The Partial molar property of a particular component in a mixture measures the contribution of that component to the mixture property. It is the property of a component when it is in admixture with one or many components.

\[ \overline{M} = \frac{\partial(nM)}{\partial n_i} \]
Partial Molar Volume: \[ \overline{V} = \frac{\partial(nV)}{\partial n_i} \]
Partial Molar Enthalpy: \[ \overline{H} = \frac{\partial(nH)}{\partial n_i} \]

Chemical Potential \( \mu_i \) of a component i in a solution is the partial molar free energy in the solution \( G_i \). It is used as an index of Chemical equilibrium.

\[ \overline{\mu_i} = \frac{\partial(nG)}{\partial n_i} \]

3. Give the classification of non-ideal solutions. (May 2011)
Non ideal solutions are broadly classified into two types, those positively deviating from ideality and those negatively deviating from ideality. Excess functions indicate the deviations from ideal solution behavior.

It is the rate of change of the total solution property with respect to number of moles of a particular, component at constant T and P. The partial molar properties of the components of the mixture vary with composition because the environment of each type of molecule, changes as the composition changes. The intermolecular forces also get changed resulting in the changes in thermodynamic properties.

5. State Henry’s law. (May 2011)
Fugacity of a component in a solution is directly proportional to the concentration.

\[ f_i \propto x_i K_i \]

6. Mention the characteristics of ideal solutions (May/June 2013, 16)
An ideal solution is one in which all molecules are of same size and all forces between molecules are equal obey ideal gas equations are called ideal solutions.

7. What is the condition for the Phases to be in equilibrium in a multiple phase system?
For the multiple phase system at the same T and P to be in equilibrium, the chemical potential of each species should be same in all phases.

8. What are the methods available for determining Partial Molar Properties? (May 2014)
(1). Analytical Method
(2). Graphical Method.
(3). Tangent intercept Method.
A solution in which the partial molar volumes of the components are the same as their molar volumes in
the pure state is called an ideal solution. In non-ideal solution molecules do interact and they occupy some
space.

10. Explain the Graphical Method of determining Partial Molar Property.
When the data of variation of $V$ with respect to $n_i$ is available a plot of $V$ versus $n_i$ is constructed.
Taking slope of the tangent at the point under consideration, gives partial molar property.

11. Explain the Tangent intercept method used to determine the Partial Molar Property.
Molar property is plotted against mole fraction of one component and the tangent drawn to the curve at
the desired point gives partial molar property.

12. What are ideal gas mixtures?
Ideal gas mixtures are those whose molecules have no influence on one another. Each molecule in the
mixture exists independent to the others, its properties are unaffected by the presence of different
molecules.

13. Explain the analytical method of determining the partial Molar Property.
Analytical method: If the volume of a solution is known of its composition, the partial molar volume of a
constituent may be found by partial differentiation with respect to the amount of the constituent.

14. Define fugacity and Fugacity coefficient.(May 2016)
Fugacity is the term equivalent to pressure applicable to non ideal solution and is a measure of effective
pressure. The ratio of fugacity to the pressure is referred to as fugacity coefficient.

15. What is Lewis Randall Rule?
The fugacity of each species in an ideal solution is proportional to its mole fraction, the proportionality
constant is the fugacity of pure species i in the same physical state as the solution and at the same T and
P.

$$f_i^{id} = x_i f_i$$

16. What are excess properties?(May 2016)
Mathematical formalism of excess properties $M^E$ is analogous to that of the residual properties. It is the
difference between actual property value of a solution and the value it would have as an ideal solution at
the same T, P and composition.

17. Give Gibb’s Duhem’s equation.

$$\left( \frac{\partial M}{\partial P} \right)_{T,x} dp + \left( \frac{\partial M}{\partial T} \right)_{P,x} dT - \sum x_i dM_i = 0$$

18. What is standard state?
A Standard state is a particular state of a species at Temperature T and at specified conditions of
Pressure, composition and physical condition as gas, liquid or solid.

The Partial pressure/fugacity of a solute over the solution is proportional to its mole fraction in the
solution.

$$f_i = x_i H_i \quad \text{or} \quad p_i = x_i H_i$$

20. State Raoult’s law.
The partial pressure of a solute over the solution is the product of its liquid phase mole fraction and its
pure component vapor pressure. This is true for ideal solutions.

21. **Which is the standard state for gasses?**
   For gases two standard states are common.
   (i). The pure component gas in its ideal state at 1 bar. \(a_i = f_i\)
   (ii). The pure component gas at the pressure of the system. \(a_i = f_i/f^o_i = \frac{x_i f_i}{f^o_i} \]

22. **Which is the standard state for liquids?**
   (i). The pure component liquid at a pressure of 1 bar. (ii).
   The pure liquid at the pressure of the system.

23. **Gibb’s free energy function is referred to as generating function. Explain.**
   When Gibb’s energy as a function of T and P is known, one can estimate all other thermodynamic properties. Gibbs energy function implicitly represents complete property information and hence referred to as a generating function.

24. **What is the phase rule variable for non reacting system? Mention its application.**
   \(F = C - P + 2\)
   where \(F\) is degrees of freedom, \(C\) is number components and \(P\) is number of Phases.

25. **Differentiate between molar volume and partial molar volume?**
   Molar volume of a pure compound is the volume occupied by one mole of the chemical, partial molar volume is the term referred to the volume occupied by one mole of the chemical is solution, which is in association with other solutes.

