What is meant by colligative properties?

These are certain properties of the solution which do not depend on the nature of the solute, but depend on the number of solute particles or molecules produced in the solution. These properties are called colligative properties (colligative: from Latin: co- = together, ligare = to bind, i.e., depending on the collection). These are:

1) Lowering of vapor pressure of the solvent,
2) Elevation of boiling point of the solvent,
3) Depression of freezing point of the solvent,
4) Osmotic pressure of the solution.

Colligative properties are the properties for only dilute solutions containing non-volatile, non-electrolyte and non-associated solute and the solution behave ideally.

What is ideal solution? What are the conditions for a solution to be an ideal?

An ideal solution is one where all the components behave ideally like an ideal gas mixture. In an ideal solution of the two components A and B, the average A-B interaction of the mixture are identical to the average A-A and B-B interaction in pure liquids. Examples are benzene-toluene, benzene-diethyl ether, etc.

If it satisfies the following conditions:
1) An ideal solution obeys Raoult's law.
2) The entropy change due to mixing is normal, i.e., \( \Delta S_{mix} = 0 \).
3) The entropy change due to mixing is zero, i.e., \( \Delta S_{mix} = 0 \).
4) There is no change in total volume due to mixing, i.e., \( \Delta V_{mix} = 0 \).
5) The change in free energy due to mixing is zero, i.e., \( \Delta G_{mix} = 0 \) at constant temperature and pressure.

What is ideally dilute solution?

A different kind of limit is reached if in a solution, the solute mole fraction approaches 0, so that all solutes are present in a low concentration. Such a solution is called ideally dilute. In such cases, due to high dilution, the solute molecules interact essentially only with the solvent molecules.
Hence from equations (1) and (2), we get

\[ \mu_i(x) = \mu_i^0(x) + RT \ln x_i \]

since \( x_i < 1 \), so \( RT \ln x_i \) is a negative quantity. Therefore,

\[ \mu_i(x) < \mu_i^0(x) \]

That is, the chemical potential of a solvent in solution is always less than that of a pure solvent. According to Raoult’s law, the vapour pressure of the two liquids forming the ideal solution may be given as follows.

\[ P_A = x_A P_A^0 \text{ and } P_B = x_B P_B^0 \]

Total pressure, \[ P = P_A + P_B = x_A P_A^0 + x_B P_B^0 \]

Is the lowering of chemical potential of a solvent in an ideal solution, an enthalpy effect or an entropy effect?

Explain, or give the molecular interpretation for lowering of vapour pressure.

The addition of a non-volatile solute to the solvent will lead to a decrease in the chemical potential of a liquid. But the chemical potential of the vapour will remain unchanged. The physical basis for lowering of chemical potential can not be in the modification of the magnitude of intermolecular forces, because lowering of vapour pressure takes place even in case of ideal solution. Thus, since it is not an enthalpy effect; it must be an entropy effect.

If a liquid is kept in a vessel evaporation takes place because this leads to more random gas. This is a process leading to increase in entropy at constant temperature. When a solute is added there is extra randomness in the liquid phase. Consequently, the tendency of the solute to go to the vapour phase decreases. In a closed vessel there will be lesser amount in the vapour phase. Thus, the vapour pressure of the solvent decreases due to addition of a non-volatile solute.

Show graphically, the lowering of vapour pressure of the solvent in the solution.

The vapour pressure of a pure solvent increases with rise in temperature. This is shown by AB in the following vapour pressure vs. temperature diagram. When a non-volatile solute is dissolved in the solvent, the vapour pressure of the solvent in solution will be lower than that of the pure solvent at any
The vapour pressure of the solvent in the solution increases with rise in temperature as shown by CD in the same diagram.

The lowering of vapour pressure is given by EF
\[ P_v^0 - P_v \]
Here, \( P_v^0 \) is the vapour pressure of the pure solvent and \( P_v \) is the vapour pressure of the solvent in solution.

Hence from the diagram, the vapour pressure of the solvent in solution is always less than that of the pure solvent.

Derive, thermodynamically, Raoult's law for vapour pressure lowering of the solvent in solution containing non-volatile solute. Or,

Derive thermodynamically, the expression for lowering of vapour pressure of solvent in solution containing non-volatile solute, and show that it is a colligative property.

Let us consider an ideal solution containing non-volatile solute in a cylinder covered by a piston and let us reduce the pressure isothermally until the solution begins to vaporise. There will be liquid and vapour phase in equilibrium at a particular temperature. For equilibrium between liquid and its vapour phase, we have
\[ \mu_i (L) = \mu_i (V) \]
where \( \mu_i (L) \) and \( \mu_i (V) \) are the chemical potential of the solute in liquid and its vapour phase respectively.

Now, the chemical potential, \( \mu_i (L) \) is given by
\[ \mu_i (L) = \mu_i^0 (T, P) + RT \ln x_i \]
where \( x_i \) is the mol-fraction of the solute in solution and \( \mu_i^0 (T) \) is given by
\[ \mu_i (V) = \mu_i^0 (T) + RT \ln (P_1/p^0) \]
where \( P_1 \) is the vapour pressure of the solvent in solution and \( P^0 \) is the standard pressure of 1.0 atm.

Therefore, chemical potential of a species is energy that can be absorbed or released due to a change in the particle number of a given species in a chemical reaction or phase transition.
\[ R_1^\circ(T, P) + RT \ln x_1 = R_2^\circ(T) + RT \ln \left( \frac{P}{P_1^\circ} \right) \quad (1) \]

Now, if \( P_1^\circ \) be the vapour pressure of the pure solvent at the same temperature, then for the equilibrium between pure solvent and its vapour, equation (1) will be:

\[ \Delta R_1^\circ(T, P) = R_1^\circ(T) + RT \ln \left( \frac{P}{P_1^\circ} \right) \quad (2) \]

Hence from equations (1) and (2), we get

\[ RT \ln \left( \frac{P}{P_1^\circ} \right) = R_1^\circ(T) \]

or,

\[ RT \ln \left( \frac{P}{P_1^\circ} \right) = RT \ln \left( \frac{P}{P_1^\circ} \right) \]

or,

\[ \frac{P}{P_1^\circ} \cdot \frac{x_1}{x_1} = \frac{P}{P_1^\circ} \]

or,

\[ P = P_1^\circ \]

or,

\[ \frac{P}{P_1^\circ} = x_1 \quad (3) \]

In equation (3), \( x_1 < 1 \), hence \( P \) is always less than \( P_1^\circ \), i.e., the vapour pressure of the solvent in solution will always lower than the vapour pressure of the pure solvent.

Now, if the solute is non-volatile, then \( x_1 = 1 - x_2 \), where \( x_2 \) is the mol-fraction of the solute in the solution. Hence equation (3) becomes

\[ \frac{P}{P_1^\circ} = 1 - x_2 \]

or,

\[ 1 - \frac{P}{P_1^\circ} = x_2 \]

or,

\[ \frac{P_1^\circ - P}{P_1^\circ} = x_2 \]

or,

\[ \frac{\Delta P}{P_1^\circ} = x_2 \quad (4) \]

where \( P_1^\circ - P \), is the lowering of vapour pressure of the solvent and \( \frac{\Delta P}{P_1^\circ} \) is called the relative lowering of vapour pressure of the solvent in solution. According to equation (2), for a dilute solution the relative lowering of vapour pressure is equal to the mol-fraction of the solute in solution. This is known as Raoult's law.

