the system in its initial state. The change in internal energy ΔE is related to Q and W transferred between the system and its surroundings the equation also expresses the fact that work and heat are equivalent ways of changing the internal energy of the system.

Work of Expansion Against a Constant Pressure

We first discuss the work term. Because of its importance in thermodynamics, initial focus is on the work produced by varying the volume of a system (i.e., expansion work or compression work) against a constant opposing external pressure, P_{ex}. Imagine a vapor confined in a hypothetical cylinder fitted with a weightless, frictionless piston of area A. If a constant external pressure P_{ex} is exerted on the piston, the total force is $P_{ex} \times A$ because P = Force/Area. The vapor in the cylinder is now made to expand by increasing the temperature, and the piston moves a distance h. The work done against the opposing pressure in one single stage is

$$\mathbf{W = - P_{ex} \times A \times h}$$

Now A × h is the increase in volume, $\Delta V = V_2 - V_1$, so that, at constant pressure,

$$\mathbf{W = - p\, \Delta V = - P_{ex}\, (v2 - v1)}$$

Lec 2

Reversible Processes

The hypothetical case of water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston. The apparatus is immersed in a constant-temperature bath maintained at the same temperature as the water in the cylinder.

By definition, the vapor pressure of water at its boiling point is equal to the atmospheric pressure, represented by a set of weights equivalent to the atmospheric pressure of 1 atm; therefore, the temperature is 100°C. The process is an isothermal one, that is, it is carried out at constant temperature.

Now, if the external pressure is decreased slightly by removing one of the infinitesimally small weights, the volume of the system increases and the vapor pressure falls infinitesimally. Water then evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant and bring about the vaporization. During this process, a heat exchange between the system and the temperature bath will occur.

On the other hand, if the external pressure is increased slightly by adding an infinitesimally small weight, the system is compressed and the vapor pressure also rises infinitesimally. Some of the water condenses to reestablish the equilibrium vapor pressure, and the liberated heat is absorbed by the constant-temperature bath.

If the process could be conducted infinitely slowly so that no work is expended in supplying kinetic energy to the piston, and if the piston is considered to be frictionless so that no work is done against the force of friction, all the work is used to expand or compress the vapor. Then, because this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be reversible. If the pressure on the system is increased or decreased rapidly or if the temperature of the bath cannot adjust instantaneously to the change in the system, the system is not in the same thermodynamic state at each moment, and the process is **irreversible**.

Although no real system can be made strictly reversible, some are nearly so. One of the best examples of reversibility is that involved in the measurement of the potential of an electrochemical cell using the **potentiometric method**.

Maximum Work

The work done by a system in an isothermal expansion process is at a maximum when it is done reversibly. This statement can be shown to be true by the following argument. No work is accomplished if an ideal gas expands freely into a vacuum, where P = 0, because any work accomplished depends on the external pressure. As the external pressure becomes greater, more work is done by the system, and it rises to a maximum when the external pressure is infinitesimally less than the pressure of the gas, that is, when the process is reversible. Of course, if the external pressure is continually increased, the gas is compressed rather than expanded, and work is done ***on*** the system rather than ***by*** the system in an isothermal reversible process.

So from the ideal gas law **$PV= nRT$**

Where n is the number of moles of gas

R is the gas constant

$$W= - p \Delta V$$

$$W= - nRT (\Delta V/V)$$

$$W= - nRT \ln(V2/V1)$$

And from boyles law **$V2/V1=P1/P2$**

Then **$W_{max} = - nRT \ln(P1/P2)$**

Then the maximum work done for a system that is expanded in reversible fashion is where P_{ex} was replaced by P because the external pressure is only infinitesimally smaller than the pressure of the system. In similar fashion, it can be deduced that the minimum work in a reversible compression of the system will also lead to equation above, because at each stage P_{ex} is only infinitesimally larger than P.

Note that in expansion, $V_2 > V_1$, and $\ln(V_2/V_1)$ is a positive quantity; therefore, the work is done by the system, so that its energy decreases (**negative sign**). When the opposite is true, $V_2 < V_1$, and $\ln(V_2/V_1)$ is negative due to gas compression, work is done on the system, so that its energy increases (**positive sign**). The process itself determines the sign of W and ΔE.

Heat content (enthalpy):

When the work of expansion is done at constant pressure (in most chemical studies where the reaction vessel is open to the atmosphere and P= 1 atm approximately), so by using the equation, $W = -P\,\Delta V = -P(V_2 - V_1)$ and under these conditions, the first law can be written as

$$\Delta E = Q_p - P(V_2 - V_1)$$

$$(E_2 - E_1) = Q_p - P(V_2 - V_1)$$

where Q_P is the heat absorbed at constant pressure. Rearranging the equation results in

$$Qp = (E_2 + PV_2) - (E_1 + PV_1)$$

The term E + PV is called the heat content or enthalpy (H), and the increase in enthalpy, ΔH, is equal to the heat absorbed by the system at **constant pressure**. It is the heat required to increase the internal energy and to perform the work of expansion, as seen by substituting H in equation above:

$$Q_p = H_2 - H_1 = \Delta H$$

and the first law equation become:

$$\Delta H = \Delta E + P\,\Delta V$$

When a chemical process is carried out at constant pressure, the heat evolved or absorbed, per mole, can be identified as ΔH (this heat is independent of the number of steps and the mechanism of the reaction. It depends only on the initial and final conditions. specific symbols and names have been devised to identify ΔH with particular processes.

For example, the heat absorbed by solid on melting is called the heat of fusion and labeled ΔH_f or ΔH_m.

For a chemical reaction ΔH is called a heat of reaction. The heat of reaction may be positive (heat is absorbed) called endothermic or negative (heat is evolved) called exothermic.

ΔH^o is the heat content at standard condition (25 C^o, 1 atm pressure)

ΔH is expressed as cal/mole.

In solution reactions, the P Δ V terms are not significant, so that ΔH [congruent] ΔE. This close approximation does not hold, however, for reactions involving gases.

Table: Modified First-Law Equations for Processes Occurring Under Various Conditions

Specific condition		**Process**	**Common means for establishing the condition**	**Modification for the first law dE=dq + dw under the stated condition**
Constant heat	$dq = 0$	Adiabatic	Insulated vessel	$dE = dw$
Reversible process at constant temperature	$dT = 0$	isothermal	Constant temp bath	$dW = W_{max}$
Constant volume	$dV = 0$	Isometric (isochoric)	Closed vessel of constant volume	$dW=-pdV=0$ $dE=Qv$
Constant pressure	$dP = 0$	isobaric	Reaction occurring in an open container at constant atmospheric pressure	$dH = Qp$ $dE=dH-Pdv$

Heat capacity: The molar heat capacity C , is defined as the heat q required to raise the temperature of one mole of the substance by one degree

$$C = q/dT$$

Differential and integral heat of solution: When a mole of a solute dissolved, the heat absorbed or liberated is not a constant quantity but varies with the concentration of the solution.

Thermochemistry : It is the study that deals with the heat changes accompanying isothermal chemical reactions at constant pressure or volume, from which values of ΔH or ΔE can be obtained.

Heat of Formation

For any reaction represented by the chemical equation

aA + bB = cC + dD

the enthalpy change can be written as

$$\Delta H = \sum \overline{H}_{\text{products}} - \sum \overline{H}_{\text{reactants}}$$
$$\Delta H = c\overline{H}_{\text{C}} + d\overline{H}_{\text{D}} - a\overline{H}_{\text{A}} - b\overline{H}_{\text{B}}$$

where $\overline{H}$ = enthalpy per mole (called the molar enthalpy) and a, b, c, and d are stoichiometric coefficients. It is known that only the molar enthalpies of compounds, either as reactants or products, contribute to the change of enthalpy of a chemical reaction.

Hess's Law and Heat of Combustion

It is not possible to directly measure the heats of formation of every known compound in equation . Incomplete or side reactions often complicate such determinations. However, Hess showed that because ΔH depends only on the initial and final states of a system, thermochemical equations for several steps in a reaction could be added and subtracted to obtain the heat of the overall reaction.

The principle is known as Hess's law of constant heat summation and is used to obtain heats of reaction that are not easily measured directly.

The Efficiency of a Heat Engine

An important consideration is that of the possibility of converting heat into work. The spontaneous character of natural processes and the limitations on the conversion of heat into work constitute the second law of thermodynamics. Falling water can be made to do work owing to the difference in the potential energy at two different levels, and electric work can be done because of the difference in electric potential. A heat engine (such as a steam engine) likewise can do useful work by using two heat reservoirs, a “**source**” and a “**sink**,” at two different temperatures. Only part of the heat at the source is converted into work, with the remainder being returned to the sink (which, in practical operations, is often the surroundings) at the lower temperature. The fraction of the heat, Q, at the source converted into work, W, is known as the efficiency of the engine:

$$\text{Efficiency} \equiv \frac{W}{Q}$$

The efficiency of even a hypothetical heat engine operating without friction cannot be unity because W is always less than Q in a continuous conversion of heat into work according to the second law of thermodynamics.

Imagine a hypothetical steam engine operating reversibly between an upper temperature T hot and a lower temperature T cold. It absorbs heat Q hot from the hot boiler or source, and by means of the working substance, steam, it converts the quantity W into work and returns heat Q cold to the cold reservoir or sink. Carnot proved that the efficiency of such an engine, operating reversibly at every stage and returning to its initial state (cyclic process), could be given by the expression

$$\frac{W}{Q_{\text{hot}}} = \frac{Q_{\text{hot}} - Q_{\text{cold}}}{Q_{\text{hot}}}$$

It is known that heat flow in the operation of the engine follows the temperature gradient, so that the heat absorbed and rejected can be related directly to temperatures. Lord Kelvin used the ratios of the two heat quantities Q hot and Q cold of the Carnot cycle to establish the Kelvin temperature scale:

$$\frac{Q_{\text{hot}}}{Q_{\text{cold}}} = \frac{T_{\text{hot}}}{T_{\text{cold}}}$$

By combining equations, we can describe the efficiency by

$$\text{Efficiency} = \frac{Q_{\text{hot}} - Q_{\text{cold}}}{Q_{\text{hot}}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

It is observed from equation that the higher T hot becomes and the lower T cold becomes, the greater is the efficiency of the engine. When T cold reaches absolute zero on the Kelvin scale, the reversible heat engine converts heat completely into work, and its theoretical efficiency becomes unity. This can be seen by setting T cold = 0. Because absolute zero is considered unattainable, however, an efficiency of 1 is impossible, and heat can never be completely converted to work.

If T hot = T cold, the cycle is isothermal and the efficiency is zero, confirming the earlier statement that heat is isothermally unavailable for conversion into work.

Lec 3

Example

One mole of water in equilibrium with its vapor is converted into steam at 100°C and 1 atm. The heat absorbed in the process (i.e., the heat of vaporization of water at 100°C) is about 9720 cal/mole. What are the values of the three first-law terms Q, W, and ΔE?