**PART B**

1. **Derive the Gibbs Duhem equation with the assumptions. Derive the various forms of Gibbs Duhem equation (NOV 2014,2016)(May 2016) (May 2011) (May/ June 2014)**
   
   Consider a binary solution made up of components 1 and 2 whose mole fractions in the solution are \(x_1\) and \(x_2\) respectively. Equation can be written as
   \[x_1 d\mu_1 + x_2 d\mu_2 = 0\]
   where \(\mu_1\) and \(\mu_2\) are the chemical potentials of components 1 and 2 respectively. This can be rearranged as
   \[x_1 d\mu_1 = -x_2 d\mu_2\]
   Dividing by \(dx_1\) and noting that \(dx_1 = -dx_2\) in binary mixtures, the above result gives
   \[\frac{\partial\mu_1}{\partial x_1} = x_2 \frac{\partial\mu_2}{\partial x_2}\]

   Introducing the relationship between chemical potential and the fugacity Equation into the above, we get
   \[\frac{\partial ln f_1}{\partial x_1} = x_2 \frac{\partial ln f_2}{\partial x_2}\]

   Since activity \(a_i = f_i / f^o_i\), fugacities in Equation may be replaced in terms of activity as
Since \( f_i^0 \), the fugacity in the standard state, is independent of the composition of the solutions,

\[
\frac{\partial \ln (f_i^0)}{\partial x_i} = 0
\]

Thus the Gibbs – Duhem equation in terms of activity is

\[
\frac{\partial \ln a_1}{\partial x_1} = x_2 \frac{\partial \ln a_1}{\partial x_2}
\]

By Equation, \( a_i = \gamma_i x_i \). Substitute this into Equation and thus the most important and widely used form of the Gibbs-Duhem equation that involving the activity coefficients, is obtained.

\[
x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_1 x_2}{\partial x_2}
\]

The second terms on both sides of the above equation vanish, as they are equal to unity. Therefore

\[
x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}
\]

As the activity coefficients directly measure the departure from the ideal solution behavior, Equation is the most useful form of the Gibbs-Duhem equation.

The various forms of Gibbs-Duhem equations are rigorous thermodynamic relations that are valid for conditions of constant temperature and pressure. They tell us that the partial molar properties of a mixture cannot change independently; in a binary mixture, if the partial molar property of one of the component increases, the partial molar properties of the other should decrease.

**Gibbs-Duhem equations find wide applications in solution thermodynamics.** These include:

a) In the absence of complete experimental data on the properties of the solution, Gibbs-Duhem equations may be used to calculate additional properties. For example, if experimental data are available for the activity coefficient of one of the components in a binary solution over certain concentration range, the activity coefficient of the other component over the same composition range can be estimated using Gibbs-Duhem equations. This is particularly useful wherever the volatilities of the two components differ markedly. The measurements usually give the activity coefficient of the more volatile component whereas that of the less volatile component is calculated using Equation. Thermodynamics properties of some high boiling liquids (e.g. polymers) dissolved in a volatile liquid (say, benzene) can be computed by measuring the partial pressure of the latter in the solution.

b) Thermodynamics consistency of experimental data can be tested using Gibbs-Duhem equations. If the data on the partial molar property of each component measured directly in experiments satisfy the Gibbs-Duhem equations, it is likely that they are reliable, but if they do not satisfy the Gibbs-Duhem equation, it is certain that they are incorrect.

c) Gibbs-Duhem equations can be used for the calculation of partial pressure from isothermal total pressure data. Suppose that in an experimental investigation of vapour-liquid equilibrium, the total
pressures are measured. The Gibbs-Duhem equation facilitates the calculation of the composition of other phase thereby reducing the experimental work considerably.

d) Partial pressure data can be obtained from isobaric boiling point data using Gibbs-Duhem equations. The isobaric $T$-$x$ data can be easily converted to $x$-$y$ data.

These equations find application in various other situations such as in the derivation of the relationship between Henry’s law and Raoult’s law for a real solution, in proving the essential criterion that the vapour and liquid composition are the same for an azeotropic mixture etc.

2. Calculate the partial molar volumes of methanol and water in a 40% (mol) method solution given the following data at 1 bar and 298 K. (May 2013)

<table>
<thead>
<tr>
<th>X</th>
<th>$\text{V} \times 10^3 , \text{m}^3/\text{mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0181</td>
</tr>
<tr>
<td>0.114</td>
<td>0.0203</td>
</tr>
<tr>
<td>0.197</td>
<td>0.0219</td>
</tr>
<tr>
<td>0.249</td>
<td>0.0233</td>
</tr>
<tr>
<td>0.495</td>
<td>0.0283</td>
</tr>
<tr>
<td>0.692</td>
<td>0.0329</td>
</tr>
<tr>
<td>0.785</td>
<td>0.0352</td>
</tr>
<tr>
<td>0.892</td>
<td>0.0379</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0407</td>
</tr>
</tbody>
</table>

where $x$ (mole fraction of methanol)

$X$ - mole fraction of methanol
$Y = \text{V} \times 10^3 \, \text{m}^3/\text{mol}

Thus $\text{V} = 0.026 \, X \times 10^{-6} \, \text{m}^3/\text{mol}$

Partial molar volume of methanol = $0.0407 \times 10^{-6} \, \text{m}^3/\text{mol}$
Partial molar volume of water = $0.0162 \times 10^{-6} \, \text{m}^3/\text{mol}$

3. At 300K and 1 bar the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $\text{V} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} \, x - 2.64 \times 10^{-6} \, x^2$ where $x$ is the mole fraction of the benzene and $\text{V}$ has the units of $\text{m}^3/\text{mol}$. Find the expressions for the partial molar volumes of benzene and cyclohexane. (MAY 2011, NOV 2015)

The molar volume of the solution as a function of composition is given:

$\text{V} = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} \, x_1 - 2.64 \times 10^{-6} \, x_1^2$

Where $x_i$ = mole fraction of component 1 (in this case, benzene). By Equation,

$\overline{V}_1 = \text{V} - x_2 \frac{\partial \text{V}}{\partial x_2}$

$\overline{V}_1 = \text{V} + (1-x_1) \frac{\partial \text{V}}{\partial x_1}$

Differentiating Equation we get

$\overline{V}_1 = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} \, x_1 - 2.64 \times 10^{-6} \, x_1^2 + (1-x_1) \left(-16.8 \times 10^{-6} - 5.28 \times 10^{-6} \, x_1\right)$