If \( n_1, n_2 \) are the gm-moles of the solvent and the solute respectively, then we have
Hence equation (5) becomes:

\[ \frac{\Delta p}{p_0} = \frac{n_2}{n_1 + n_2} \]

If the solution is dilute, then \( n_1 \gg n_2 \); so that

\[ n_1 + n_2 = n_1 \]

Therefore, equation (5) can be written as:

\[ \frac{\Delta p}{p_0} = \frac{n_2}{n_1} \]

For a definite quantity of a given solvent both \( n_1 \) and \( p_0 \) are constant. Therefore, according to equation (6), we have:

\[ \Delta p \propto n_2 \]

Which means that equimolar quantity of any non-volatile solute dissolved in same quantity of the solvent will produce the same lowering of vapour pressure. Also, lowering of vapour pressure is a colligative property as it depends only on the amount of solute, i.e., the number of solute particles, but not on their nature.

**Determination of molecular weight:**

Since \( n_1 = \frac{W_1}{M_1} \) and \( n_2 = \frac{W_2}{M_2} \)

where \( W_1, W_2 \) are masses of the solvent and the solute, and \( M_1, M_2 \) are their respective molar masses.

Substituting \( n_1, n_2 \) in equation (6), we get:

\[ \frac{\Delta p}{p_0} = \frac{W_2/M_2}{W_1/M_1} = \frac{W_2 \cdot M_1}{W_1 \cdot M_2} \]

or

\[ \sqrt{M_2} = \frac{p_0 \cdot W_2 \cdot M_1}{W_1 \cdot (\Delta p)} \]

If all the quantities on the R.H.S in equation (7) are known, then \( M_2 \), the molar mass of the solute, in the solution can be determined.

**Positive deviation from Raoult's law:** Acetone, ether, benzene, chloroform, etc.

**Negative deviation from Raoult's law:** Chloroform, acetone, methanol, acetone, etc.
The relative lowering of vapour pressure is independent of temperature. — comment on the statement.

Let $p^0$ be the vapour pressure of the pure solvent at a particular temperature $T$ and $p_1$ be the vapour pressure of the solvent in solution at the same temperature. Then the relative lowering of vapour pressure is

$$
\frac{p^0 - p_1}{p^0} = \frac{\Delta P}{p^0}
$$

Now, according to Clausius-Clapeyron equation, for the equilibrium between pure solvent and its vapour, we have

$$
\frac{\ln p^0}{dT} = \frac{Le}{RT^2}
$$

where $Le$ is the latent heat of evaporation per mole of the pure solvent and $p^0$ is the vapour pressure of the pure solvent.

Again, for the equilibrium between solvent in solution and its vapour, we have

$$
\frac{\ln p_1}{dT} = \frac{Le}{RT^2}
$$

where $p_1$ is the vapour pressure of the solvent in solution and $Le$ is the latent heat of evaporation per mole of the solvent in solution.

Now, subtracting equation 1 from equation 2, we get

$$
\frac{\ln p_1 - \ln p^0}{dT} = \frac{Le - Le}{RT^2}
$$

or

$$
\frac{d}{dT} \ln \left( \frac{p_1}{p^0} \right) = \frac{Le - Le}{RT^2}
$$

or

$$
\frac{d}{dT} \ln \left( \frac{1 - \frac{p_1 - p^0}{p^0}}{p_1 - p^0} \right) = \frac{Le - Le}{RT^2}
$$

If the solution is dilute, then $p_1 - p^0$ is very small and so $\ln \left( \frac{1 - \frac{p_1 - p^0}{p^0}}{p_1 - p^0} \right) \approx -\left( \frac{p_1 - p^0}{p^0} \right)$. Therefore equation 2 becomes

$$
-\frac{d}{dT} \left( \frac{p_1 - p^0}{p^0} \right) = \frac{Le - Le}{RT^2}
$$

or

$$
\frac{d}{dT} \left( \frac{p_1^0 - p_1}{p^0} \right) = -\left( \frac{Le - Le}{RT^2} \right)
$$

or

$$
\frac{d}{dT} \left( \frac{\Delta P}{p^0} \right) = -\left( \frac{Le - Le}{RT^2} \right)
$$

Therefore the above assertion may be true only if $(Le - Le)$ is zero.
i.e., \( \Delta L = L_c \) where \( \Delta L \) is the latent heat of evaporation of the solvent in solution is equal to the latent heat of evaporation of the pure solvent. Hence, the relative lowering of evaporation of the pure solvent is independent of temperature. If vapour pressure may be independent of temperature, then the relative lowering of vapour pressure of a dilute solution is independent of temperature only if the differential heat of solution is zero.

Suggest a method for experimental measurement of vapour pressure lowering of the solvent.

By Oswald-Walker method (transpiration method)

The relative lowering of vapour pressure can be obtained without measuring the vapour pressure of the solvent in solution and the pure solvent separately. This method may be obtained as follows:

A stream of dry air is slowly passed through a previously weighed series of U-tubes containing the solvent in solution in the following figure.

```
\[ \text{Solvent in Solution} \quad \text{Pure Solvent} \quad \text{Absorbent CaCl}_2 \]
```

The air takes up vapour from the solution until it is saturated up to the pressure \( P_1 \), which is the vapour pressure of the solvent in solution at that temperature. The actual loss of vapour from the U-tube is obtained by subsequently weighing the U-tube. The loss of weight, \( W \), is proportional to \( P_1 \), i.e.,

\[ W_1 = k P_1 \]

or, \( W_1 = k P_1 \)

where \( k \) is a constant of proportionality.

The air (already saturated with vapour up to pressure \( P_1 \)) is next passed through another series of U-tubes also previously weighed and containing the pure solvent. Since the vapour pressure of pure solvent is greater than \( P_1 \), the air will take up some more vapours from pure solvent until it is saturated to the pressure \( P_1 \), which is the vapour pressure of the
pure solvent. The U-tubes are weighed again to obtain the loss of weight, \( W_2 \) which is required to saturate the air from pressure \( P_i \) to \( P_i^0 \). Therefore,

\[
\frac{W_2}{P_i^0 - P_i} = K
\]

or,

\[
W_2 = K (P_i^0 - P_i)
\]

Finally, the air is passed through a weighed series of U-tubes containing an absorbent for the vapour of the solvent. For example, anhydrous calcium oxide is used, if the solvent is water. The increase in weight is the measure of vapour required to saturate the air up to \( P_i^0 \). Therefore,

\[
W_1 + W_2 = K P_i^0
\]

Hence

\[
\frac{P_i^0 - P_i}{P_i^0} = \frac{W_2/K}{W_1 + W_2} = \frac{W_2}{W_1 + W_2}
\]

Since the quantities of the R.H.S. are known, the relative lowering of vapour pressure is obtained. The temperature must be kept constant throughout the experiment.

**Elevation of boiling point**

Show graphically, the elevation of boiling point of the solvent in the solution.