The amount of heat absorbed is the heat of vaporization, given as 9720 cal/mole. Therefore,

Q = 9720cal/mole

The work W performed against the constant atmospheric pressure is obtained by using equation W = -nRT ln(V_2/V_1). Now, V_1 is the volume of 1 mole of liquid water at 100°C, or about 0.018 liter. The volume V_2 of 1 mole of steam at 100°C and 1 atm is given by the gas law, assuming that the vapor behaves ideally:

$$V_2 = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.6 \text{ liters}$$

It is now possible to obtain the work,

W = -(1 mole)(1.9872 cal/K mole)(398.15 K) ln (30.6/0.018)

W = -5883 cal

The internal energy change ΔE is obtained from the first-law expression,

ΔE = 9720 - 5883 = 3837 cal

Example

A steam engine operates between the temperatures of 373 and 298 K. (a) What is the theoretical efficiency of the engine? (b) If the engine is supplied with 1000 cal of heat Q_{hot}, what is the theoretical work in ergs?

$$\text{Efficiency} = \frac{W}{Q_{\text{hot}}} = \frac{373 - 298}{373} = 0.20, \quad \text{or} \quad 20\%$$

$$W = 1000 \times 0.20 = 200 \text{ cal}$$

$$200 \text{ cal} \times 4.184 \times 10^7 \text{ ergs/cal} = 8.36 \times 10^9 \text{ ergs}$$

Entropy (S) and Disorder:

Entropy can be defined as the measure of randomness or disorder in the universe. Is a quantitative measure of increasing the probability of spontaneous process. From statistical mechanics we had seen that ΔS increases during a spontaneous process, so these results give us :

$\Delta S < 0$ for non spontaneous processes

$\Delta S = 0$ for a system at equilibrium

$\Delta S > 0$ for spontaneous (reversible) processes

Example: conceder a container with rigid walls. Only thermal interactions change the energy. If the system initially contains two phases, ice and water, then after some passage of time the ice will melt as heat is transferred into the system. All systems tend to an increase freedom of motion (increase in entropy). The ice is more ordered , so that the final state (liquid) has higher entropy than the initial state (solid).

Second law of thermodynamic

Spontaneous processes always proceeds in the direction of increased the entropy; when the system finally reaches the equilibrium, the net entropy change undergone by the system and its surrounding is equal to zero

Examples:

1- Heat flows spontaneously only from hot to cold places
2- Gases expand naturally from higher to lower pressure
3- Heat does not spontaneously flow from a cold body to a hot body.
4- Spontaneous processes are not thermodynamically reversible.
5- It is impossible to convert heat into work by means of a constant temperature cycle.
6- All natural processes are accompanied by a net gain in entropy of the system and its surroundings.

Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a pure crystalline substance is zero at absolute zero because the crystal arrangement must show the greatest orderliness at this temperature. As a consequence of the third law, the temperature of absolute zero (0 K) is not possible to reach even though sophisticated processes that use the orientation of electron spins and nuclear spins can reach very low temperatures of 2×10^{-3} and 10^{-5} K, respectively.

The third law cannot be applied to the super-cooled liquids because their entropy at 0^{o} K is probably not zero.

States of matter

Binding Forces Between Molecules

For molecules to exist as aggregates in gases, liquids, and solids, intermolecular forces must exist. Like intramolecular bonding energies found in covalent bonds, intermolecular bonding is largely governed by electron orbital interactions. The key difference is that covalency is not established in the intermolecular state. **Cohesion**, or the attraction of like molecules, and **adhesion**, or the attraction of unlike molecules, are manifestations of intermolecular forces. Repulsion is a reaction between two molecules that forces them apart.

For molecules to interact, these forces must be balanced in an energetically favored arrangement. Briefly, the term energetically favored is used to describe the intermolecular distances and intramolecular conformations where the energy of the interaction is maximized on the basis of the balancing of attractive and repulsive forces. At this point, if the molecules are moved slightly in any direction, the stability of the interaction will change by either increase in attraction (when moving the molecules away from one another) or an increase in repulsion (when moving the molecules toward one another).

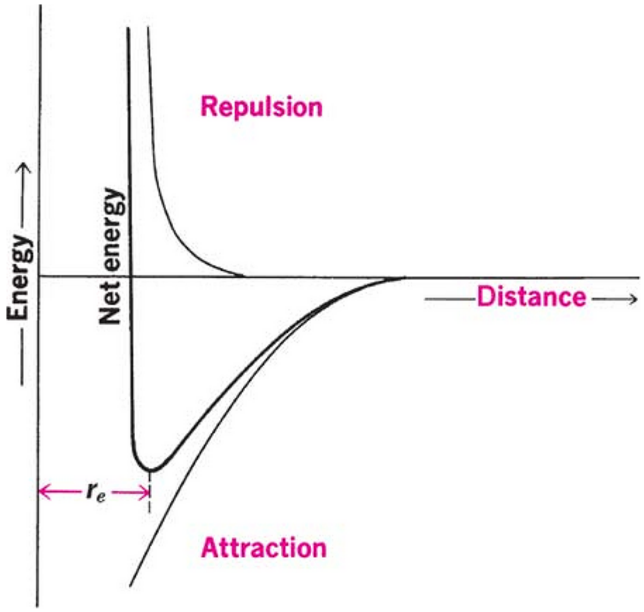
Knowledge of these forces and their balance (equilibrium) is important for understanding not only the properties of gases, liquids, and solids, but also interfacial phenomena, flocculation in suspensions, stabilization of emulsions, compaction of powders in capsules, dispersion of powders or liquid droplets in aerosols, and the compression of granules to form tablets.

Repulsive and Attractive Forces

When molecules interact, both repulsive and attractive forces operate. As two atoms or molecules are brought closer together, the opposite charges and binding forces in the two molecules are closer together than the similar charges and forces, causing the molecules to attract one another. The negatively charged electron clouds of the molecules largely govern the balance (equilibrium) of forces between the two molecules. When the molecules are brought so close that the outer charge clouds touch, they repel each other like rigid elastic bodies. Thus, attractive forces are necessary for molecules to cohere, whereas repulsive forces act to prevent the molecules from interpenetrating and annihilating each other.

i.e. the importance of these forces is that the attraction forces are necessary for molecules to cohere each other and repulsive forces are necessary in order the molecules don’t destroy each other.

Stable matter : when the attractive forces are in equilibrium with repulsive forces



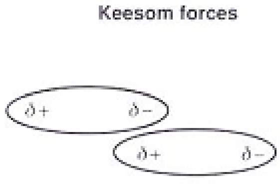
Repulsive and attractive energies and net energy as a function of the distance between molecules.

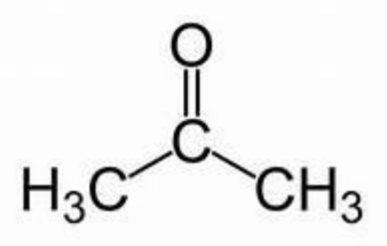
Types of intermolecular forces

Vander waal's forces

Van der Waals forces relate to nonionic interactions between molecules, yet they involve charge–charge interactions and it includes three types

a- Dipole _ dipole forces (Keesom forces) (1-7 kcal / mole)
occur between two polar molecules when came together where they arrange themselves so that the partial positive charge become toward the partial negative charge.
Example : Acetone

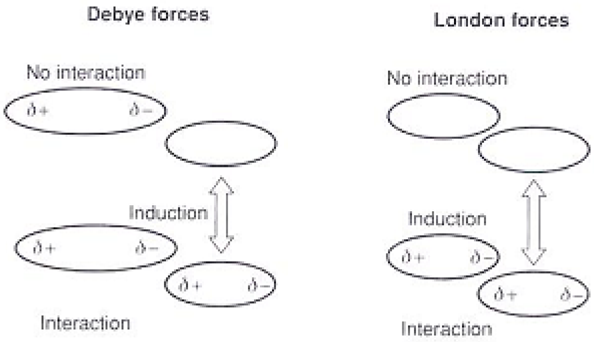




b- Dipole-induced dipole(Debye interactions) (1-3 kcal / mole)

In this case polar molecule can produce temporarily electric dipole from non polar molecule that is easily polarized.

c- Induced dipole _ induced dipole forces (London attractions) (0.5 -1 kcal / mole)



The attractive forces between non polar molecules when they come close to each other they induce each other to become dipole molecules. These forces are originated from molecular internal vibration, this vibration will induce dipole in the neighboring atom of other molecules.

One of the applications of this bond is the condensation of non polar gas.

Ion _ dipole forces and Ion-Induced Dipole Forces

In addition to the dipolar interactions known as van der Waals forces, other attractions occur between polar or nonpolar molecules and ions. These types of interactions account in part for the solubility of ionic crystalline substances in water; the cation, for example, attracts the relatively negative oxygen atom of water and the anion attracts the hydrogen atoms of the dipolar water molecules.

a- Ion – dipole forces (1-7 kcal/mole):

It occurs between ionic and polar molecules because ions have strong charge so a partial charge end of the dipole will be attracted to the ion

Example is the solubility of sodium chloride each sodium ion will attract the negative partial charge (oxygen) of water molecule and chloride ion will attract the positive partial charge (hydrogen) of water molecules.

b- Ion- induced dipole forces :

It occurs between ionic molecules and nonpolar molecules

Example:

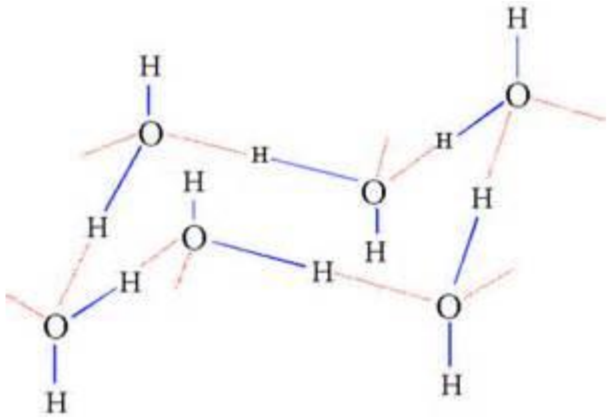
$$I_2 + K^+I^- = K^+I_3^-$$

So we add potassium iodide to iodine preparation in order to form a soluble complex in which the K^+ ion will induce a dipole in the non polar iodine molecule and attract to it by ion- induced dipole attraction.

Hydrogen bonds (2-7 kcal/mole) :

Interaction between molecules containing hydrogen atom and strongly electronegative atoms (N , F, O)because of the small size of hydrogen atom; it can move close to the electronegative atom and form a hydrogen bond (hydrogen bridge).