$= 92.6 \times 10^{-6} - 5.28 \times 10^{-6} \, x_1 + 2.64 \times 10^{-6} \, x_1^2$
Using Equation $V_2$ can be found out.

\[
\bar{V}_2 = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} x_1 - 2.64 \times 10^{-6} x_1^2 - x_1 (-16.8 \times 10^{-6} \times 5.28 \times 10^{-6} x_1)
\]

\[
= 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2
\]

The partial molar volume of benzene:

\[
\bar{V}_1 = 92.6 \times 10^{-6} - 5.28 \times 10^{-6} x_1 + 2.64 \times 10^{-6} x_1^2
\]

The partial molar volume of cyclohexane:

\[
\bar{V}_2 = 109.4 \times 10^{-6} + 2.64 \times 10^{-6} x_1^2
\]

4. Discuss the Methods for the determination of partial molar properties.

**Method 1 (Analytical):** If the volume of a solution is known as a function of its composition, the partial molar volume of a constituent may be found by partial differentiation with respect to the amount of that constituent.

\[
\bar{V}_1 = \left( \frac{\partial \bar{V}}{\partial n_i} \right)_{P,T,n_j}
\]

**Method 2 (Graphical):** Let $V^i$, the volume of the solution containing a fixed amount of one of the constituents (say, $n_1$) is known for several values of the amount of other constituent (say, $n_2$). We may plot $V^i$ against $n_2$. See Fig. 7.2. The slope of the tangent to the curve is

\[
\text{Slope of tangent} = \left( \frac{\partial V}{\partial n_2} \right)_{P,T,n_1}
\]

Which, by definition is $\bar{V}_2$, the partial molar volume of component 2. The volume of solution is assumed, so large that no significant change in composition occurs when $n_2$ is changed. This method has limitation of not yielding values of $\bar{V}_1$ directly. Also, it is not advisable to use this method for determination of $\bar{V}_2$ when $n_2$ is large compared to $n_1$. The method of tangent intercepts is free from such limitations and is therefore preferred for the determination of partial molar properties.

**Method 3 (The tangent-intercept method):** This is a graphical method widely used for the determination of partial molar properties of both components in a binary solution. The molar volume $v$ is plotted against mole fraction of one of the components (say, $x_2$, the mole fraction of component 2). To determine the partial molar volumes, draw the tangent to the curve at the desired mole fraction. The intercept that this tangent makes with the vertical axis at $x_2 = 1$ gives $\bar{V}_2$ and the intercept on the vertical axis gives $\bar{V}_1$. 
To prove this result, consider a binary solution containing \( n_1 \) moles of component 1 and \( n_2 \) moles of component 2. Let the total volume be \( V^t \) and let \( V \) be the molar volume. Then

\[
V^t = nV = (n_1 + n_2)V
\]

Differentiating Equation with respect to \( n_1 \), keeping \( n_2, T \) and \( P \) constant

\[
\left( \frac{\partial V^t}{\partial n_1} \right)_{p, T, n_2} = \frac{\partial V}{\partial n_1} = V + \left(n_1 + n_2\right) \left( \frac{\partial V}{\partial n_1} \right)_{n_2}
\]

The mole fraction \( x_2 \) is given by

\[
x_2 = \frac{n_2}{n_1 + n_2}
\]

Differentiating Equation with respect to \( n_1 \) keeping \( n_2 \) constant, we get

\[
\left( \frac{\partial x_2}{\partial n_1} \right)_{n_2} = -\frac{x_2}{(n_1 + n_2)^2} = -\frac{x_2}{n_1 + n_2}
\]

which can be rearranged as

\[
\frac{n_1 + n_2}{\partial n_1} = -\frac{x_2}{\partial x_2}
\]

Equation can be substituted into Equation to yield the following:

\[
\bar{V}^t = V - x_2 \frac{\partial V}{\partial x_2}
\]

Similarly it can be shown that

\[
\bar{V}^t
\]
In Figure, the length $BD = BE + ED$, where $BE$ is the slope of the tangent at $P$ times the length $PE$. That is,

$$BE = (1 - x_2) \left( \frac{\partial V}{\partial x_2} \right)$$

And $ED = V$, the molar volume at the molar fraction $x_2$, Thus

$$BD = V + (1-x_2) \left( \frac{\partial V}{\partial x_2} \right)$$

Which, by Equation is $V_2$, similarly, the length

$$AC = FC - FA = V - x_2 \left( \frac{\partial V}{\partial x_2} \right) = \overline{V_1}$$

The above methods are applicable for the determination of various other partial molar properties also. Of the various mixture properties, only the volume can be determined absolutely. For the determination of other properties like $G_i$, $H_i$, etc., it becomes necessary to work with property changes on mixing like $\Delta G$, $\Delta H$, etc.

5. The volume of an aqueous solution of NaCl at 298K was measured for a series of molalities (moles of solute per kg of solvent) and it was found that the volume varies with molality according to the following expression. $V = 1.003 \times 10^{-3} + 0.1662 \times 10^{-4} m + 0.177 \times 10^{-5} m^{1.5} + 0.12 \times 10^{-6} m^2$. Where $m$ is the molality and $V$ is in $m^3$. Calculate the partial molar volumes of components at $m=0.1$ mol/Kg. (MAY 2014)

The partial molar volume of NaCl:

$$\overline{V_1} = \left( \frac{\partial V}{\partial n_1} \right)_{n_2} = \left( \frac{\partial V}{\partial m} \right)_{n_2}$$

$$V = 1.003 \times 10^{-3} + 0.1662 \times 10^{-4} m + 0.177 \times 10^{-5} m^{1.5} + 0.12 \times 10^{-6} m^2$$

Substituting $m=0.1$ in the above equation we get, $V = 1.0047 \times 10^{-4} m^3/mol$