A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. Let \( T_b \) be the boiling temperature of the pure solvent and its vapour pressure equals to 1 atm at this temperature. But at this temperature solution will have a vapour pressure lower than 1 atm and hence it will not boil. Further, with increase in temperature say to \( T_b' \), the vapour pressure over the solution rises to 1 atm when the solution would boil. This means that the solvent in solution has a higher boiling point than that of the pure solvent. The increase in boiling temperature i.e., the elevation of boiling point of the solvent in solution is given by

\[
\Delta T_b = T_b' - T_b
\]

This is shown in the following vapour pressure vs. temperature diagram.
Give the molecular interpretation for the elevation of boiling point of the solvent in solution. Or, why is the boiling point of a solvent elevated when a non-volatile solute is added to it?

The addition of a non-volatile solute to the solvent will lead to a decrease in the chemical potential of the liquid. But the chemical potential of the vapour will remain unchanged. The physical basis for lowering of chemical potential can not be in the modification of intermolecular forces, because the magnitude of intermolecular forces, in case of elevation of boiling point takes place even in case of ideal solution. Thus, since it is not an enthalpy effect, it must be an entropy effect.

If a liquid is kept in a vessel, evaporation takes place because this lead to increase in randomness. This is a process leading to increase in entropy at constant temperature, when a solute is added, there is extra randomness in the liquid. Consequently, the tendency of the solvent to go to the vapour phase decreases, in a closed vessel, the vapour phase decreases. In a closed vessel, there will be lesser amount of the solvent will decrease. Thus, the vapour pressure of the solvent will decrease. Thus, the vapour pressure of the solvent pressure means elevation of boiling point. However, because there is higher randomness in a solution in comparison to solvent, the same process (\( \Delta G = \Delta H - T \Delta S \)) can arise only at higher temperature. Thus, the boiling point of a solvent in solution is elevated.

Derive, thermodynamically, the expression for elevation of boiling point of a solvent in solution containing non-volatile non-electrolyte solute with assumptions and approximations.

Let us consider a cylinder covered by a piston in which there is pure solvent in equilibrium with its vapour, at normal boiling temperature, \( T_b \) and under constant external pressure of \( P_b \). At equilibrium, the chemical potential of the pure solvent in both phases are equal; i.e.,

\[
\mu^0_L = \mu^0_v
\]

where \( \mu^0_L \), \( \mu^0_v \) are the chemical potential of the solvent in liquid and vapour phases respectively.
Now, a small amount of a non-volatile solute is added, so that a solution of solute mole-fraction \( x_2 \) results. As a result, the chemical potential of the solvent is reduced to \( \mu_1^* (T) \). But the chemical potential of the vapour phase remains unchanged. The equilibrium can be re-established by increasing the temperature from \( T_b \) to \( T_b' \), so that \( \mu_1^* (T) \) changes to \( \mu_1 (T) \) and \( \mu_2 (T) \) changes to \( \mu_2 (T) \). Thus, at new equilibrium, \( \mu_1 (T) = \mu_1^* (T) \) i.e.,
\[
d\mu_1 (T) = d\mu_1^* (T)
\]

Now,
\[
\mu_1 (T) = f (T, x_2)
\]
and
\[
\mu_2 (T) = f (T) \text{ only}
\]

Therefore,
\[
d\mu_1 (T) = \left[ \frac{\partial \mu_1 (T)}{\partial T} \right]_{P, x_2} dT + \left[ \frac{\partial \mu_1 (T)}{\partial x_2} \right]_{P, T} dx_2
\]

and
\[
d\mu_2 (T) = \left[ \frac{\partial \mu_2 (T)}{\partial T} \right]_{P, x_2} dT + \left[ \frac{\partial \mu_2 (T)}{\partial x_2} \right]_{P, T} dx_2
\]
with these, equation 1 becomes
\[
\left[ \frac{\partial \mu_1 (T)}{\partial T} \right]_{P, x_2} dT + \left[ \frac{\partial \mu_1 (T)}{\partial x_2} \right]_{P, T} dx_2 = \left[ \frac{\partial \mu_2 (T)}{\partial T} \right]_{P, x_2} dT + \left[ \frac{\partial \mu_2 (T)}{\partial x_2} \right]_{P, T} dx_2
\]

But for a closed system, we have
\[
\frac{d\mu_1}{d\mu_2} = \frac{-S_1}{V_1} \frac{dT}{dP} \implies \left[ \frac{\partial \mu_1}{\partial T} \right]_{P, x_2} = -\frac{\partial S_1}{\partial x_2}
\]
where \( S_1 \) and \( V_1 \) are the partial molar entropy and volume of the solvent respectively.

Thus, from equations 2 and 3, we have
\[
-\frac{\partial S_1}{\partial x_2} \frac{dT}{dP} + \left[ \frac{\partial \mu_1^* (T)}{\partial x_2} \right]_{P, T} dx_2 = -\frac{\partial S_1}{\partial x_2} \frac{dT}{dP} + \left[ \frac{\partial \mu_1^* (T)}{\partial x_2} \right]_{P, T} dx_2
\]

For a dilute solution, when Raoult's law is valid, we have
\[
\mu_1 = \mu_1^* (T, P) + RT \ln x_1
\]
where \( x_1 \) is the mole fraction of the solvent in the solution.

Thus,
\[
\left[ \frac{\partial \mu_1}{\partial x_2} \right]_{T, P} = 0 + RT \left[ \frac{\partial \ln x_1}{\partial x_2} \right]_{T, P}
\]

Now, we have \( x_1 = 1 - x_2 \). Therefore,
\[
\left[ \frac{\partial \mu_1}{\partial x_2} \right]_{T, P} = RT \left[ \frac{\partial \ln (1-x_2)}{\partial x_2} \right]_{T, P}
\]

For a dilute solution, \( x_2 \) is very small, so that \( \ln (1-x_2) = -x_2 \). Thus, we get
\[
\frac{\partial H_v}{\partial x_2} \bigg|_{T, P} = -RT
\]

Hence, from equations (4) and (5), we have
\[
\beta_1 (\omega - \omega') - RT \frac{dx_2}{dt} = -S_1 \omega \frac{d\omega}{dt}
\]
or,
\[
[S_1(\omega) - S_1(\omega')] \frac{d\omega}{d\tau} = RT \frac{dx_2}{dt}
\]

or,
\[
\Delta S_v \frac{d\tau}{dT} = RT dx_2
\]

where \( \Delta S_v \) is the partial molar entropy change during vaporisation, but \( \Delta S_v = \frac{\Delta H_v}{T} \), where \( \Delta H_v \) is the partial molar enthalpy change during vaporisation.

Hence equation (6) becomes
\[
\frac{\Delta H_v}{T} \frac{d\tau}{dT} = RT dx_2
\]
or,
\[
x_2 = \frac{\Delta H_v}{R} \int \frac{d\tau}{T^2} = \int \frac{L_v}{R} \left[ \frac{1}{T_B} - \frac{1}{T_b} \right] \frac{dT}{T^2}
\]
or,
\[
x_2 = \frac{L_v}{R} \left[ \frac{T_B - T_b}{T_B T_b} \right] = \frac{L_v}{R} \cdot \frac{\Delta T_b}{T_b^2}
\]

[where \( \Delta T_b = T'_b - T_b \), is called the elevation of boiling point and \( T'_b \approx T_b \) for a dilute solution.]

or,
\[
\Delta T_b = \frac{RT_B}{L_v} \cdot x_2
\]

The equation (8) is the law for the elevation of boiling point of a solvent in solution in terms of latent heat of vaporisation of the solvent, the boiling point of the solvent and the mole fraction of the solute in solution.