Example: water



(structure of water)

The H – bond in water is responsible for most of unusual properties of water (such as high boiling point & low vapor pressure)

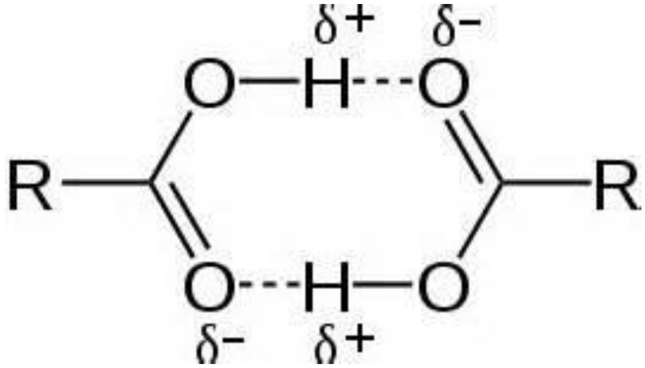
<u>Note</u> : for liquid evaporation all the H – bonds should be broken (so we need a high temp.)

while for the melting of solids (ice) 1/6 of the H- bonds should broken

Q/ which one have a higher B.P water or alcohol?

Answer: water because it have two H- bonds while alc. Have only one.

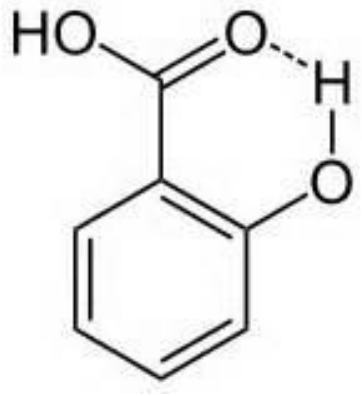
H –bond in carboxylic acid is strong enough to give (dimer) even in the vapor state



While hydrogen florid exist as polymer

-------HF----- HF-----HF-----HF------HF-------

*some times the H-bonds occurs intramolecular example salicylic acid



Ionic bonds(100-200 Kcal/mole):

It is the attraction between the oppositely charged molecules

Covalent bonds (100- 150 kcal/mole).

Lec 4

States of matter

The Gaseous State

Gas molecules have vigorous and rapid motion that result in collisions not only with one another but also with the walls of the container in which they are confined.

Hence, they exert a pressure (a force per unit area) expressed in **dynes/cm^2**, **atm.** or in **mm Hg** because of the use of the barometer in pressure measurement. Another important characteristic of a gas, its volume, is usually expressed in **liters** or (**1 cm^3 = 1 mL**). The temperature involved in the gas equations is given according the absolute or Kelvin scale. Zero degrees on the centigrade scale is equal to 273.15 Kelvin (K).

1 atm = 760 mm Hg

= 76 cm Hg

= 1.0133×10^6 dyne/cm^2

Ideal gas properties:

1- The particles of the gas do not attract one another (no intermolecular forces), but instead move with complete independence; this statement applies only at low pressures.

2- The total volume of gases molecules is so small as to be negligible in relation to the volume of the space in which the molecules are confined while the real gases composed of molecules of finite volume.

3- The particles exhibit continuous random motion owing to their kinetic energy. The average kinetic energy, E, is directly proportional to the absolute temperature of the gas.

4- The molecules exhibit perfect elasticity; that is, there is no net loss of speed or transfer of energy after they collide with one another and with the molecules in the walls of the confining vessel.

5- The ideal gas can be compressed or cooled but with out liquification (remain gas) while the real gas can be compressed, cooled and converted to liquid (liquification).

Q/ which one have larger volume, the real gas or Ideal gas ?

Ans./

Under standard conditions (1 atm , 0 C^o , 1 mole)

At this conditions the calculated volume of ideal gas is (**22.414 L**)

While the measured volume of real gas is (**22.207 L**)

Therefore $V_{ideal} > V_{real}$

Q/ under wt conditions the real gas is converted or behave as Ideal gas ?

Ans./ by increasing the temp. and decreasing the pressure

For example at 10 C° and 0.9 atm the calculated volume of the ideal gas 25.78 L while in the laboratory and under the same conditions we can measure the real gas volume which is 25.69 L.

By increasing the temp to 20 C° and decreasing the pressure to 0.7 atm the calculated volume of ideal gas is 34.32 L which is the same as the measured volume of real gas.

So under these conditions of temp and pressure the real gas behave as ideal gas (we can apply the ideal gas law).

This phenomena can be explained by the fact that as the temp increased, the kinetic energy of gas molecules will increase causing them to speed up in their motion and this speed can overcome the intermolecular forces acting between them, so real gas behave as ideal gas.

The same effect will be gained by decreasing the pressure until the forces approach zero which is the property of ideal gas.

Note: in ideal gas, the absence of attraction between particles will cause them to hit the wall of container with force that depend on speed and size of the particles while in real gases, the presence of attraction between molecules will pull the particles to the centre of container and slow it down which will decrease the force of collision with the container wall and hence the pressure will decrease.

So $V_{\text{ideal}} > V_{\text{real}}$

$P_{\text{ideal}} > P_{\text{real}}$

The Ideal Gas Law

Boyle's law relates the volume and pressure of a given mass of gas at constant temperature,

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = k$$

The law of **Gay-Lussac and Charles** states that the volume and absolute temperature of a given mass of gas at constant pressure are directly proportional,

$$V \propto T \quad \text{or} \quad V = kT$$

These equations can be combined to obtain the familiar relationship

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Thus, one can conclude that although P, V, and T change, the ratio PV/T is constant and can be expressed mathematically as

$$\frac{PV}{T} = R \quad \text{or} \quad PV = RT$$

in which R is the constant value for the PV/T ratio of an ideal gas. This equation is correct only for 1 mole (i.e., 1 g molecular weight) of gas; for n moles it becomes

$$PV = nRT$$

To obtain a numerical value for R, let us proceed as follows. If 1 mole of an ideal gas is chosen, its volume under standard conditions of temperature and pressure (i.e., at 0°C and 760 mm Hg) has been found by experiment to be 22.414 liters.

$$\begin{aligned} 1 \text{ atm} \times 22.414 \text{ liters} &= 1 \text{ mole} \times R \times 273.16 \text{ K} \\ R &= 0.08205 \text{ liter atm/mole K} \end{aligned}$$

The molar gas constant can also be given in energy units by expressing the pressure in dynes/cm^2 (1 atm = 1.0133×10^6 dynes/cm^2) and the volume in the corresponding units of cm^3 (22.414 liters = 22,414 cm^3). Then

$$\begin{aligned} R = \frac{PV}{T} &= \frac{(1.0133 \times 10^6) \times 22.414}{273.16} \\ &= 8.314 \times 10^6 \text{ erg/mole K} \end{aligned}$$

or, because 1 joule = 10^7 ergs,

$$R = 8.314 \text{ joules/mole K}$$

The constant can also be expressed in cal/mole deg, employing the equivalent 1 cal = 4.184 joules:

$$R = \frac{8.314 \text{ joules/mole deg}}{4.184 \text{ joules/cal}} = 1.987 \text{ cal/mole deg}$$

Liquid states of matter:

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

A dispersion consists of at least two phases with one or more dispersed (internal) phases contained in a single continuous (external) phase.

The term phase is defined as a distinct homogeneous part of a system separated by definite boundaries from other parts of the system.

Solution: is a mixture of two or more components that form a single phase that is homogenous down the molecular level, it is mostly consist of solute and solvent.

The diameter of particles in coarse dispersions is greater than ~500 nm (0.5 µm). Two common pharmaceutical coarse dispersions are emulsions (liquid–liquid dispersions) and suspensions (solid–liquid dispersions). A 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.

Commonly, the terms component and constituent are used interchangeably to represent the pure chemical substances that make up a solution. The constituent present in the greater amount in a binary solution is arbitrarily designated as the solvent and the constituent in the lesser amount as the solute.

Physical Properties of Substances

In the field of thermodynamics, physical properties of systems are classified as **extensive properties**, which depend on the quantity of the matter in the system (e.g., mass and volume), and **intensive properties**, which are independent of the amount of the substances in the system (e.g., temperature, pressure, density, surface tension, and viscosity of a pure liquid).

The physical properties of substances can be classified as:

a- **Colligative properties** depend mainly on the number of particles in a solution. Such as osmotic pressure, vapor pressure lowering, freezing point depression, and boiling point elevation. In considering the colligative properties of solid-in-liquid solutions, it is assumed that the solute is nonvolatile and that the pressure of the vapor above the solution is provided entirely by the solvent.

b- **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 such as molecular weight.

c- **Constitutive properties** depend on the arrangement and to a lesser extent on the number and kind of atoms within a molecule. These properties give clues to the constitution of individual compounds and groups of molecules in a system.

Many physical properties may be partly additive and partly constitutive. The refraction of light, electric properties, surface and interfacial characteristics, and the solubility of drugs are at least in part constitutive and in part additive properties

Types of Solutions

A solution can be classified according to the states in which the solute and solvent occur, and because three states of matter (gas, liquid, and crystalline solid) exist, nine types of homogeneous mixtures of solute and solvent are possible. These types, together with some examples, are given in Table 1

Table 1 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

Electrolyte and non electrolyte solutions:

The solutes (whether gases, liquids, or solids) are divided into two main classes: nonelectrolytes and electrolytes. **Nonelectrolytes** are substances that do not ionize when dissolved in water and therefore do not conduct an electric current through the solution. Examples of nonelectrolytes are sucrose, glycerin, naphthalene, and urea.

Electrolytes are substances that dissolve in water and form ions in solution (anion and cation), conduct electric current, and show apparent “anomalous” colligative properties; that is, they produce a considerably greater freezing point depression and boiling point elevation than do nonelectrolytes of the same concentration. Examples of electrolytes are hydrochloric acid, sodium sulfate, ephedrine, and phenobarbital.

Electrolytes may be subdivided further into strong electrolytes which are completely ionized and conduct a strong electrical current such as sodium chloride, and weak electrolytes that are only slightly ionized in aqueous solution and conduct electrical current weakly (eg. ephedrine and phenobarbital are weak electrolytes).

Expression	**Symbol**	**Definition**
Molarity	M, c	Moles (gram molecular weights) of solute in 1 liter of solution
Normality	N	Gram equivalent weights of solute in 1 liter of solution
Molality	*m*	Moles of solute in 1000 g of solvent

Concentration Expressions

Table 2 Concentration Expressions

Mole fraction	*X*,N	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		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

Example 1: Solutions of Ferrous Sulfate

An aqueous solution of exsiccated ferrous sulfate was prepared by adding 41.50 g of FeSO4 to enough water to make 1000 mL of solution at 18°C. The density of the solution is 1.0375 and the molecular weight of FeSO4 is 151.9. Calculate (a) the molarity; (b) the molality; (c) the mole fraction of FeSO4, the mole fraction of water, and the mole percent of the two constituents; and (d) the percentage by weight of FeSO4.

Example 2: Calculation of Equivalent Weight

(a) What is the number of equivalents per mole of **K_3PO_4**, and what is the equivalent weight of this salt? (b) What is the equivalent weight of **KNO_3**? (c) What is the number of equivalents per mole of **$Ca_3(PO_4)_2$**, and what is the equivalent weight of this salt?