Differentiating the above equation,

$$\overline{V_1} = 0.1662 \times 10^{-4} + 0.177 \times 1.5 \times 10^{-5} m^{0.5} + 0.12 \times 2 \times 10^{-6} m$$

$$= 0.1662 \times 10^{-4} + 0.2655 \times 10^{-5} m^{0.5} + 0.24 \times 10^{-6} m$$

Substituting $m=0.1$ in the above equation we get, $\overline{V_1} = 0.1748 \times 10^{-4} m^3/mol$. Therefore,

$$V = n_1\overline{V_1} + n_2\overline{V_2} = m\overline{V_1} + \frac{1000}{18} \overline{V_2}$$

$$\overline{V_2} = (1.0047 \times 10^{-3} - 0.1 \times 0.1748 \times 10^{-4}) \times \frac{18}{1000} = 18.05 \times 10^{-6} m^3/mol$$

Partial molar volume of water = $18.05 \times 10^{-6} m^3/mol$

Partial molar volume of NaCl = $17.48 \times 10^{-6} m^3/mol$
6. (a) The Henry’s law constant oxygen in water at 298 K is $4.4 \times 10^4$ bars. Estimate the solubility of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bars. (MAY 2011)

(b) What is excess property? Explain (MAY 2011)

(a) We know that,

$$x_i = \frac{p_i}{K_i}$$

Substituting $K = 4.4 \times 10^4$ bar and $p_i = 0.25$ bar, we get $x_i = 0.0568 \times 10^{-4}$. For very dilute solution,

$$x_{O_2} = \frac{\text{Moles of oxygen}}{\text{Moles of oxygen + moles of water}} \approx \frac{\text{Moles of oxygen}}{\text{Moles of water}}$$

Therefore, the solubility of oxygen is $0.0568 \times 10^{-4}$ moles per mole of water. Or,

$$0.0568 \times 10^{-4} \times 32 \times 1/18 = 0.101 \times 10^{-4} \text{ kg oxygen per kg water.}$$

(b) **Excess properties:**

The difference between the property of a real solution and that of an ideal solution is important in chemical thermodynamics, especially in the treatment of phase equilibria. The excess property, $M^E$, is defined as the difference between an actual property and the property that would be calculated for the same temperature, pressure and composition by the equations for an ideal solution.

$$M^E = M - M^{id} \quad \text{--------------------------- 1}$$

$M$ is the maolar property of the solution and $M^{id}$ is the property of an ideal solution under the same conditions. The excess property change of mixing is defined in a similar manner.

$$\Delta M^E = \Delta M - \Delta M^{id} \quad \text{--------------------------- 2}$$

$\Delta M^E$ is the excess property change of mixing, $\Delta M$ and $\Delta M^{id}$ are the property changes of mixing for a real solution and an ideal solution respectively, both under the same conditions. As

$$\Delta M = M - \Sigma x_i M_i \quad \text{--------------------------- 3}$$

Eqn 2 can be written as $\Delta M^E = M - M^{id} \quad \text{--------------------------- 4}$

Comparing above equations $\Delta M^E = M^E \quad \text{--------------------------- 5}$

Let us consider the excess volume $V^E$ of a solution. $V^E = \Delta V^E = \Delta V - \Delta V^{id}$

Since ideal solution involves no volume change of mixing, $\Delta V^{id} = 0$
Effect of pressure:
The effect of pressure on fugacity is given by

\[
\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{V_i}{RT}
\]

The fugacity of I, \( f_i \), is written as

\[
\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{V_i}{RT}
\]

Combining both equations, we get,

\[
\left(\frac{\partial \ln \frac{\overline{f}_i}{f_i}}{\partial P}\right)_T = \frac{\overline{V}_i - V_i}{RT}
\]

But,

\[
\frac{\overline{f}_i}{f_i} = \gamma_i x_i,
\]

So,

\[
\left(\frac{\partial \ln \gamma_i x_i}{\partial P}\right)_T = \frac{\overline{V}_i - V_i}{RT}
\]

As mole fraction \( x_i \) is independent of pressure, i.e.

\[
(\partial \ln x_i / \partial P) = 0,
\]

we get,

\[
\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T = \frac{\overline{V}_i - V_i}{RT}
\]

Effect of temperature:
The effect of temperature on fugacity is given by

\[
\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{H_i^0 - H_i}{RT^2}
\]
For a substance $i$,
\[
\left( \frac{\partial \ln \bar{f}_i}{\partial T} \right)_P = \frac{H_i^0 - \bar{H}_i}{RT^2}
\]
Combining both equations, and
\[
\bar{f}_i / f_i = \gamma_i \chi_i
\]
x$_i$ is independent of temperature, we get
\[
\left( \frac{\partial \ln \gamma_i}{\partial T} \right)_P = \frac{H_i - \bar{H}_i}{RT^2}
\]


The chemical potential of component $I$, is same as partial molar free energy $\bar{G}_i$. It is denoted by $\mu_i$. It is defined as,
\[
\mu_i = \bar{G}_i = \left[ \frac{\partial G'}{\partial n_i} \right]_{T,P,n_j}
\]
The total Gibb's free energy of a solution is
\[
G' = f\left(P, T, n_1, n_2, \ldots, n_k\right)
\]
The total differential,
\[
dG' = \left[ \frac{\partial G'}{\partial P} \right]_{T,n} dP + \left[ \frac{\partial G'}{\partial T} \right]_{P,n} dT + \sum_{i=1}^{i=k} \left[ \frac{\partial G'}{\partial n_i} \right]_{P,T,n_j} dn_i
\]
\[
\sin ce, \mu_i = \left[ \frac{\partial G'}{\partial n_i} \right]_{T,P,n_j}
\]
\[
dG' = \left[ \frac{\partial G'}{\partial P} \right]_{T,n} dP + \left[ \frac{\partial G'}{\partial T} \right]_{P,n} dT + \sum \mu_i dn_i
\]
For a closed system,
\[
dG' = V' dP - S' dT
\]
At constant pressure and temperature,
Therefore,

\[
\left[ \frac{\partial G'}{\partial P} \right]_T = V'
\]

\[
\left[ \frac{\partial G'}{\partial T} \right]_P = -S'
\]

Therefore,

\[
dG' = V'\,dP - S'\,dT + \sum \mu_i \,dn_i
\]

At constant temperature and pressure,

\[
\left[ dG' \right]_{T,P} = \sum \mu_i \,dn_i
\]

The change in free energy, is because of the change in number of moles,

\[
G' = \sum \mu_i n_i
\]

Thus, for a binary solution,

\[
G' = x_1 \mu_1 + x_2 \mu_2
\]

The chemical potential is the contribution to Gibb’s free energy and is an important property used in phase and chemical equilibria.
UNIT 2 – PHASE EQUILIBRIA

PART – A

It states that for any closed system formed initially from the given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed.