Since \( T_b \) and \( L_v \) are constant for a given solvent, therefore the elevation of boiling point of the solvent in solution is directly proportional to the mole fraction of the solute and is independent of the nature of the solute.

\( \text{If} \; n_1, n_2 \; \text{are the gm-moles of solvent and solute respectively, then} \)
\[ x_2 = \frac{n_2}{n_1 + n_2} \]

For a dilute solution, \( n_1 \gg n_2 \) and thus,

\[ x_2 = \frac{n_2}{n_1} \quad (\text{Since } n_1 + n_2 = n_1) \]

Hence, equation (8) becomes

\[ \Delta T_b = \frac{R T_b^2}{L_v} \cdot \frac{n_2}{n_1} \quad (9) \]

If the solute is non-electrolyte, then

\[ n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2} \]

where \( W_1, W_2 \) are the masses of solvent and solute respectively and \( M_1, M_2 \) are their respective molar masses. Therefore, equation (9) becomes

\[ \Delta T_b = \frac{RT_b^2}{L_v} \cdot \frac{W_2}{W_1} \cdot \frac{M_1}{M_2} \quad \text{Molarity} \quad \text{Amount of solute in Gram-mole per} \]

\[ = \frac{RT_b^2}{L_v/M_1} \cdot \frac{W_2}{M_2 W_1} \quad 1000 \text{gm of solvent} \]

\[ = \frac{RT_b^2}{L_v} \cdot \frac{W_2}{M_2 W_1} \]

where \( L_v \) is the latent heat of vaporisation per gm of the solvent. Therefore,

\[ \Delta T_b = \frac{RT_b^2}{L_v \times 1000} \cdot \frac{1000 \times W_2}{M_2 W_1} \]

or,

\[ \Delta T_b = K_b \cdot \frac{W_2}{M_2 W_1} \quad (10) \]

where \( K_b = \frac{RT_b^2}{L_v \times 1000} \) is a constant for a given solvent and is called ebullioscopic constant or molal elevation constant and \( m = \frac{W_2}{M_2 W_1} \) is called the molality of the solution. The equation (10) is the appropriate relation between elevation of boiling point and the molality of the solution.

Assumptions:

1. The solute is non-volatile and non-electrolyte.
2. The solution is ideal and also dilute.
3. Raoult's law is valid.
4. \( L_v \) is independent on temperature.
Ceramics

The word ceramic is derived from the greek term *keramos*, which means “potter’s clay” and *keramikos* means “clay products”. Till 1950s, the most important types of ceramics were the traditional clays, made into pottery, bricks, tiles etc. Ceramic artefacts play an important role in historical understanding of the technology and culture of the people who lived many years ago.

A ceramic material is an inorganic, non-metallic material and is often crystalline. Traditional ceramics are basically clays. The earliest application was in pottery. Most recently, different types of ceramics used are alumina, silicon carbide etc. Latest advancements are in the bio-ceramics with examples being dental implants and synthetic bones.

A comparative analysis of ceramics with other engineering materials is shown in table 1. The purpose of presenting this comparative analysis is to show importance of ceramics among different engineering metals and polymers. This comparison would enable to justify application areas of ceramics.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ceramic</th>
<th>Metal</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Low</td>
<td>High</td>
<td>Lowest</td>
</tr>
<tr>
<td>Hardness</td>
<td>Highest</td>
<td>Low</td>
<td>Lowest</td>
</tr>
<tr>
<td>Ductility</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Thermal / Electrical conductivity</td>
<td>Mostly low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

Properties of Ceramic materials
The properties of the materials depend upon the types of atoms present, the types of bonding between the atoms and the way the atoms are packed together. A wide range of properties of ceramics can be obtained due to the variation in crystal structure of ceramics. The crystal structure of ceramics is relatively more complex than metals. Depending upon the bonding, there exits different types of properties in ceramics. Type of Bonding in Ceramics leads to:

1. high melting point
2. low thermal expansion
3. high elastic modulus
4. high hardness
5. good chemical resistance
6. brittleness
Applications

- Pottery products, sanitary ware, floor and roof tiles
- Crucibles, kiln linings, other refractories
- High end applications such as in ceramic matrix composites, tiles in space shuttle, bullet proof jackets, disk brakes, ball bearing applications, bio-ceramics

Classification of ceramics materials

Ceramics can be classified in diverse ways i.e. there are number of ways to classify the ceramic materials. Most commonly, the ceramics can be classified on the following basis:

Based on composition
1. Silicate ceramics
2. Oxide ceramics
3. Non-oxide ceramics
4. Glass ceramics

Based on applications
1. Glasses (Containers, household, optical glasses)
2. High performance advanced ceramics (Sensors, engine rotors, valve bearings)
3. Traditional vitreous ceramics (Sanitary ware, tiles, bricks)
4. Natural Ceramics(Rocks & minerals, bones)
5. Cement & Concrete (Structural, composites)

Classification based on composition

(i) Silicate ceramics

Silicates are materials generally having composition of silicon and oxygen. Four large oxygen (o) atoms surround each smaller silicon (Si) atom as shown in figure.

The main types of silicate ceramics are based either on aluminosilicates or on magnesium silicates. Out of these two, the former include clay-based ceramics such as porcelain, earthenware, stoneware, bricks etc. while the latter consists of talc-based technical ceramics such as steatite, cordierite and forsterite ceramics. Silicate ceramics are traditionally categorized into coarse or fine and, according to water absorption, into dense (< 2% for fine and < 6% for coarse) or porous ceramics (> 2% and > 6%, respectively).

(ii) Oxide ceramics

Oxide ceramics include alumina, zirconia, silica, aluminium silicate, magnesia and other metal oxide based materials. These are non-metallic and inorganic compounds by nature that include oxygen, carbon, or nitrogen. Oxide ceramics possess the following properties:

(a) High melting points
(b) Low wear resistance
(c) An extensive collection of electrical properties
These types of ceramics are available with a variety of special features. For example, glazes and protective coatings seal porosity, improved water or chemical resistance, and enhanced joining to metals or other materials.

Oxide ceramics are used in a wide range of applications, which include materials and chemical processing, radio frequency and microwave applications, electrical and high voltage power applications and foundry and metal processing.

Aluminium oxide ($\text{Al}_2\text{O}_3$) is the most important technical oxide ceramic material. This synthetically manufactured material consists of aluminium oxide ranging from 80% to more than 99%.

Structure of aluminium oxide

(iii) Non-Oxide ceramics
The use of non-oxide ceramics has enabled extreme wear and corrosion problems to be overcome, even at high temperature and severe thermal shock conditions. These types of ceramics find its application in different spheres such as pharmaceuticals, oil and gas industry, valves, seals, rotating parts, wear plates, location pins for projection welding, cutting tool tips, abrasive powder blast nozzles, metal forming tooling etc.

(iv) Glass ceramics
These are basically polycrystalline material manufactured through the controlled crystallization of base glass. Glass-ceramic materials share many common characteristics with both glasses and ceramics. Glass-ceramics possess an amorphous phase and more than one crystalline phases. These are produced by a controlled crystallization procedure. Glass-ceramics holds the processing advantage of glass and has special characteristics of ceramics.

Glass-ceramics yield an array of materials with interesting properties like zero porosity, fluorescence, high strength, toughness, low or even negative thermal expansion, opacity, pigmentation, high temperature stability, low dielectric constant, machinability, high chemical durability, biocompatibility, superconductivity, isolation capabilities and high resistivity. These properties can be altered by controlling composition and by controlled heat treatment of the base glass.