- K_3PO_4 represents 3 Eq/mole, and its equivalent weight is numerically equal to one third of its molecular weight, namely, (212 g/mole) ÷ (3 Eq/mole) = 70.7 g/Eq.
- The equivalent weight of KNO_3 is also equal to its molecular weight, or 101 g/Eq.

- The number of equivalents per mole for $Ca_3(PO_4)_2$ is 6 (i.e., three calcium ions each with a valence of 2 or two phosphate ions each with a valence of 3). The equivalent weight of $Ca_3(PO_4)_2$ is therefore one sixth of its molecular weight, or 310/6 = 51.7 g/Eq.

Example 3: For a complex salt such as monobasic potassium phosphate (potassium acid phosphate), KH_2PO_4 (molecular weight, 136 g), the equivalent weight depends on how the compound is used. If it is used for its potassium content, the equivalent weight is identical to its molecular weight, or 136 g. When it is used as a buffer for its hydrogen content, the equivalent weight is one half of the molecular weight, 136/2 = 68 g, because two hydrogen atoms are present. When used for its phosphate content, the equivalent weight of KH_2PO_4 is one third of the molecular weight, 136/3 = 45.3 g, because valence of phosphate is 3.

Ideal and Real Solutions

Ideal solution as one in which 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. Stated another way, no shrinkage or expansion occurs when the substances are mixed. The constitutive properties, for example, the vapor pressure, refractive index, surface tension, and viscosity of the solution, are the weighted averages of the properties of the pure individual constituents.

Mixing substances with similar properties forms ideal solutions. For example, 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**. When 100 mL of sulfuric acid is combined with 100 mL of water, however, the volume of the solution is about 180 mL at room temperature, and the mixing is attended by a considerable evolution of heat; the solution is said to be nonideal, or **real**.

Lec 5

Liquefaction of Gases:

When a gas is cooled, it loses some of its kinetic energy in the form of heat, and the velocity of the molecules decreases. If pressure is applied to the gas, the molecules are brought within the sphere of the van der Waals interaction forces and pass into the liquid state. Because of these forces, liquids are considerably denser than gases and occupy a definite volume. The transitions from a gas to a liquid and from a liquid to a solid depend not only on the temperature, but also on the pressure to which the substance is subjected.

If the temperature is elevated sufficiently, a value is reached above which it is impossible to liquefy a gas, irrespective of the pressure applied.

This temperature, above which a liquid can no longer exist, is known as the ***critical temperature***. The pressure required to liquefy a gas at its critical temperature is the ***critical pressure***, which is also the highest vapor pressure that the liquid can have. The further a gas is cooled below its critical temperature, the less pressure is required to liquefy it. Based on this principle, all known gases have been liquefied.

The critical temperature serves as a rough measure of the attractive forces between molecules, for at temperatures above the critical value, the molecules possess sufficient kinetic energy so that no amount of pressure can bring them within the range of attractive forces that cause the particles to "stick" together.

Methods for Achieving Liquefaction:

One of the ways to liquefy a gas is to subject it to intense cold by the use of freezing mixtures. Other methods depend on the cooling effect produced in a gas as it expands. Thus, suppose we allow an ideal gas to expand so rapidly that no heat enters the system. Such an expansion, termed an adiabatic expansion, may be achieved by carrying out the process in a vacuum flask, which effectively insulates the contents of the flask from the external environment.

The work that has to be done to bring about expansion therefore must come from the gas itself at the expense of its own heat energy content. As a result, the temperature of the gas falls. If this procedure is repeated a sufficient number of times, the total drop in temperature is sufficient to cause liquefaction of the gas.

Aerosols:

Gases can be liquefied by increasing pressure, provided we work below the critical temperature. When the pressure is reduced, the molecules expand and the liquid reverts to a gas. This reversible change of state is the basic principle involved in the preparation of pharmaceutical aerosols. In such products, the drug is dissolved or suspended in a 'propellant', a material that is liquid under the pressure conditions existing inside the container and forms a gas under normal atmospheric conditions.

Chlorofluorocarbons and hydrofluorocarbons have traditionally been utilized as propellants in these products because of their physicochemical properties, However, in the face of increasing environmental concerns (ozone depletion) their use is tightly regulated which has led to the increased use of other gases such as nitrogen and carbon dioxide.

Vapor Pressure of Liquids

Translational energy of motion (kinetic energy) is not distributed evenly among molecules; some of the molecules have more energy and hence higher velocities than others at any moment. When a liquid is placed in an evacuated container at a constant temperature, the molecules with the highest energies break away from the surface of the liquid and pass into the gaseous state, and some of the molecules subsequently return to the liquid state, or condense.

When the rate of condensation equals the rate of vaporization at a definite temperature, the vapor becomes saturated and a dynamic equilibrium is established. The pressure of the saturated vapor above the liquid is then known as the **equilibrium vapor pressure**. If a manometer is fitted to an evacuated vessel containing the liquid, it is possible to obtain a record of the vapor pressure in millimeters of mercury. The presence of a gas, such as air, above the liquid decreases the rate of evaporation, but it does not affect the equilibrium pressure of the vapor.

As the temperature of the liquid is elevated, more molecules approach the velocity necessary for escape and pass into the gaseous state. As a result, the vapor pressure increases with rising temperature.

Boiling Point:

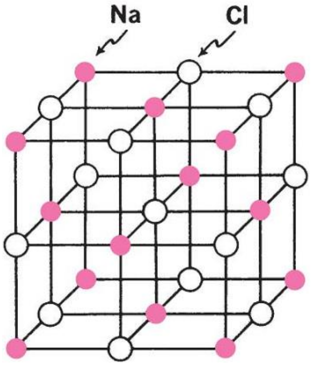
If a liquid is placed in an opened container and heated until the vapor pressure equals the atmospheric pressure, the vapor is seen to form bubbles that rise rapidly through the liquid and escape into the gaseous state. The temperature at which the vapor pressure of the liquid equals the external or atmospheric pressure is known as the boiling point. Absorbed heat is used to change liquid to vapor, and temperature does not rise until the liquid is completely vaporized.

Solids and the Crystalline State

Crystalline Solids

The structural units of crystalline solids, such as ice, sodium chloride, and menthol, are arranged in fixed geometric patterns or lattices. Crystalline solids, unlike liquids and gases, have definite shapes and an orderly arrangement of units. Gases are easily compressed, whereas solids, like liquids, are practically incompressible.

The units that constitute the crystal structure can be atoms, molecules, or ions. The sodium chloride crystal, shown in Figure bellow, consists of a cubic lattice of sodium ions interpenetrated by a lattice of chloride ions, the binding force of the crystal being the electrostatic attraction of the oppositely charged ions. In diamond and graphite, the lattice units consist of atoms held together by covalent bonds. Solid carbon dioxide, hydrogen chloride, and naphthalene form crystals composed of molecules as the building units.



The crystal lattice of sodium chloride

Polymorphism:

It is the case when a substance exists in more than 1 crystalline form but they have the same chemical formula. Differences in the crystalline form may lead to differences in physical properties as melting point, solubility, miscibility and x-ray diffraction. In case of slightly soluble drugs, this may affect dissolution rate, as a result, one polymorph may be more active therapeutically than another polymorph of the same drug. For example polymorphic state of chloramphenicol palmitate have a significant influence on the biologic availability of the drug. Another case is that of the AIDS drug ritonavir, which was marketed in a dissolved formulation until a previously unknown, more stable and less soluble polymorph appeared.

This led to recall of the product from the market.

Perhaps the most common example of polymorphism is the contrast between a diamond and graphite, both of which are composed of crystalline carbon. In this case, high pressure and temperature lead to the formation of a diamond from elemental carbon. It should be noted that a diamond is a less stable (metastable) crystalline form of carbon than is graphite. Actually, the imperfections in diamonds continue to occur with time and represent the diamond converting, very slowly at the low ambient temperature and pressure, into the more stable graphite polymorph.

Solvates

Because many pharmaceutical solids are often synthesized by standard organic chemical methods, purified, and then crystallized out of different solvents, residual solvents can be trapped in the crystalline lattice. This creates a cocrystal termed a solvate. The presence of the residual solvent may dramatically affect the crystalline structure of the solid depending on the types of intermolecular interactions that the solvent may have with the crystalline solid.

Amorphous Solids

Amorphous solids as a first approximation may be considered supercooled liquids in which the molecules are arranged in a somewhat random manner as in the liquid state. Substances such as glass and many synthetic plastics are amorphous solids. They differ from crystalline solids in that they tend to flow when subjected to sufficient pressure over a period of time, and they do not have definite melting points.

Amorphous substances, as well as cubic crystals, are usually ***isotropic***, that is, they exhibit similar properties in all directions. Crystals other than cubic are ***anisotropic***, showing different characteristics (electric conductance, refractive index, crystal growth, rate of solubility) in various directions along the crystal.

Whether a drug is amorphous or crystalline has been shown to affect its therapeutic activity. Thus, the crystalline form of the antibiotic novobiocin acid is poorly absorbed and has no activity, whereas the amorphous form is readily absorbed and therapeutically active. This is due to the differences in the rate of dissolution. Once dissolved, the molecules exhibit no memory of their origin.

X-Ray Diffraction:

X-rays are diffracted by crystals just as visible light is dispersed into a color spectrum by a ruled grating. This is due to the fact that x-rays have wavelengths of about the same magnitude as the distance between the atoms or molecules of crystals (about 1.54 Å for most laboratory instruments using Cu Kα radiation; the C—C bond is about 1.5 Å).

Melting Point and Heat of Fusion:

The temperature at which a liquid passes into the solid state is known as the freezing point. It is also the melting point of a pure crystalline compound. The freezing point or melting point of a pure crystalline solid is strictly defined as the temperature at which the pure liquid and solid exist in equilibrium.