2. Define the terms Phase and component.
Phase is that part of the system which is physically distinct, chemically homogeneous and mechanically separable.
Component is nothing but chemical species that is present in different phases of the system.

3. What is phase rule as applicable to a reacting system?
The criterion of phase equilibrium is valid even when chemical reactions occur within the system. However, the phase rule needs modification for it to be applicable for reacting systems. This is because for each independent reaction occurring, and additional constraint is imposed on the system. Thus the number of degrees of freedom will be reduced by one for each independent chemical reaction. If \( r \) independent reactions occur in the system, then the phase rule becomes

\[ F = C - \pi - r + 2 \]

For example, considering a system containing five components distributed between two phases. If the number of independent chemical reactions occurring is one, then the number of degrees of freedom will be 5-2-1+2 = 4

4. Define Gibb’s Phase rule. (Nov 2013)
Gibbs phase rule is one which gives the number of variables that must be arbitrarily specified to fix all remaining phase rule variables.
\[ F = 2 - \pi + N \]
where \( F \) is degrees of freedom, \( \pi \) is number of phases and \( N \) is the number of chemical species.

Bubble point is the temperature at which first bubble of the vapor is produced, that is when the saturated liquid is further heated.
Dew point is the temperature at which first drop of liquid condenses from a saturated vapor upon cooling.

6. For a heterogeneous multicomponent system, what is the general criterion of phase equilibrium? (May/June 2013)
A heterogeneous closed system is made up of two or more phases with each phase behaving as open system within the overall closed system. Because each phase consists of two or more components in different proportions, it is necessary that the criterion of multicomponent phase equilibrium be developed in terms of partial molar free energies or the chemical potentials of the components.

Relative volatility of a binary mixture is the ratio of pure component vapor pressure of volatile component to the pure component vapor mixture of second component.
8. Give Clausius Clapayron equation and explain the terms.

\[ \ln \frac{P_2^s}{P_1^s} = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \]

where \( \Delta H \) is heat of vaporization assumed to be constant, in the temperature range of \( T_1 \) to \( T_2 \). \( P_1^s \) and \( P_2^s \) are the saturation pressures at temperatures at \( T_1 \) to \( T_2 \) respectively.

9. Give the importance of Vapor liquid equilibrium.
The most commonly encountered coexisting phases in industrial practice are vapor and liquid. To quantify the mass transfer between them, the departure of the system form equilibrium is very important and hence VLE data.

10. Write Clapayron equation and explain the terms involved.

\[ \frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \]

Where \( \Delta H \) and \( \Delta V \) are the enthalpy and volume changes accompanying a process. It predicts the dependence of equilibrium pressure on temperature when two phases of a given substance coexist.

11. What is the criterion applicable for low pressure VLE problems?
At low pressures fugacity coefficient is assumed to be one since the vapor phase behaves ideally.

\[ y_i P = y_i x_i P_{i, sat} \]

12. What is Boiling point diagram? (May/ June 2014)
The boiling point diagrams are plots of temperature as ordinate against composition of liquid and vapor as abscissa.

13. What is equilibrium diagram?
Equilibrium diagram is a plot in which equilibrium vapor composition is taken as the ordinate and corresponding liquid phase composition is taken as abscissa.

14. Differentiate between minimum boiling and maximum boiling azeotropes?
Minimum boiling azeotropes are those showing positive deviation from ideality and maximum boiling azeotropes are those showing negative deviation from ideality.

15. What are azeotropes? Give examples.
Azeotropes are constant boiling mixtures. They are formed by solution showing large positive or negative deviation from ideality.

16. What is the effect of pressure on azeotropes? (May/ June 2014)
The azeotropic composition shifts continuously with change is pressure. In some cases changing in pressure may eliminate azeotropism from the system.
17. Give the fundamental relationship in the study of VLE.
\[ \Phi_i y_i P = \gamma_i x_i P_{sat} \]

18. What are partially miscible and immiscible systems? Give an example each.
Partially miscible systems are those in which the components are miscible only within a temperature range either above or below or in between two temperatures. Ex: Phenol water system.
Immiscible systems are those in which components are not at all miscible irrespective of temperatures of the system. Ex: Benzene – Water.

19. What are the applications of Ternary liquid equilibrium?
Ternary liquid equilibrium finds application in three component systems like extraction, leaching.

20. Write any two activity composition models.
Margules Model and Vanlaar Model.

21. What do you mean by saying a system is in equilibrium?
When a system of multiple phases is in equilibrium, then there should not be energy, momentum and mass transfer between the phases. That is all phases must have same T and P and each species in all phases must have same chemical potential.

22. Write down the condition of Criteria for liquid/liquid equilibrium.
Two liquids will be in equilibrium when they are in thermal, chemical and mechanical equilibrium.
That is when the chemical potential of the chemicals present in both the liquids are same and the system is at same Temperature and pressure.

23. What are partially miscible systems? Give examples.
Partially miscible systems are those in which the solubility of one liquid in another liquid is seen only under certain conditions are temperature.

24. Give the applications of Clausius Clapayron equation
Clausius Clapayron equation is extensively used in mass transfer operations, to quantify the energy requirements.