Classification based on application

(i) Glasses
Glasses are based on Silicate ($\text{SiO}_2$) along with other additives to shrink the melting point and to impart special characteristic properties. Glasses are mainly used in the manufacturing of the following products:

- containers
- households
- optical glasses etc.
(ii) **High performance advanced ceramics**
These are basically special ceramics having outstanding measures in terms of toughness, wear resistance, electrical properties, etc. Its applicative demand has rose to a larger extent in the last decade and finds its need in cutting tool, grinding, bearing, sensor, laser, superconductor, insulators, electrical transmission components, spark plugs, and microelectronic chip substrates, magnetic ceramics (computer memories), nuclear fuels (based on UO$_2$), bioceramics (artificial teeth and bones), etc.

(iii) **Traditional vitreous ceramics**
All the clay-based products within ceramics come under this category. Applications are easily noticeable in porcelain, sanitary ware, tiles, bricks, refractories etc.

(iv) **Cement and concrete**
Cement and concrete ceramics are basically multiphase materials that is these materials exist in more than one phase.

(v) **Natural ceramics**
Natural ceramics include rocks, minerals, ores that are extracted from the earth and are produced by the laws of nature. Bones also come under natural ceramics.
Refractories

Refractories are inorganic nonmetallic material which can withstand high temperature without undergoing physico – chemical changes while remaining in contact with molten slag, metal and gases. It is necessary to produce range of refractory materials with different properties to meet range of processing conditions. The refractory range incorporates fired, chemically and carbon bonded materials that are made in different combinations and shapes for diversified applications.

**Need of a refractory**
To minimize heat losses from the reaction chamber.
To allow thermal energy dependent conversion of chemically reactive reactants into products because metallic vessels are not suitable.

In steelmaking, the physico-chemical properties of the following phases are important:

**Slag**: Mixture of acidic and basic inorganic oxides like SiO$_2$, P$_2$O$_5$, CaO, MgO, FeO, etc.; temperature varies in between 1400℃ to 1600℃.

**Molten steel**: Iron containing carbon, silicon, manganese, phosphorous, tramp elements, non metallic inclusions, dissolved gases like nitrogen, oxygen and hydrogen and different alloying elements like Cr, Ni, Nb, Mo, W, Mo etc.; temperature 1600℃

**Gases**: CO, CO$_2$, N$_2$, Ar containing solid particles of Fe$_2$O$_3$, Fe$_3$O$_4$ etc.; temperature 1300℃ to 1600℃.

The above phases are continuously and constantly in contact with each other and are in turbulent motion.

**Refractory requirements:**
The refractory materials should be able to withstand
• High temperature
• Sudden changes of temperature
• Load at service conditions
• Chemical and abrasive action of phases

The refractory material should not contaminate the material with which it is in contact.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Melting point (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (pure sintered)</td>
<td>2800</td>
</tr>
<tr>
<td>CaO(limit)</td>
<td>2571</td>
</tr>
<tr>
<td>SiC pure</td>
<td>2248</td>
</tr>
</tbody>
</table>
Properties required in a refractory
The diversified applications of refractory materials in several different types of industries require diversified properties to meet the physico-chemical and thermal requirements of different phases. In some industrial units more than one phase are present e.g. in steel-making vessels slag /metal /gases are simultaneously present in the vessel at high temperatures. In the heat treating furnaces solid/reducing or oxidizing gases are simultaneously present.

Types of refractory materials
This can be discussed in several ways, for example chemical composition of refractory or use of refractory or method of manufacture or in terms of physical shape. Below is given type of refractory depending on its chemical composition and physical shape.

a) Chemical composition
Refractories are composed of either single or multi-component in organic compounds with non metallic elements.

Acid refractory
The main raw materials used are SiO₂,ZrO₂ and alumino- silicate. They are used where slag and atmosphere are acidic. They cannot be used under basic conditions. Typical refractories are fireclay, quartz and silica.

Basic refractory
Raw materials used are CaO,MgO, dolomite and chrome-magnesite. Basic refractories are produced from a composition of dead burnt magnesite, dolomite, chrome ore.
   a) Magnesite: Chrome combinations have good resistance to chemical action of basic slag and mechanical strength and volume stability at high temperatures.
   b) Magnesite: Carbon refractory with varying amount of carbon has excellent resistance to chemical attack by steelmaking slags.
   c) Chromite- Magnesite refractory: used in inner lining of BOF and side walls of soaking pits.( basic refractory)
   d) Magnesite: Basic refractory in nature. Magnesite bricks cannot resist thermal stock, loose strength at high temperature and are not resistant to abrasion.

Neutral refractory
Neutral refractory is chemically stable to both acids and bases. They are manufactured from Al₂O₃,Cr₂O₃ and carbon.

b) Physical form
Broadly speaking refractory materials are either bricks or monolithic.
**Bricks**

Shaped refractories are in the form the bricks of some standard dimensions. These refractories are machine pressed and have uniform properties. Special shapes with required dimensions are hand molded and are used for particular kilns and furnaces. Different types are:

i) Ramming refractory material is in loose dry form with graded particle size. They are mixed with water for use. Wet ramming masses are used immediately on opening.

ii) Castables refractory materials contain binder such as aluminate cement which imparts hydraulic setting properties when mixed with water. These materials are installed by casting and are also known as refractory concretes.

iii) Mortars are finely ground refractory materials, which become plastic when mixed with water. These are used to fill the gap created by a deformed shell, and to make wall gas tight to prevent slag penetration. Bricks are joined with mortars to provide a structure.

iv) Plastic refractories are packed in moisture proof packing and pickings are opened at the time of use. Plastic refractories have high resistance to corrosion.

**Monolithic**

Monolithic refractories are replacing conventional brick refractories in steel making and other metal extraction industries. Monolithic refractories are loose materials which can be used to form joint free lining. The main advantages of monolithic linings are:

- Greater volume stability
- Better spalling tendency
- Elimination of joint compared with brick lining
- Can be installed in hot standby mode
- Transportation is easier

Monolithic refractories can be installed by casting, spraying etc. Ramming masses are used mostly in cold condition so that desired shapes can be obtained with accuracy.
Polymers

A polymer is a long molecule formed by the joining together of thousands of small molecular units by chemical bonds. Due to their large size, they are called as macromolecules.

The chemical process leading to the formation of polymer is known as polymerization. Small molecules which combine with each other to form polymer molecules are known as monomers. The no. of monomeric units contained in the polymer is known as degree of polymerization.

\[ n \left( CH_2 = CH_2 \right) \rightarrow \left( CH_2 = CH_2 \right)_n \]

- Ethene
- Monomer
- Polymer
- Polyethylene, PE

\[ n \text{ is degree of polymerisation, } 10^4 (a) \text{ mol} \]

Notes

Functionality:

- No. of bonding sites in monomer
- CH₂=CH-X (b) functional
  - vinyl
  - (two sites)
Polymer classification

Based on structure/shape
  - Linear
  - Branched
  - Cross-linked

Based on physical state
  - Amorphous: LDPE, Rubber
  - Semi-crystalline: HDPE, Nylon, Polyester

Based on its behaviour when heated to processing temp.
  - Thermoplastic: PE, PP, PVC, Nylon, PET
  - Thermoset: PF, UF, MF, Epoxy, etc.