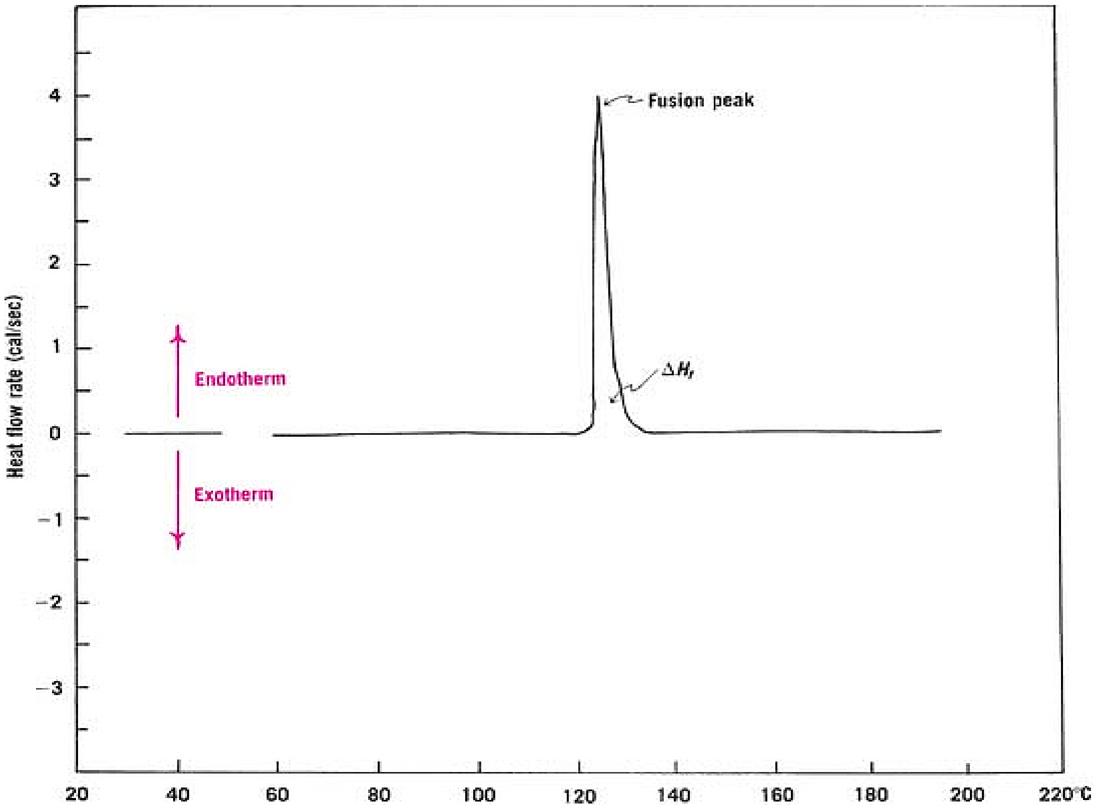
The heat (energy) absorbed when 1 g of a solid melts or the heat liberated when it freezes is known as the latent heat of fusion, and for water at 0°C it is about 80 cal/g (1436 cal/mole). The heat added during the melting process does not bring about a change in temperature until all of the solid has disappeared because this heat is converted into the potential energy of the molecules that have escaped from the solid into the liquid state.

Thermal Analysis

A number of physical and chemical effects can be produced by temperature changes, and methods for characterizing these alterations upon heating or cooling a sample of the material are referred to as thermal analysis. The most common types of thermal analysis are **DSC**, differential thermal analysis (**DTA**), and thermomechanical analysis (**TMA**). These methods have proved to be valuable in pharmaceutical research and quality control for the characterization and identification of compounds, the determination of purity, polymorphism solvent, and moisture content, amorphous content, stability, and compatibility with excipients.

Differential Scanning Calorimetry

In DSC, heat flows and temperatures are measured that relate to thermal transitions in materials. Typically, a sample and a reference material are placed in separate pans and the temperature of each pan is increased or decreased at a predetermined rate. When the sample, for example, benzoic acid, reaches its melting point, in this case 122.4°C, it remains at this temperature until all the material has passed into the liquid state because of the endothermic process of melting. A temperature difference therefore exists between benzoic acid and a reference, indium (melting point [mp] = 156.6°C), as the temperature of the two materials is raised gradually through the range 122°C to 123°C. A second temperature circuit is used in DSC to provide a heat input to overcome this temperature difference. In this way the temperature of the sample, benzoic acid, is maintained at the same value as that of the reference, indium. The difference is heat input to the sample, and the reference per unit time is fed to a computer and plotted as dH/dt versus the average temperature to which the sample and reference are being raised. The data collected in a DSC run for a compound such as benzoic acid are shown in the thermogram Figure.



Thermogram of a drug compound

Differential scanning calorimetry is a measurement of heat flow into and out of the system. In general, an endothermic (the material is absorbing heat) reaction on a DSC arises from desolvations, melting, glass transitions, and, more rarely, decompositions. An exothermic reaction measured by DSC is usually indicative of a decomposition (energy is released from the bond breaking) process and molecular reorganizations such as crystallization.

Lec 6

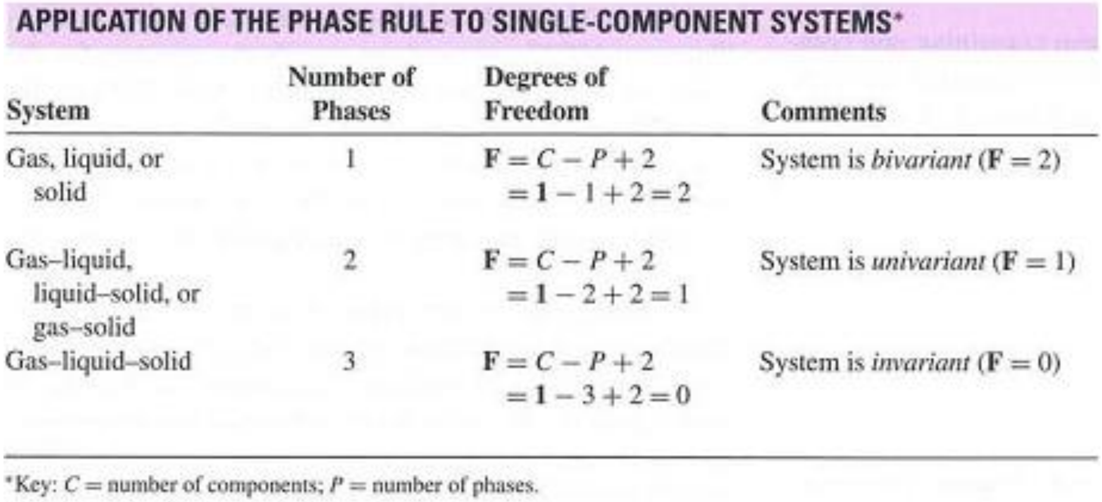
The Phase Rule:

The phase rule is a useful device for relating the effect of the least number of independent variables (e.g., temperature, pressure, and concentration) upon the various phases (solid, liquid, and gaseous) that can exist in an equilibrium system containing a number of components. Phase rule is expressed as follows:

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

Where **F** is number of degrees of freedom in system, **C** is number of components, and **P** is number of phases present.

The number of degrees of freedom is the least number of intensive variables (temperature, pressure, concentration, refractive index, density, viscosity, etc.) that must be fixed to describe the system completely and here lies the utility of the phase rule.



APPLICATION OF THE PHASE RULE TO SINGLE-COMPONENT SYSTEMS*

System	Number of Phases	Degrees of Freedom	Comments
Gas, liquid, or solid	1	$F = C - P + 2$ $= 1 - 1 + 2 = 2$	System is *bivariant* ($F = 2$)
Gas–liquid, liquid–solid, or gas–solid	2	$F = C - P + 2$ $= 1 - 2 + 2 = 1$	System is *univariant* ($F = 1$)
Gas–liquid–solid	3	$F = C - P + 2$ $= 1 - 3 + 2 = 0$	System is *invariant* ($F = 0$)

*Key: C = number of components; P = number of phases.

Systems Containing One Component

We consider a system containing one component, namely, that for water, which is illustrated in Figure bellow. The curve OA in the P–T (pressure–temperature) diagram in the Figure is known as the vapor pressure curve. Its upper limit is at the **critical temperature**, 374°C for water, and its lower end terminates at 0.0098°C, called the **triple point**. Along the vapor pressure curve, vapor and liquid coexist in equilibrium. Curve OC is the sublimation curve, and here vapor and solid exist together in equilibrium. Curve OB is the melting point curve, at which liquid and solid are in equilibrium. The negative slope of OB shows that the freezing point of water decreases with increasing external pressure.

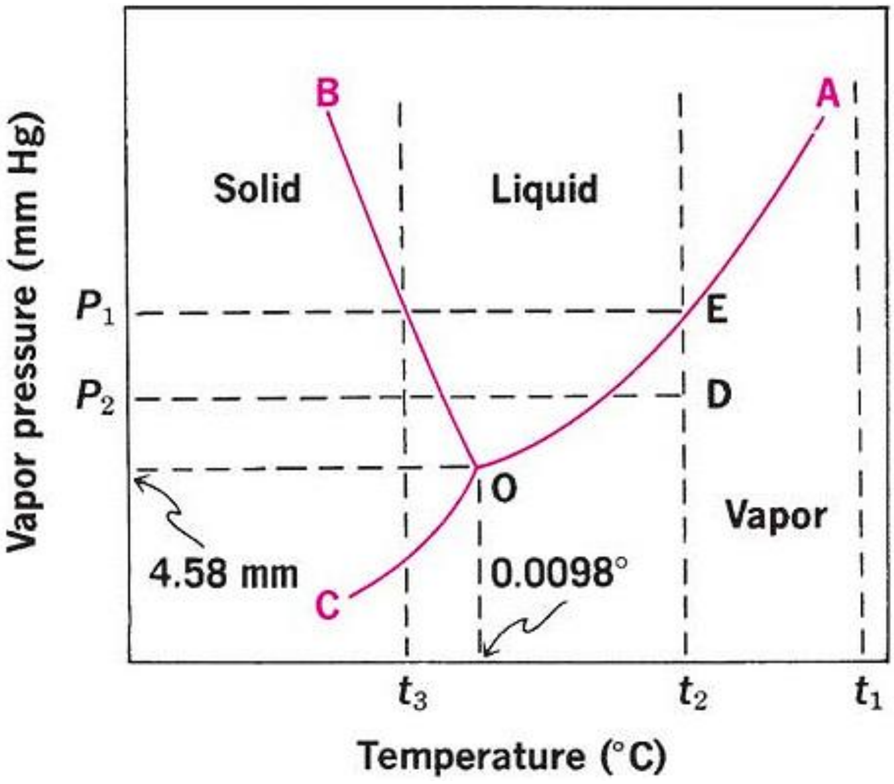
The result of changes in pressure (at fixed temperature) or changes in temperature (at fixed pressure) becomes evident by referring to the phase diagram. If the temperature is held constant at **t1**, where water is in the gaseous state above the critical temperature, no matter how much the pressure is raised (vertically along the dashed line), the system remains as a gas. At a temperature **t2** below the critical temperature, water vapor is converted into liquid water by an increase of pressure because the compression brings the molecules within the range of the attractive intermolecular forces. It is interesting to observe that at a temperature below the triple point, say **t3**, an increase of pressure on water in the vapor state converts the vapor first to ice and then at higher pressure into liquid water. This sequence, vapor → ice → liquid, is due to the fact that ice occupies a larger volume than liquid water below the triple point. At the triple point, all three phases are in equilibrium, that is, the only equilibrium is at this pressure at this temperature of 0.0098°C (or with respect to the phase rule, $F = 0$). As was seen in Table, in any one of the three regions in which pure solid, liquid, or vapor exists and $P = 1$, the phase rule gives

$$F = 1 - 1 + 2 = 2$$

Therefore, we must fix two conditions, namely temperature and pressure, to specify or describe the system completely. This statement means that if we were to record the results of a scientific experiment involving a given quantity of water, it would not be sufficient to state that the water was kept at, say, 76°C. The pressure would also have to be specified to define the system completely. If the system were open to the atmosphere, the atmospheric pressure obtaining at the time of the experiment would be recorded. Conversely, it would not be sufficient to state that liquid water was present at a certain pressure without also stating the temperature.