25. What is the criterion for Phase equilibrium in terms of fugacity and chemical potential?
\[ \mu_i^\alpha = \mu_i^\beta = \mu_i^\beta = \ldots \]

26. What assumption with which Clapayron equation yields Clausius – Clapayron equation?
Clausius assumed that the vapor behaves ideally and introduced ideal gas equation in to Clapeyron equation, which resulted in Clausius-Clapeyron equation.

27. What are azeotropes? How do you categorize an azeotrope?(Nov 2015,2016)
Azeotropes are constant boiling mixtures. They are formed by solution showing large
positive or negative deviation from ideality. Ex: Benzene – Ethanol mixture. Alcohol – water mixture.

Minimum boiling azeotropes are those showing positive deviation from ideality and maximum boiling azeotropes are those showing negative deviation from ideality.

28. **What is Poyting correction?**

For high pressure VLE problems, the equation employed is,

\[
\Phi_i \gamma_i P = \gamma_i x_i P_i^s \exp \left[ \frac{V_i (P - P_i^s)}{RT} \right]
\]

The exponential term in the above equation is called the Poyting correction.

**PART B**

1. **Prove that if Raoult’s law is valid for one constituent of a binary mixture over the whole concentration range it must also apply to the other component. (MAY 2011, 2013, NOV 2014)**

Assume that Raoult’s Law is obeyed by component 1 in a binary mixture. Then

\[
\overline{P}_1 = x_1 P_i^s
\]

Raoult’s law is obeyed by ideal solution when the vapour phase behaves as an ideal gas whereas Lewis – Randall rule is obeyed by ideal solutions irrespective of whether the gas phase is ideal or not.

So for component 1, we can write

\[
\overline{f}_1 = x_1 f_i
\]

\[
d(\ln \overline{f}_1) = d(\ln x_1)
\]

\[
\frac{d(\ln \overline{f}_1)}{d(\ln x_1)} = 1 \quad --- (1)
\]

Gibbs – Duhem equation relates fugacities of components in a binary mixture as

\[
x_1 \frac{d(\ln \overline{F}_1)}{dx_1} = x_2 \frac{d(\ln \overline{F}_2)}{dx_2}
\]

Rearranging this equation

\[
\frac{d(\ln \overline{F}_1)}{d(\ln x_1)} = \frac{d(\ln \overline{F}_2)}{d(\ln x_2)} \quad --- (2)
\]

This equation is sometimes referred to as Duhem – Margules equation comparing equation (1) with (2) we see that

\[
\frac{d(\ln \overline{F}_2)}{d(\ln x_2)} = 1
\]

\[
d(\ln \overline{F}_2) = d(\ln x_2)
\]

Nothing that \( \overline{F}_2 = F_2 \) when \( x_2 = 1 \) the above equation can be integrated
\[
\int_{b}^{1} d\left(\ln \bar{f}_2\right) = \int_{1}^{x_2} d\left(\ln x_2\right)
\]

\[
\frac{\ln \bar{f}_2}{f_2} = \frac{\ln x_2}{1}
\]

(or)

\[
\frac{\bar{F}_2}{f_2} = x_2
\]

(i.e) \(\bar{f}_2 = x_2 f_2\), which is the Lewis – Randal rule for component 2. If the vapour is an ideal gas, this can be equally written as

\[
\bar{P}_2 = x_2 P^S_2
\]

This is Raoult’s law for component 2. The conclusion to be drawn from the above derivation is that if Raoult’s law is applicable to one of the constituents of a liquid mixture at all concentrations it must be applicable to be other constituent as well.

2. The azeotrope of the ethanol benzene system has a composition of 44.8% ethanol with a boiling point of 341.4 K at 101.3 KPa. At this temperature the vapor pressure of ethanol is 68.9 KPa and the vapor pressure of Benzene is 67.4 KPa. What are the activity coefficients in a solution containing 10% alcohol? (MAY 2011)

Let benzene be component 1 and alcohol component 2. For the azeotrope

\[
\gamma_1 = \frac{P}{P^S_1} = \frac{1013}{68.9} = 1.4702 \quad \gamma_1 = \frac{P}{P^S_1} = \frac{1013}{67.4} = 15030
\]

\(X_1=0.552\) and \(x_2 = 0.448\). Substituting these values in Eq. the constants A and B in the van Laar equation can be evaluated.

\[
A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = \ln 1.4702 \left(1 + \frac{0.448 \times \ln 15030}{0.552 \times \ln 1.4702}\right)^2 = 1.3305
\]

\[
B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = \ln 15030 \left(1 + \frac{0.552 \times \ln 1.4702}{0.448 \times \ln 1.5030}\right) = 1.9106
\]

For a solution containing 10% alcohol \(x_1 = 0.90\) and \(x_2 = 0.1\). For calculating the activity coefficient at this concentration, van Laar equations, Equation are used.
\[
\ln \gamma_1 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2} = \frac{1.3305 \times 0.1^2}{[(1.3305/1.9106)0.9 + 0.1]^2} = 0.02519
\]
\[
\ln \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)x_2]^2} = \frac{1.9106 \times 0.9^2}{[0.9 + (9106/13305)0.1]^2} = 1.4210
\]

Therefore, \( \gamma_1 = 1.0255 \) and \( \gamma_2 = 4.1412 \).