Based on end use
  - Fibres
  - Plastics
  - Elastomers
  - Films
  - Adhesives
  - Paints
  - Membranes
Based on tacticity, p, m, R, side groups all on the main chain:
- Isotactic
- Syndiotactic
- Atactic
- Random around the main chain

Based on origin:
- Natural
- Synthetic

Based on conductance:
Polymer mostly be insulator, but they are conducting polyammon polymers.

Based on environment-friendly:
Polymer can be degradable or biodegradable.

Starch-based PE

Based on type of monomers:
- Polar: PET, Nylon
- Non-polar: PE, PP

Based on no. of monomers:
- Homopolymers: PE, PP, PVC
- Copolymers: PE, PP

---

Notes

Polymers advantage:
- Low density
- Resistant to corrosion
- Insulation
- Flexibility (Rubber)
- Complex shape and reproducible dimension
- Variety of colour
- Tailor-made
Disadvantages:
- Lower strength and stiffness
- Temperature limitations: low heat resistance
- Time-dependent properties
- Combustible

Polymerization: It is a process by which simple molecules join together by chemical bonds to form very large molecules.

Opening of double bond:

\[ n \text{CH}_2=\text{CH}_2 \rightarrow (\text{CH}_2=\text{CH}_2)_n \]

Opening of ring:

\[ \text{HO} \quad \rightarrow \quad (\text{HO})_n \]

S. valerobetone  \quad \rightarrow \quad \text{polyester}

Molecules having two functions:

\[ n \text{HOOC-(CH}_2)_2-\text{COOH} + n \text{H}_2 \text{N-CH}_2\text{N-(CH}_2)_2\text{NH}_2 \]

Acrylic acid  \quad \rightarrow \quad \text{Hexamethylene diamine}

\[ \text{[C-(CH}_2)_2-H-N-(CH}_2)_2-N-H]_n \]

Nylon 6,6
Polymerisation
1. Addition
2. Condensation

Addition:
Polymer has same empirical formula as that of monomers.
No molecule is formed as by-product during polymerisation.
Polymer is an exact multiple of original monomeric molecule

\[ n(CH=CH) \rightarrow \text{CH}_2-\text{CH}_2 \]

\[ R \]

\[ n \]

R = H, CH₃, Cl, C₆H₅

Polymer PE PP PVC PS

Condensation Polymerisation:
Condensation of two different bi (or) poly functional monomers having functional groups which have affinity for each other.

- COOH and -OH;  -COOH and -NH₂

\[ n \cdot \text{HO-C-OH} + n \cdot \text{HOC}-(\text{CH}_2)_2-\text{OH} \rightarrow \text{HO}-\text{(CO)\text{-(CH}_2\text{)\text{O}-}} \]

Terephthalic acid
Ethylene
Polyethylene
Terephthalate
Thermodynamics of polymerization reaction

\[ \Delta G = \Delta H - T \Delta S \]

\( \Delta H \): enthalpy of polymerization
\( \Delta S \): entropy of polymer - entropy of monomer
\( T \): polymerization temp.

\( \Delta H \): \text{\textasciitilde}vive (\textit{exo}\text{thermic})
\( \Delta S \): \text{\textasciitilde}vive

Increase in temp. increases T\Delta S value.
\( \Delta H \) does not change significantly at a specific temp., where \( \Delta G = 0 \), now the polymerization reaction is said to be dynamic equilibrium.

The temp. \( T \) at which equilibrium is attained is known as ceiling temp. \( T_c \)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>styrene</th>
<th>( \alpha )-methyl styrene</th>
<th>methyl methacrylate</th>
<th>ethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_c ) (°C)</td>
<td>310</td>
<td>61</td>
<td>220</td>
<td>693</td>
</tr>
</tbody>
</table>
Notes

\[ M_{n-1}^* + M \xrightarrow{t_{dp}} M_n \]

\[ \Delta \mu^o = \Delta H^o - T \Delta S^o \]

\[ \Delta G^o = -RT \ln K \]

\[ K = \frac{t_{dp}}{t_{dp}} \]

\[ t_{dp} [M_{n-1}^*][M] = t_{dp} [M_n^*] \]

\[ [M_{n-1}^*] = [M_n^*] \]

\[ T = \frac{\Delta H^o}{\Delta S^o + R \ln [M]_c} \]

Equilibrium monomer conc.

\[ \ln [M]_c = \frac{\Delta H^o - \Delta S^o}{RT_c \Delta S^o} \]
Floor temp. $T_f$

The temp. below which no appreciable amount of polymerisation.

The optimum temp. for polymerisation fall between $T_f$ and $T_e$

Endo thermo polymerisation

$\Delta H = +ive$

$\Delta S = +ive$

Polymerisation of octene $S_8$

$S\rightarrow S-S-S\rightarrow S_8\rightarrow S-S_{n-1}S_n\rightarrow$ chain ended.

Floor temp. $160^\circ C$

Addition

Condensation

Presence of double bond

Two reactive func.

Two different bi-(or)

No by-products is formed

By-products is formed

Homo-chain polymer

Hetero-chain polymer

Thermoplastic

Thermo-plastic (or) thermostet

Growth of chain in at one

Growth of chain occurs at minimum of two active centres

PE

Nylon-6

PVC

Nylon-66

PS

PET
Polyethylene

\[ n \text{ CH}_2 = \text{CH}_2 \rightarrow \left\{ \text{CH}_2 - \text{CH}_2 \right\}_n \] addition

\[ n \cdot \text{Br} + (\text{CH}_2)_n \cdot \text{Br} \xrightarrow{2n - \text{Na}} \left\{ (\text{CH}_2)_n \right\}_n \] condensation

- Polymer I
  - Very hard, tough solid, mp 115 - 135°C

- Polymer II
  - Low Mwt, waxy solid, mp 87 - 105°C
Step growth polymerization

Monomer $\rightarrow$ Dimer $\rightarrow$ Trimer $\rightarrow$ Oligomers $\rightarrow$ Polymer

Monomer disappears early in the reaction

Degree of polymerization and molecular weight increases steadily throughout the reaction

Longer time is required for getting high molecular weight.

Addition

$$\text{CH}_3\text{C} = \text{O} + \text{HO-}R'\text{OH} \rightarrow \text{CH}_2\text{H}_2\text{N} = \text{C} = \text{O} - \text{R'-O}$$

Dimercyanate

Condensation

$$\text{Cl} = \text{C} = \text{Cl} + \text{HO-(CH}_2\text{)}_2\text{-OH} \rightarrow 2\text{nHCl} + \left[\text{HO-(CH}_2\text{)}_2\text{-CH}_2\text{COO}^-\right]_n$$

Benzoyl chloride, ethylene glycol, polymerization

Nylon 66

$$\text{nHO-C(CH}_2\text{)}_4\text{-OH} + \text{nH}_2\text{N-}-(\text{CH}_2\text{)}_6\text{-NH}_2$$

$$\rightarrow 2\text{nH}_2\text{O}$$

$$\left[\text{HO-(CH}_2\text{)}_4\text{-H-(CH}_2\text{)}_6\text{-NH}^-\right]_n$$

It proceeds by stepwise intramolecular condensation.
Chain growth polymerisation

It proceeds by chain mechanism and high M.wt. polymers are formed after start of the reaction.