Along any three of the curves where two phases exist in equilibrium, $F = 1$ (see Table). Hence, only one condition need be given to define the system. If we state that the system contains both liquid water and water vapor in equilibrium at 100°C, we need not specify the pressure, for the vapor pressure can have no other value than 760 mm Hg at 100°C under these conditions. Similarly, only one variable is required to define the system along line OB or OC. Finally, at the triple point where the three phases—ice, liquid water, and water vapor—are in equilibrium, we saw that F = 0.

As already noted, the triple point for air-free water is 0.0098°C, whereas the freezing point (i.e., the point at which liquid water saturated with air is in equilibrium with ice at a total pressure of 1 atm) is 0°C.



Phase diagram for water at moderate pressures

Escaping Tendency

This concept say that the heat in the hotter body has a greater escaping tendency than that in the colder one. Temperature is a quantitative measure of the escaping tendency of heat, and at thermal equilibrium, when both bodies finally have the same temperature, the escaping tendency of each constituent is the same in all parts of the system.

A quantitative measure of the escaping tendencies of material substances undergoing physical and chemical transformations is **free energy**. For a pure substance, the free energy per mole, or the molar free energy, provides a measure of escaping tendency; for the constituent of a solution, it is the partial molar free energy or chemical potential that is used as an expression of escaping tendency.

The free energy of 1 mole of ice is greater than that of liquid water at 1 atm above 0°C and is spontaneously converted into water because

$$\Delta G = G_{liq} - G_{ice} < 0$$

At 0°C, at which temperature the system is in equilibrium, the molar free energies of ice and water are identical and $\Delta G = 0$. In terms of escaping tendencies, the escaping tendency of ice is greater than the escaping tendency of liquid water above 0°C, whereas at equilibrium, the escaping tendencies of water in both phases are identical.

Lec 7

Ideal Solutions and Raoult's Law

In an ideal solution of two volatile liquids, 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:

$$P_A = P_A^o X_A$$

$$P_B = P_B^o X_B$$

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. The vapor pressures of the pure components are $p_A°$ and $p_B°$, respectively, and the total vapor pressure is equal to (p_A + p_B).

For example, if the vapor pressure of ethylene chloride in the pure state is 236 mm Hg at 50°C, then in a solution consisting of a mole fraction of 0.4 ethylene chloride and 0.6 benzene, the partial vapor pressure of ethylene chloride is 40% of 236 mm, or 94.4 mm.

The vapor pressure–composition curve for the binary system benzene and ethylene chloride at 50°C is shown in Figure 1 bellow. The three lines represent the partial pressure of ethylene chloride, the partial pressure of benzene, and the total pressure of the solution as a function of the mole fraction of the constituents.

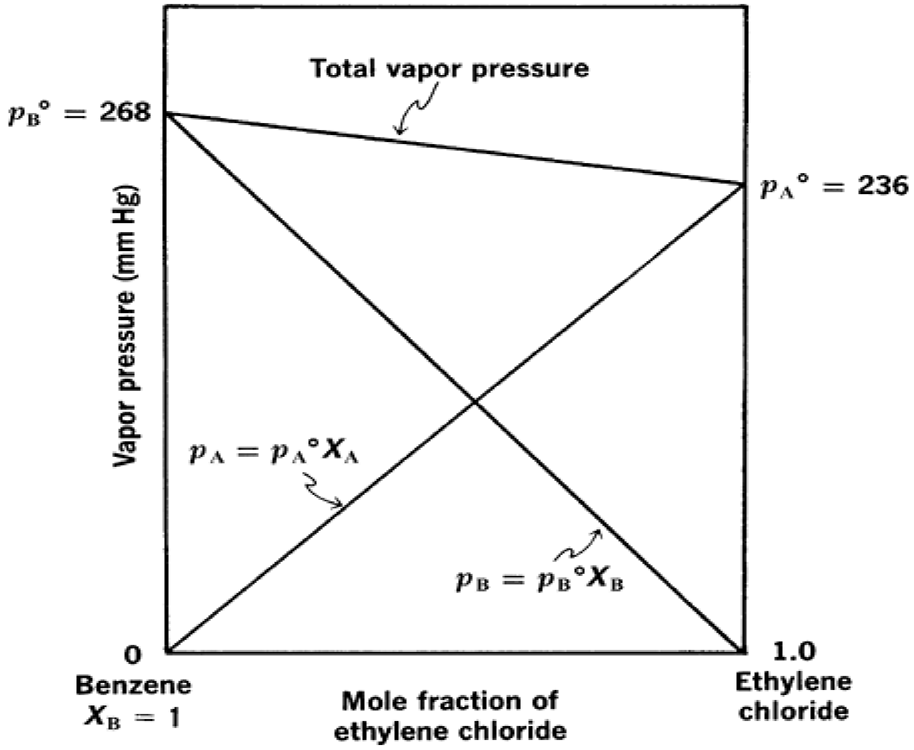


Fig 1. Vapor pressure–composition curve for an ideal binary system.

Real Solutions

For the real solutions, two types of deviation from Raoult's law are recognized, **negative deviation** and **positive deviation**.

When the "adhesive" attractions between molecules of different species exceed the "cohesive" attractions between like molecules, the vapor pressure of the solution is less than that expected from Raoult's ideal solution law, and negative deviation occurs. If the deviation is sufficiently great, the total vapor pressure curve shows a minimum, as observed in **Figure 2**, where A is chloroform and B is acetone.

Chloroform and acetone manifest such an attraction for one another through the formation of a hydrogen bond, thus further reducing the escaping tendency of each constituent. This pair forms a weak compound,**$[Cl_3C\text{-}H\ldots O{=}C(CH_3)_2]$** that can be isolated and identified. Reactions between dipolar molecules, or between a dipolar and a nonpolar molecule, may also lead to negative deviations. The interaction in these cases, however, is usually so weak that no definite compound can be isolated.

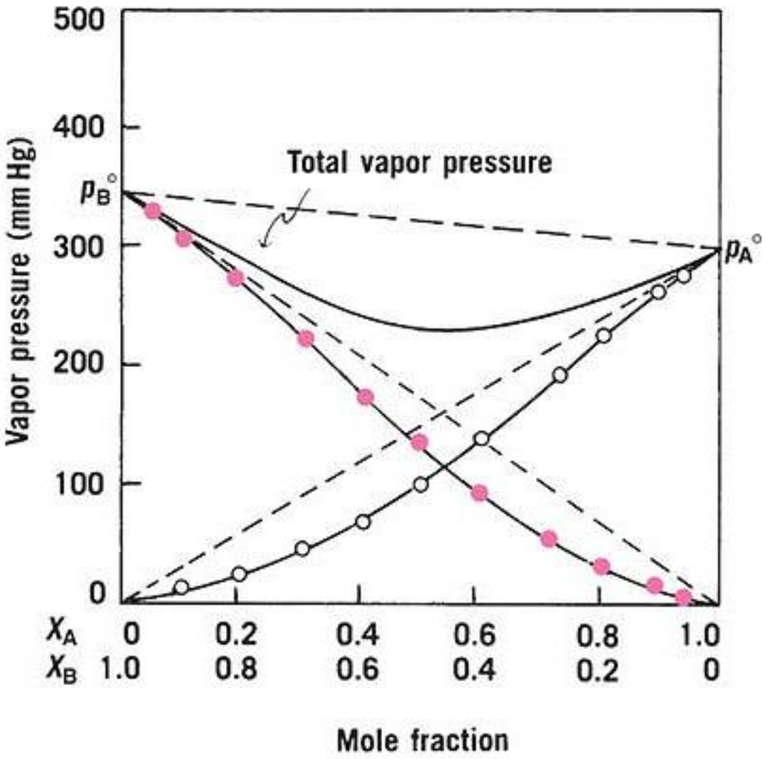
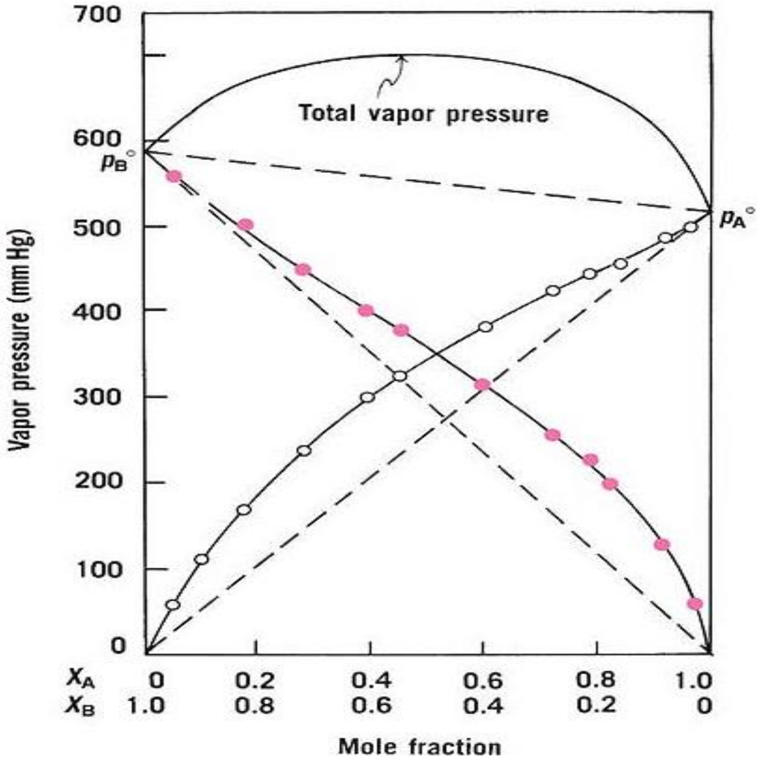


Fig.2. Vapor pressure of a system showing negative deviation from Raoult's law.

When the interaction between A and B molecules is less than that between molecules of the pure constituents, the presence of B molecules reduces the interaction of the A molecules, and A molecules correspondingly reduce the B—B interaction. Accordingly, the dissimilarity of polarities or internal pressures of the constituents results in a greater escaping tendency of both the A and the B molecules. The partial vapor pressure of the constituents is greater than that expected from Raoult's law, and the system is said to exhibit positive deviation.

The total vapor pressure often shows a maximum at one particular composition if the deviation is sufficiently large. An example of positive deviation is shown in **Figure 3**. Liquid pairs that demonstrate positive deviation are benzene and ethyl alcohol, carbon disulfide and acetone, and chloroform and ethyl alcohol.