3. **Explain the different methods to check the consistency of VLE data. (MAY 2011, JUNE 2012)**

Consistency tests for VLE data are based on Gibb’s Duhem equations. They are

i) **Using slope of \( \ln \gamma \) curves**

The Gibb’s Duhem equations in terms of activity coefficient is

\[
x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P}
\]

\[
x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = - (1 - x_1) \left( \frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P}
\]

When \( \ln \gamma \) is plotted against \( x_1 \), and the slopes of the tangent is measured at any selected composition of \( x_1 \). If both slopes have the opposite sign – data consistent; else inconsistent.
ii) Using data at mid point
The van Laar equation is

\[ \ln \gamma_1 = A x_1^2 = \frac{A x_1^2}{[(A/B) x_1 + x_2]^2}; \quad \ln \gamma_2 = B x_2^2 = \frac{B x_2^2}{[x_1 + (B/A) x_2]^2} \]

By putting \( x_1 = x_2 = 0.5 \), we get

\[ \frac{\ln \gamma_1}{B} = \frac{\ln \gamma_2}{A} = \frac{AB}{(A + B)^2} \]

When \( \ln \gamma \) is plotted against \( x_1 \), the data is consistent if
- Both curves are at same level in the end point
- The curve lowest at the mid point is highest at the end point
Otherwise, the data is inconsistent.

iii) Redlich-Kister method:
Also known as the zero area method. It can be used for testing data, when the activity coefficient is available over the entire range.
The excess free energy is

\[ \Delta G^E = RT \sum x_i \ln \gamma_i \]
For a binary solution, it can be written as,  \( \Delta G^E = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \)

Differentiating with respect to \( x_1 \),

\[
\frac{d(\Delta G^E)}{dx_1} = RT \left[ \frac{\ln \gamma_1}{\gamma_2} + x_1 \frac{d(\ln \gamma_1)}{dx_1} + (1 - x_1) \frac{d(\ln \gamma_2)}{dx_1} \right]
\]

Also, substituting the following solution into the above equation

\[
x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = -(1 - x_1) \left( \frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P}
\]

We get

\[
\frac{d(\Delta G^E)}{dx_1} = RT \ln \frac{\gamma_1}{\gamma_2}
\]

When the above equation is integrated between \( x_1=0 \) to \( x_1=1 \) (\( \Delta G^E=0 \) at both points), we get

\[
0 - 0 = RT \int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1
\]

\[
\int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1 = 0
\]

Thus, when \( \ln (\gamma_1/\gamma_2) \) is plotted against \( x_1 \), the net area of the curve should be zero. Then the data is consistent. Else it is inconsistent.

![Graph showing the net area of the curve]

iv) Using co existence equation:

The activity coefficients can be written as

\[
\gamma_1 = \frac{y_1 P}{x_1 P^*}, \quad \gamma_2 = \frac{y_2 P}{x_2 P^*}
\]

Substituting the above in Gibb’s-Duhem equation, we get,

\[
x_1 \, d \ln \gamma_1 = -(1 - x_1) \, d \ln \gamma_2
\]

\[
x_1 \, d \ln \frac{y_1 P}{x_1 P^*} = -(1 - x_1) \, d \ln \frac{y_2 P}{x_2 P^*}
\]

As the saturation pressures are constant at constant temperature, we get,

\[
d \ln P = \frac{y_1 - x_1}{y_1 (1 - y_1)} \, dy_1
\]

On rearranging , we arrive at the co-existence equation which can be used to test the consistency of VLE data.

\[
\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1 (1 - y_1)}
\]
v) **Using partial pressure data:**

Gibb’s duhem equation in term of fugacity can be re written as

\[
x_1 \frac{d \ln \bar{p}_1}{dx_1} = -x_2 \frac{d \ln \bar{p}_2}{dx_1}
\]

\[
x_1 \frac{\bar{p}_1}{d\bar{p}_1} = -x_2 \frac{\bar{p}_2}{d\bar{p}_2}
\]

The partial pressure of both components are plotted against mole fraction and slopes are determined at selected composition.

Data consistent if the absolute values of these slopes are the same. Else the data is inconsistent.

4. **Show that for a stable liquid phase, the fugacity of each component in a binary mixture always increases with increase in concentration at constant temperature and pressure.** (May 2016)

The excess free energy of mixing was defined in chapter. It was shown there that

\[
\Delta G^E = \Delta G - \Delta G^{id}
\]

\[
\Delta G^E = G^E = RT \sum x_i \ln \gamma_i
\]

\[
\Delta G^{id} = RT \sum x_i \ln x_i
\]

Combining these there equations we find that

\[
\Delta G = RT \sum x_i \ln (\gamma_i x_i)
\]

\[
\frac{\Delta G}{RT} = \sum x_i \ln (\gamma_i x_i) = x_1 \ln (\gamma_1 x_1) + x_2 \ln (\gamma_2 x_2)
\]

Differentiating this with respect to \(x_1\),

\[
\frac{d}{dx_1} \left( \frac{\Delta G}{RT} \right) = \frac{d}{dx_1} \left[ x_1 \ln (\gamma_1 x_1) + x_2 \ln (\gamma_2 x_2) \right] = \ln (\gamma_1) - \ln (\gamma_2) + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + x_2 \frac{\partial \ln \gamma_2}{\partial x_1}
\]