Longer reaction time have little effect on M.wt but improves the yield.

At any stage, either unreacted monomer or high M.wt. polymer is there.

No oligomers are there.

Initiators are used. (free radical, cationic, or anionic)

R^+ Na^–

Addition

High m.wt. polymers can be synthesized from vinyl monomers by radical (or) ionic polymerisation.

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \quad \text{CH}_2=\text{CH} \\
& \quad \text{CH}_2=\text{CH} \quad \text{X} \\
& \quad \text{X} \rightarrow \text{Cl} \\
& \quad \text{X} \rightarrow \text{CH}_3 \\
& \quad \text{Y} \rightarrow \text{COOCH}_3
\end{align*}
\]
Notes

condensation

\[
\begin{align*}
\text{Friedel-Crafts} \\
\text{Monomer} \\
\text{Trimer}
\end{align*}
\]

3. active site

Chain growth (addition) Polymersiation

\[
\text{CH}_2=\text{CH}-\text{R} \quad \text{R} \Rightarrow \text{H, CH}_3, \text{Cl, CN, Ph etc}
\]

Mechanism:

1. Chain initiation: \( M \xrightarrow{I} M^* \)
2. Chain propagation: \( M^* + M \rightarrow M_1^*; M_1^* + M \rightarrow M_2^* \)
3. Chain termination: \( M_n^* + M \rightarrow M_n^+ \)

\( M_n^* \Rightarrow M_n \)

\( M_n^+ \Rightarrow \text{activated fusing polymer chain} \)

\( M_n \Rightarrow \text{inactive polymer molecule} \)

Free radical

\text{ionic polymerization} \Rightarrow 1. Cationic 2. Anionic

\text{coordinate reaction}
Free radical

Phenyl radical

Benzoyl peroxide

Acetone

Isobutyl nitrite (AIBN)

Chain initiation

\[ \text{In} \rightarrow 2R' \]

\[ R' + CH=CH \overset{R'}{\rightarrow} R-CH=CH \]

Chain propagation

\[ R-CH=CH + CH=CH \overset{R'}{\rightarrow} R\left[CH=CH\right]CH=CH \]

[Diagram of benzoyl peroxide and related reactions]
Propagating step determines:
  - Rate of polymerization
  - Mw of polymer
  - Structure of chain
  - Mode of monomer addition

Chain termination (mainly):
  - Radical recombination

\[
\text{Me-CH}_2\text{-CH} + \text{CH}_2\text{-CH}_2\text{-ML} \rightarrow \text{Me-CH}_2\text{-CH-CH}_2\text{-CH}_2\text{-ML}
\]

\[
\text{Me-CH}_2\text{-CH} + \text{R}^* \rightarrow \text{Me-CH}_2\text{-CH-R}
\]

At \( T = 60^\circ C \)

Polyethylene and acrylonitrile
Disproportionation

\[ \text{CH}_3-\text{C}^\cdot + \text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \rightarrow \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH} + \text{H}^\cdot - \text{CH} \]

At \( T > 60^\circ C \), PMMA and vinylacetaldehyde

\[ \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \]

Reactions with polymerization inhibitors

\[ \text{CH}_2=\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \]

Chain transfer

\[ \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{C}^\cdot + \text{CH}_2=\text{CH}_2 \]
Notes

Branching and cross-linking

\[ \text{Monomer} + \text{CH}_2=\text{CH} \rightarrow \text{Monomer} \]

Monomer for free radical polymerization
Ethylene and vinyl derivatives \( \text{CH}_2=\text{CH} \)
Acrylic acid derivative \( \text{CH}_2=\text{CH} \)
Butadiene, isoprene, chloroprene

Notes

Ionic Polymerisation

Cationic
Dependence on formation and propagation of ionic species
Relatively low (or moderate) temp
(necessary to suppress termination, favour chain breaking reactions)

Monomers with EWG (\(-\text{OME}, -\text{OT}, -\text{Ph}, \text{etc}\))
Presence of Lewis and Friedel-Craft catalysts (\(\text{AlCl}_3, \text{BF}_3, \text{SbCl}_5 \text{etc}\))
Generation of carbocation
High rate even at low temp
\(\alpha\)-methylstyrene, isobutylene
Chain initiation

\[ \text{SnCl}_2 + H_2O \rightarrow [\text{SnCl}_2\cdot OH]^- + H^+ \]

\[ \text{CH}_2 = \text{CH} + H^+ \rightarrow \text{CH}_3 - \text{CH} \]

Chain propagation

\[ \text{CH}_3 - \text{CH} + n \cdot \text{CH}_2 = \text{CH} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH} \]

\[ \text{ph} \quad \text{ph} \quad \text{ph} \]

Chain termination

\[ \text{CH}_5 - \text{CH} + [\text{CH}_2 - \text{CH}]^- + \text{CH}_2 = \text{CH} \rightarrow \text{CH}_3 - \text{CH} \{\text{CH}_2 - \text{CH}_2\} - \text{CH}_2 \]

\[ \text{ph} \quad \text{ph} \quad \text{h} \quad \text{ph} \quad \text{ph} \quad \text{ph} \]

\[ + H^+ \]

Depolymerization

\[ \text{BF}_3 + \text{H}_2\text{O} \rightarrow [\text{BF}_3\cdot \text{OH}]^+ + \text{H}^+ \]
**Notes**

**Anionic polymerization**

Monomer with EWG:

$$R - C - H \rightarrow R - C^\ominus \leftrightarrow R - C$$

$$\begin{array}{c}
\text{chain initiation,} \\
\text{CH}_2 = C - CH_3 + K^+\text{NH}_4^- \rightarrow H_2NCH_2C^\ominus K^+\text{COOH}
\end{array}$$

**Chain propagation**

$$\begin{array}{c}
\text{CH}_3 - C^\ominus + K^+\text{NH}_4^- \rightarrow \text{CH}_3C^\ominusCH + K^+\text{NH}_4^-
\end{array}$$

Living polymer

Living polymers are polymerizations in which propagating centers do not undergo either transfer or terminal reaction.
Notes

Coordination polymerisation
Zeisler Natta

$\text{TiCl}_3$ and $\text{Al (C}_2\text{H}_5)_3 \rightarrow \text{Bimetallic}$

\[
\text{Et} \quad \text{Et} + \text{Cl} \rightarrow \text{EtCl} \rightarrow \text{Et} + \text{C}_2\text{H}_5
\]

\[
\text{Et} - \text{Al} - \text{Et} \rightarrow \text{Et} + \text{C}_2\text{H}_5
\]

\[
\text{Et} \quad + n\text{CH}_2=\text{CH} \quad \rightarrow \quad \text{EtCH}_2=\text{CH}_2
\]

\[
\text{CH}_3-\text{CH}=(\text{CH}_2-\text{CH})_n \rightarrow \text{EtCH}_2-\text{CH}_2 \rightarrow \text{EtCH}_2-\text{CH}_2
\]

Termination

\[\text{Et} \quad \text{Et} \quad \text{Et} \]

\[\text{Et} \quad \text{Et} \quad \text{Et} \]

\[\text{Et} \quad \text{Et} \quad \text{Et} \]
Notes

Stereoregular

Propylene \rightarrow \text{ tactic } \rightarrow \text{ high MP, hardopération property}

Linear free from branching

Stereoregularity control about \text{ c-c bond}

\text{ cis-1,4-polyisoprene (identical with natural rubber) }

\text{ cis-1,4-linear }

CH_2 = CH-CH = CH \rightarrow \left[ \begin{array}{c}
\text{ cis} \\
\text{ cis}
\end{array} \right]_m

\text{ cis-1,4-linear }

Notes

Co-polymerization

m \text{ CH}_2 = \text{ CH} + n \text{ CH}_2 = \text{ CH} \rightarrow \left[ \text{ CH}_2 = \text{ CH} \right]_m \left[ \text{ CH}_2 = \text{ CH} \right]_m

\text{ Polyacrylonitrile (PAN) vinyl chloride }

m \text{ CH}_2 = \text{ CH} + n \text{ C=C} \rightarrow \left[ \text{ CH}_2 = \text{ CH} \right]_m \left[ \text{ CH}_2 = \text{ CH} \right]_m

\text{ Styrere butadiene rubber, oil and petrol resistance }

\text{ ph}
Number average Mw (\( \bar{M}_n \))

Determined from colligative properties.