Raoult's law does not apply over the entire concentration range in a nonideal solution. It describes the behavior of either component of a real liquid pair only when that substance is present in high concentration and thus is considered to be the solvent. Raoult's law can be expressed as

$$\mathbf{P_{solvent} = P^{o}_{solvent}\, X_{solvent}}$$

Henry's Law

The vapor pressure of volatile solute is equal to its mole fraction multiplied by *characteristic proportionality constant* of the solute

$$\mathbf{P_{solute} = \mathit{K}_{solute}\, X_{solute}}$$

Henry's law applies to the solute and Raoult's law applies to the solvent in dilute solutions of real liquid pairs.

Colligative Properties

When a nonvolatile solute is combined with a volatile solvent, the vapor above the solution is provided solely by the solvent. The solute reduces the escaping tendency of the solvent, and, on the basis of Raoult's law, the vapor pressure of a solution containing a nonvolatile solute is lowered proportional to the relative number.

Lowering of the Vapor Pressure

According to Raoult's law, the vapor pressure, p_1, of a solvent over a dilute solution is equal to the vapor pressure of the pure solvent, $p_1°$, times the mole fraction of solvent in the solution, X_1. Because the solute under discussion here is considered to be nonvolatile, the vapor pressure of the solvent, p_1, is identical to the total pressure of the solution, p.

It is more convenient to express the vapor pressure of the solution in terms of the concentration of the solute rather than the mole fraction of the solvent, and this may be accomplished in the following way. The sum of the mole fractions of the constituents in a solution is unity:

$$X_1=1- X_2$$

where X_1 is the mole fraction of the solvent and X_2 is the mole fraction of the solute. Raoult's equation can be modified:

$$P = P_1^o (1-X_2) \longrightarrow P_1^o - P = P_1^o X_2 \longrightarrow P_1^o - P / P_1^o = X_2$$

$\Delta p = p_1° - p$ is the lowering of the vapor pressure and $\Delta p/p_1°$ is the relative vapor pressure lowering. The relative vapor pressure lowering depends only on the mole fraction of the solute, X_2, that is, on the number of solute particles in a definite volume of solution. Therefore, the relative vapor pressure lowering is a colligative property.

Elevation of the Boiling Point

The normal boiling point is the temperature at which the vapor pressure of the liquid becomes equal to an external pressure of 760 mm Hg. A solution will boil at a higher temperature than will the pure solvent owing to the fact that the nonvolatile solute lowers the vapor pressure of the solvent. This is the colligative property called boiling point elevation (the more of the solute that is dissolved, the greater is the effect).

The ratio of the elevation of the boiling point, ΔT_b, to the vapor pressure lowering, $\Delta p = p° - p$, at 100°C is approximately a constant at this temperature; it is written as

$$\Delta T_b / \Delta p = k$$

$$\Delta T_b = \Delta p\, k$$

Moreover, because p° is a constant, the boiling point elevation may be considered proportional to $\Delta p/p°$, the relative lowering of vapor pressure. By Raoult's law, however, the relative vapor pressure lowering is equal to the mole fraction of the solute; therefore,

$$\Delta T_b = K X_2$$

Because the boiling point elevation depends only on the mole fraction of the solute, it is a colligative property.

In dilute solutions, X_2 is equal approximately to $m/(1000/M_1)$, so the equation can be written as

$$\Delta T_b = (kM_1/1000)m = K_b\, m$$

where ΔT_b is known as the **boiling point elevation** and K_b is called the **molal elevation constant** or the **ebullioscopic constant**. K_b has a characteristic value for each solvent. It may be considered as the boiling point elevation for an ideal 1 m solution. Stated another way, K_b is the ratio of the boiling point elevation to the molal concentration in an extremely dilute solution in which the system is approximately ideal.

The proportionality between ΔT_b and the molality is exact only at infinite dilution, at which the properties of real and ideal solutions coincide. The ebullioscopic constant, K_b, of a solvent can be obtained experimentally by measuring ΔT_b at various molal concentrations and extrapolating to infinite dilution ($m = 0$)

Depression of the Freezing Point

The normal freezing point or melting point of a pure compound is the temperature at which the solid and the liquid phases are in equilibrium under a pressure of 1 atm.

The value T_0 for water saturated with air at this pressure is arbitrarily assigned a temperature of 0°C. The triple point of air-free water, at which solid, liquid, and vapor are in equilibrium, lies at a pressure of **4.58 mm** Hg and a temperature of **0.0098°C**. It is not identical with the ordinary freezing point of water at atmospheric pressure but is rather the freezing point of water under the pressure of its own vapor.

If a solute is dissolved in the liquid at the triple point, the escaping tendency or vapor pressure of the liquid solvent is lowered below that of the pure solid solvent. The temperature must drop to reestablish equilibrium between the liquid and the solid. Because of this fact, the freezing point of a solution is always lower than that of the pure solvent. It is assumed that the solvent freezes out in the pure state rather than as a solid solution containing some of the solute.

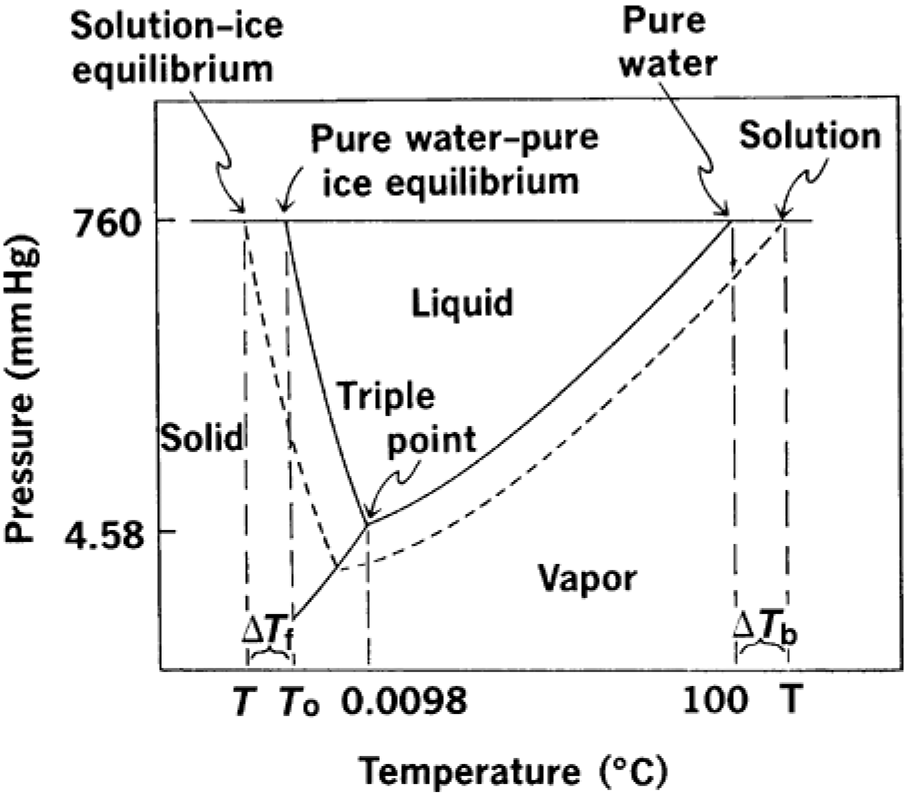


Fig. Depression of the freezing point of the solvent, water, by a solute

The more concentrated the solution, the farther apart are the solvent and the solution curves in the diagram and the greater is the freezing point depression and the equation which valid only in very dilute solutions is:

$$\Delta T_f = k\,m$$

ΔT_f is the freezing point depression, and K_f is the **molal depression constant** or the **cryoscopic constant**, which depends on the physical and chemical properties of the solvent.

The depression of the freezing point, like the boiling point elevation, is a direct result of the lowering of the vapor pressure of the solvent. The value of K_f for water is 1.86. It can be determined experimentally by measuring $\Delta T_f/m$ at several molal concentrations and extrapolating to zero concentration.

is quite useful for describing weak electrolytes, but found unsatisfactory for strong and moderately strong electrolytes.

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Osmotic Pressure

Osmosis is defined as the passage of the solvent into a solution through a semipermeable membrane. This process tends to equalize the escaping tendency of the solvent on both sides of the membrane. Escaping tendency can be measured in terms of vapor pressure or the closely related colligative property osmotic pressure. Osmosis in some cases is believed to involve the passage of solvent through the membrane by aa distillation process or by dissolving in the material of the membrane in which the solute is insoluble. In other cases, the membrane may act as a sieve, having a pore size sufficiently large to allow passage of solvent but not of solute molecules, in either case, the phenomenon of osmosis depends on the fact that the chemical potential (a thermodynamic expression of escaping tendency) of a solvent molecule in solution is less than exists in the pure solvent. Solvent therefore passes spontaneously into the solution until the chemical potentials of solvent and solution are equal. The system is then at equilibrium.

Van't Hoff and Morse Equations for Osmotic Pressure

In 1886, Jacobus van't Hoff recognized a proportionality between **osmotic pressure**, **concentration**, and **temperature**, suggested a relationship that corresponded to the equation for an ideal gas. 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

$$\pi V = n R T$$

where π is the osmotic pressure in atm, V is the volume of the solution in liters, n is the number of moles of solute, R is the gas constant, equal to 0.082 liter atm/mole deg, and T is the absolute temperature.

Ionic Equilibria

Arrhenius defined an acid as a substance that liberates hydrogen ions and a base as a substance that supplies hydroxyl ions on dissociation.

According to the Brönsted–Lowry theory, an acid is a substance, charged or uncharged, that is capable of donating a proton, and a base is a substance, charged or uncharged, that is capable of accepting a proton from an acid.

The strength of an acid or a base varies with the solvent. Hydrochloric acid is a strong acid but it is a weak acid in glacial acetic acid and acetic acid ,which is a weak acid, is a strong acid in liquid ammonia. Consequently, the strength of an acid depends not only on its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid. This is called **the basic strength of the solvent**.

In the Brönsted–Lowry classification, acids and bases may be anions such as HSO_4^- and CH_3COO^-, cations such as NH_4^+ and H_3O^+, or neutral molecules such as HCl and NH_3. Water can act as either an acid or a base and thus is amphiprotic.

According to the Lewis theory, an acid is a molecule or an ion that accepts an electron pair to form a covalent bond. A base is a substance that provides the pair of unshared electrons by which the base coordinates with an acid. Certain compounds, such as boron trifluoride and aluminum chloride, although not containing hydrogen and consequently not serving as proton donors, are nevertheless acids in this scheme. Many substances that do not contain hydroxyl ions, including amines, ethers, and carboxylic acid anhydrides, are classified as bases according to the Lewis definition.