Aromatic form. Elevation of b.p., depression of F.P.

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}
\]

\( N_i \) no of molecules of molecular weight \( M_i \).

The no. average m. wt. is defined as the total weight (w) of all molecules in a polymer sample divided by the total no. of molecules present.

Weight average molecular weight (\( \bar{M}_w \))

Light scattering and sedimentation - equilibrium method.

When the m. wt. is averaged to the weight of the molecules of each type.

\[
\bar{M}_w = \frac{\sum N_i^2 M_i}{\sum N_i M_i^2}
\]

\( N_i \) no of molecules of molecular weight \( M_i \).
Degree of polymerisation

Average no. of monomer unit present in a polymer chain

\[ \overline{DP}_n = \frac{\overline{M}_n}{M_0} \quad \overline{DP}_w = \frac{\overline{M}_w}{M_0} \]

Molecular weight distribution (PDI)

Polydispersity index as a measure of molar distribution

\[ PDI = \frac{\overline{M}_w}{\overline{M}_n} \]

monodisperse (natural polymer and synthetic polymers made by anionic polymerization)
1. A polymer sample consists of 10% by weight of macromolecules of M_w 10,000, and 90% by weight of macromolecules with M_w 100,000. Calculate $\overline{M_n}$, $\overline{M_w}$, $\overline{D_p}$, $\overline{D_p}$, and PDI.

2. In a polymer, there are 100 molecules of M_w 100, 200 molecules of M_w 1000, and 300 molecules of M_w 10,000. Find $\overline{M_n}$, $\overline{M_w}$, $\overline{D_p}$, $\overline{D_p}$, and PDI.

Notes

Corrosion

Corrosion is a process of gradual deterioration of a metal from its surface due to unwanted chemical/electrochemical action of metal with its environment.
Effects:

- Lowering of economy of operation
- Loss of useful metal property
- Increase in maintenance and production cost
- Time consumption
- Contamination of product

Types:

- Chemical (dry condition)
- Corrosion by oxides

\[ \text{M} + n\text{O}_2 \rightarrow 2\text{M}^{n+} + 2n\text{O}_3^- \rightarrow \text{M}_2\text{O}_n \]

- Low temp. alkali and alkaline earth metals (except Pt, Ag, Au)
- High temp. other metals (except Pt, Ag, Au)

- Stable Cu, Al
- Unstable Au, Pt
- Volatile Mo \rightarrow \text{MoO}_3 \rightarrow 2\text{Mo} + 3\text{O}_2 \rightarrow 2\text{MoO}_3

- Porous
Notes

Pilling - Bedworth rule:

\[
\text{Specific Volume Ratio} = \frac{\text{vol. of metal oxide}}{\text{vol. of metal}}
\]

Smaller porous

\[\text{w} \text{ Cr, Ni} \text{? Corrosion of Ni in heat 3:6 2.0 1:6 even at high temp.}\]

\[\text{vol. of oxide} \rightarrow \text{vol. of metal non-porous, Al, Cu}\]

\[< \text{oxide layer for}\]

\[\text{steam and strain} \rightarrow \text{cracks and pores}\]

Li, Na, K, Mg

Notes

corrosion by other gases (corrosion by air mainly)

\[\text{Cl}_2, \text{H}_2\text{S}\]

\[\text{quid acidic base}\]

\[\text{Ag} + \text{Cl}_2 \rightarrow 2\text{AgCl} \ (\text{Protective})\]

\[\text{legal and known balance for reddening}\]

\[\text{Sn} + 2\text{Cl}_2 \rightarrow \text{SnCl}_4 \ (\text{Volatile})\]

\[\text{or to precipitate without (old) volatilization}\]
liquid metal corrosion

Lig. metal is allowed to flow over solid at high temp.

Dissolution of solid metal into liquid

Penetration of liquid into solid

calciun (Na) leads to corrosion of Cd in nuclear reactor

Electrochemical (or) Wet corrosion (moisture)

Anode, cathode medium (H₂O)

Anode $\Rightarrow$ oxidation $\text{M}^{n+}$

Cathode $\Rightarrow$ Reduction $\text{OH}^-$, $\text{O}_2$ formed

Diffusion of metallic and non-metallic ion

Fretting of Fe

oxygen absorption

Anode

$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

Neutral (or) Weakly alkaline

$2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$
Notes

Hydrogen evolution: absence of O₂

Acidic or neutral medium, anode:

\[ 2H^+ + 2e^- \rightarrow H_2 \]

Neutral or alkaline medium, cathode:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]

Electroplating

\[ Cu^{2+} + 2e^- \rightarrow Cu \]
Notes

- Chemical  Electrochemical
- Dry  wet (electrolyte present)
- Direct chemical attack  large number of Galvanic cells
- Absorption  Electrochemical
- Homogeneous and heterogeneous surface  heterogeneous metal surface
- Corrosion is uniform  non-uniform (corrosion area is small, pitting will occur)
- Slow process  fast
- Corrosion products accumulate near anode, product accumulate at the near cathode
Notes

Electrochemical corrosion.

Galvanic (Differential metal corrosion)

Zn and Cu
Zn and Ag
Fe and Cu

Avoiding galvanic couple
Providing insulating material between two metals.

Pitting corrosion

Corrosion product

Cathode

Anode

\[ \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 2\text{e}^- \]

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \rightarrow \text{Fe(OH)}_3 \]
Crevice corrosion

[Diagram of crevice area with labeled anode and cathode]
Notes

Differential aeration

Cathode

Anode

\[ \text{Zn} \rightarrow 2\text{Zn}^{2+} + 2\text{e}^- \]

\[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \]

Notes

Corrosion inhibitors

Anodic

Molybdate, phosphate, chromate, alkaline

Cathodic

amine, mercaptan, heavy metal soap, substituted urea and thiourea

decoration (or) \( \text{NO}_2\text{SO}_3 \)

Inhibiting power: \( \text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N} \)
Cathode Protection

Sacrificial anode protection

zn, Al, Mg

[Diagram:牺牲阳极示意图]

Sacrificial zn l/y

[Diagram:牺牲阳极示意图]

Immersed cu wire

Sulphurized
Pt
Silver Hamilton
Sodium salt
Carbon

[Diagram:阴极保护示意图]

Complete circuit

+1

Buried pipe made cathode

(protected)