Acid–Base Equilibria

The ionization or proteolysis of a weak electrolyte, acetic acid, in water can be written in the Brönsted–Lowry manner as

$$\underset{\text{Acid}_1}{\text{HAc}} + \underset{\text{Base}_2}{\text{H}_2\text{O}} \rightleftharpoons \underset{\text{Acid}_2}{\text{H}_3\text{O}^+} + \underset{\text{Base}_1}{\text{Ac}^-}$$

According to the law of mass action, the velocity or rate of the forward reaction, R_f, is proportional to the concentration of the reactants:

$$R_f = k_1 \times [\text{HAc}]^1 \times [\text{H}_2\text{O}]^1$$

The speed of the reaction is usually expressed in terms of the decrease in the concentration of either the reactants per unit time. The terms rate, speed, and velocity have the same meaning here.

Sörensen's pH

The hydrogen ion concentration of a solution varies from approximately 1 in a 1 M solution of a strong acid to about 1 × 10-14 in a 1 M solution of a strong base

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

The pH of a solution can be considered in terms of a numeric scale having values from 0 to 14, which expresses in a quantitative way the degree of acidity (7 to 0) and alkalinity (7-14). The value 7 at which the hydrogen and hydroxyl ion concentrations are about equal at room temperature is referred to as the neutral point, or neutrality. The neutral pH at 0°C is 7.47, and at 100°C it is 6.15.

Buffered and Isotonic Solutions

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

The Buffer Equation

a- Weak Acid and Its Salt

The pH of a buffer solution and the change in pH upon the addition of an acid or base can be calculated by use of the buffer equation. This expression is developed by considering the effect of a salt on the ionization of a weak acid when the salt and the acid have an ion in common.

For example, when sodium acetate is added to acetic acid, the dissociation constant for the weak acid,

$$\mathrm{HAc} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{Ac^-}$$

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} = 1.75 \times 10^{-5}$$

is momentarily disturbed because the acetate ion supplied by the salt increases the [Ac-] term in the numerator. To reestablish the constant Ka at 1.75×10^{-5}, the hydrogen ion term in the numerator $[H_3O^+]$ is instantaneously decreased, with a corresponding increase in [HAc]. Therefore, the constant Ka remains unaltered, and the equilibrium is shifted in the direction of the reactants. Consequently, the ionization of acetic acid, is repressed upon the addition of the common ion, Ac^-. This is an example of the common ion effect. The pH of the final solution is obtained by rearranging the equilibrium expression for acetic acid:

$$[H_3O^+] = K_a \frac{[HAc]}{[Ac^-]}$$

If the acid is weak and ionizes only slightly, the expression [HAc] may be considered to represent the total concentration of acid, and it is written simply as [Acid]. In the slightly ionized acidic solution, the acetate concentration [Ac-] can be considered as having come entirely from the salt, sodium acetate. Because 1 mole of sodium acetate yields 1 mole of acetate ion, [Ac-] is equal to the total salt concentration and is replaced by the term [Salt]. Hence, equation is written as

$$[H_3O^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

Equation can be expressed in logarithmic form, with the signs reversed, as

$$-\log [H_3O^+] = -\log K_a - \log [\text{Acid}] + \log [\text{Salt}]$$

from which is obtained an expression, known as the buffer equation or the Henderson–Hasselbalch equation, for a weak acid and its salt:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

The term pKa, the negative logarithm of Ka, is called the dissociation exponent.

The buffer equation is important in the preparation of buffered pharmaceutical solutions; it is satisfactory for calculations within the pH range of 4 to 10.

b- Weak Base and Its Salt

Buffer solutions are not ordinarily prepared from weak bases and their salts because of the volatility and instability of the bases and because of the dependence of their pH on pKw, which is often affected by temperature changes. Pharmaceutical solutions—for example, a solution of ephedrine base and ephedrine hydrochloride—however, often contain combinations of weak bases and their salts.

The buffer equation for solutions of weak bases and the corresponding salts can be derived in a manner analogous to that for the weak acid buffers. Accordingly,

$$[OH^-] = K_b \frac{[Base]}{[Salt]}$$

and using the relationship $[OH^-] = K_w/[H_3O^+]$, the buffer equation is obtained

$$pH = pK_w - pK_b + \log \frac{[Base]}{[Salt]}$$

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Electrolyte Solutions

The first satisfactory theory of ionic solutions was that proposed by Arrhenius in 1887. The theory was based largely on studies of electric conductance by Kohlrausch, colligative properties by van't Hoff, and chemical properties such as heats of neutralization by Thomsen.

Although the theory proved quite useful for describing weak electrolytes, it was soon found unsatisfactory for strong and moderately strong electrolytes. Accordingly, many attempts were made to modify or replace Arrhenius's ideas with better ones, and finally, in 1923, Debye and Hückel put forth a new theory. It is based on the principles that strong electrolytes are completely dissociated into ions in solutions of moderate concentration and that any deviation from complete dissociation is due to interionic attractions.

Properties of Solutions of Electrolytes

Electrolysis

When, under a potential of several volts, a direct electric current (dc) flows through an electrolytic cell (Fig.bellow), a chemical reaction occurs. The process is known as electrolysis. Electrons enter the cell from the battery or generator at the cathode (road down); they combine with positive ions or cations in the solution, and the cations are accordingly reduced. The negative ions, or anions, carry electrons through the solution and discharge them at the anode (road up), and the anions are accordingly oxidized. Reduction is the addition of electrons to a chemical species, and oxidation is removal of electrons from a species. The current in a solution consists of a flow of positive and negative ions toward the electrodes, whereas the current in a metallic conductor consists of a flow of free electrons migrating through a crystal lattice of fixed positive ions. Reduction occurs at the cathode, where electrons enter from the external circuit and are added to a chemical species in solution. Oxidation occurs at the anode, where the electrons are removed from a chemical species in solution and go into the external circuit.

In the electrolysis of a solution of ferric sulfate in a cell containing platinum electrodes, a ferric ion migrates to the cathode, where it picks up an electron and is reduced:

$$Fe^{3+} + e = Fe^{2+}$$

The sulfate ion carries the current through the solution to the anode, but it is not easily oxidized; therefore, hydroxyl ions of the water are converted into molecular oxygen, which escapes at the anode, and sulfuric acid is found in the solution around the electrode. The oxidation reaction at the anode is

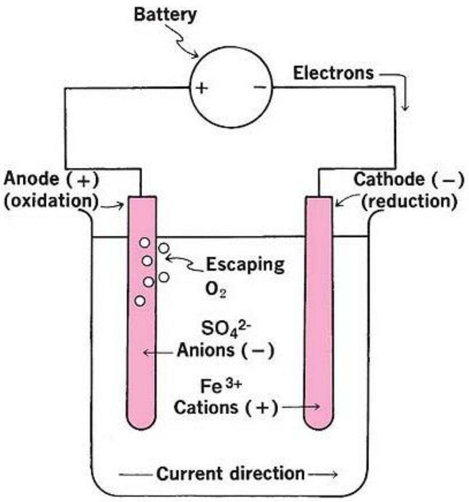
$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e$$

Platinum electrodes are used here because they do not pass into solution to any extent. When attackable metals, such as copper or zinc, are used as the anode, their atoms tend to lose electrons, and the metal passes into solution as the positively charged ion.

In the electrolysis of cupric chloride between platinum electrodes, the reaction at the cathode is

$$\frac{1}{2}Cu^{2+} + e = \frac{1}{2}Cu$$

whereas at the anode, chloride and hydroxyl ions are converted, respectively, into gaseous molecules of chlorine and oxygen, which then escape. In each of these two examples, the net result is the transfer of one electron from the cathode to the anode.



Electrolysis in an electrolytic cell

Transference Numbers

It should be noted that the flow of electrons through the solution from right to left in Figure above is accomplished by the movement of cations to the right as well as anions to the left. The fraction of total current carried by the cations or by the anions is known as the transport or transference number t_+ or t_-:

$$t_+ = \frac{\text{Current carried by cations}}{\text{Total current}}$$

$$t_- = \frac{\text{Current carried by anions}}{\text{Total current}}$$

The sum of the two transference numbers is obviously equal to unity:

$$t_+ + t_- = 1$$

The transference numbers are related to the velocities of the ions, the faster-moving ion carrying the greater fraction of current. The velocities of the ions in turn depend on hydration as well as ion size and charge. Hence, the speed and the transference numbers are not necessarily the same for positive and for negative ions. For example, the transference number of the sodium ion in a 0.10 M solution of NaCl is 0.385. Because it is greatly hydrated, the lithium ion in a 0.10 M solution of LiCl moves more slowly than the sodium ion and hence has a lower transference number, 0.317.

Theory of Electrolytic Dissociation

The original Arrhenius theory, together with the alterations that have come about as a result of the intensive research on electrolytes, is summarized as follows. When electrolytes are dissolved in water, the solute exists in the form of ions in the solution, as seen in the following equations:

$$H_2O + Na^+Cl^- \rightarrow Na^+ + Cl^- + H_2O$$

[Ionic compound]

[Strong electrolyte]

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

[Covalent compound]

[Strong electrolyte]

$$H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

[Covalent compound]

[Weak electrolyte]

The solid form of sodium chloride is marked with plus and minus signs in reaction to indicate that sodium chloride exists as ions even in the crystalline state. If electrodes are connected to a source of current and are placed in a mass of fused sodium chloride, the molten compound will conduct the electric current because the crystal lattice of the pure salt consists of ions. The addition of water to the solid dissolves the crystal and separates the ions in solution.

Hydrogen chloride exists essentially as neutral molecules rather than as ions in the pure form and does not conduct electricity. When it reacts with water, however, it ionizes according to above reaction. H_3O^+ is the modern representation of the hydrogen ion in water and is known as the hydronium or oxonium ion.

Sodium chloride and hydrochloric acid are strong electrolytes because they exist almost completely in the ionic form in moderately concentrated aqueous solutions. Inorganic acids such as HCl, HNO_3, H_2SO_4, and HI; inorganic bases as NaOH and KOH of the alkali metal family and $Ba(OH)_2$ and $Ca(OH)_2$ of the alkaline earth group; and most inorganic and organic salts are highly ionized and belong to the class of strong electrolytes.

Acetic acid is a weak electrolyte, the oppositely directed arrows in equation indicating that equilibrium between the molecules and the ions is established. Most organic acids and bases and some inorganic compounds, such as H_3BO_3, H_2CO_3, and NH_4OH, belong to the class of weak electrolytes. Even some salts (lead acetate, $HgCl_2$, HgI, and HgBr) and the complex ions $Hg(NH_3)_2{}^{+}$, $Cu(NH_3)_4{}^{2+}$, and $Fe(CN)_6{}^{3-}$ are weak electrolytes.

Faraday applied the term ion (Greek: “wanderer”) to these species of electrolytes and recognized that the cations (positively charged ions) and anions (negatively charged ions) were responsible for conducting the electric current. Before the time of Arrhenius's publications, it was believed that a solute was not spontaneously decomposed in water but rather dissociated appreciably into ions only when an electric current was passed through the solution.