By Gibbs – Duhem equation

\[
x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2} = -x_2 \frac{\partial \ln \gamma_2}{\partial x_1}
\]
When this is substituted into equation we get
\[ \frac{d}{dx_1} \left( \frac{\Delta G}{RT} \right) = \ln \left( \gamma_1 x_1 \right) - \ln \left( \gamma_2 x_2 \right) \]
Activity coefficients are defined as
\[ \gamma_1 = \frac{f_1}{x_1 f_1}, \quad \gamma_2 = \frac{f_2}{x_2 f_2} \]
Where \( f_1 \) and \( f_2 \) are the fugacities of components in solution and \( f_1 \) and \( f_2 \) are the fugacities of pure components. Substituting these into equation we get
\[ \frac{d}{dx_1} \left( \frac{\Delta G}{RT} \right) = \ln \frac{f_1}{f_1} - \ln \frac{f_2}{f_2} \]
Differentiating equation again with respect to \( x_1 \) and noting that fugacities of pure components are independent of concentration, we get
\[ \frac{d^2}{dx_1^2} \left( \frac{\Delta G}{RT} \right) = \frac{d}{dx_1} \ln f_1 - \frac{d}{dx_1} \ln f_2 \]
According to Gibbs – Duhem equations, the fugacities in a binary mixture are interrelated as indicated below.
\[ x_1 \frac{\partial \ln f_1}{\partial x_1} = x_2 \frac{\partial \ln f_2}{\partial x_2} = -x_2 \frac{\partial \ln f_2}{\partial x_1} \]
Therefore,
\[ \frac{d}{dx_1} \ln f_2 = -\frac{x_1}{x_2} \frac{d}{dx_1} \ln f_1 \]
Using this equation can be written as
\[ \frac{d^2}{dx_1^2} \left( \frac{\Delta G}{RT} \right) = \frac{d}{dx_1} \ln f_1 + \frac{x_1}{x_2} \frac{d}{dx_1} \ln f_1 = \frac{1}{x_2} \frac{d}{dx_1} \ln f_1 \]
\[ \frac{d^2 \Delta G}{dx_1^2} = \frac{RT}{x_2} \frac{d}{dx_1} \ln f_1 \]
Equation reveals that the left – hand side of the above equation is greater than zero. Therefore,
\[ \frac{RT}{x_2} \frac{d}{dx_1} \ln f_1 > 0 \]
\[ \frac{d}{dx_1} \ln f_1 > 0 \]
In a similar way, we can show that
\[ \frac{d}{dx_2} \ln f_2 > 0 \]
The last two equations imply that fugacity of components in a stable solution always increase with increase in concentration.

5. Applying the criterion for equilibrium, Derive Clausius Clapayron equation.(Nov 2015)

The Clapeyron equation using Maxwell’s relations can be written as
\[
\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}
\]

The criterion of equilibrium provides an alternate route for its derivation. Consider any two phases \(a\) and \(b\) of the same substance under equilibrium. Since \(G^a\) and \(G^b\) are both functions of temperature and pressure, and these functional relationships are different for different phases, the two phases can coexist only at such values of the temperature and pressure that \(G^a = G^b\). If the temperature and pressure are altered infinitesimally without disturbing the equilibrium, the change in the free energy must be the same in each phase.

\[
dG^a = dG^b
\]

In a phase change there is no work other than the work of expansion, so that
\[
dG = V \, dP - S \, dT
\]

Using this in equation
\[
V^a \, dP - S^a \, dT = V^b \, dP - S^b \, dT
\]

\(V\) and \(S\) are the molar volume and molar entropy of the fluid with the superscript representing the phase for which the properties correspond to. Equation can be rearranged to the following form.

\[
\frac{dP}{dT} = \frac{S^a - S^b}{V^a - V^b} = \frac{\Delta S}{\Delta V}
\]

In the above equation, \(\Delta S\) and \(\Delta V\) are the entropy change and volume change respectively, accompanying the phase change. Since the transition between phases is occurring reversibly, the entropy change can be evaluated if the latent heat of phase change is known.

\[
\Delta S = \frac{\Delta H}{T}
\]

Where \(\Delta H\) is the latent heat for the phase change. Substituting equation into equation the Clapeyron equation results.

\[
\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}
\]

This relation gives the increase in pressure that is necessary to maintain the equilibrium between phase for a pure substance when the temperature is increased. By using the following simplifications can be modified to yield the Clausius – Clapeyron equation applicable for vapour – liquid equilibria.

1. The latent heat of vaporization is constant and independent of temperature.
2. The molar volume of liquid is negligible compared to that of vapour.
3. The vapour behaves as ideal gas.

The Clausius – Clapeyron equation was derived in chapter and is reproduced below.

\[
\ln \frac{P_2^s}{P_1^s} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

Where \(P_1^s\) and \(P_2^s\) are the vapour pressures at temperatures \(T_1\) and \(T_2\) respectively.
6. Using criterion of phase equilibrium, show that the change in entropy during phase changes can be calculated from the latent heat of and the absolute temperature as \( \Delta S = \Delta H / T \). (June 2014)

Suppose that two phase a and b are in equilibrium. Using the definition of free energy

\[
G^a = H^a - TS^a \quad \text{and} \quad G^b = H^b - TS^b
\]

Here, H and S denote the enthalpy and entropy of the substance. Substituting these results, in equation,

\[
H^a - TS^a = H^b - TS^b
\]

This equation can be rearranged as,

\[
S^b - S^a = \frac{H^b - H^a}{T}
\]

The Left – hand side of the above equation is the entropy change accompanying the phase change of one mole of the substance (\( \Delta S \)), and the numerator on the right – hand side represents the enthalpy change for the phase change of one mole of the substance or the latent heat of phase change (\( \Delta H \)). That is,

\[
\Delta S = \frac{\Delta H}{T}
\]

7. The activity coefficients for component 1 in a binary solution can be represented by, \( \ln \gamma_1 = ax_2^2 + bx_2^3 + cx_2^4 \), where a, b and c are concentration independent parameters. Derive an expression for \( \gamma_2 \). (May 2014)

Equation may be written as

\[
\ln \gamma_2 = -\int_0^{x_1} \frac{x_1}{x_2} d(\ln \gamma_1)
\]

For the present case, differentiating the given equation,

\[
d \ln \gamma_2 = (2ax_2 + 3bx_2^2 + 4cx_2^3)dx_2
\]

Substituting this in the above equation we get

\[
\ln \gamma_2 = -\int_0^{x_1} (2ax_1 + 3bx_1x_2 + 4cx_1x_2^2)dx_2
\]

\[
= -\int_0^{x_1} (2ax_1 + 3bx_1(1-x_1) + 4cx_1(1-x_1)^2)dx_2
\]

\[
\ln \gamma_2 = \left( a + \frac{3b}{2} + 4c \right)x_1^2 - \left( b + \frac{4c}{3} \right)x_1^3 + 4cx_1
\]
8. Explain the triangular diagram for ternary liquid liquid phase equilibria (May 2016)

- Involving three components.
- A binary mixture of components A and C is brought in contact with a solvent B.
- The solvent B is either partially soluble in liquid A or is immiscible with it.
- The component C gets distributed in different proportions between the two insoluble phases - ‘raffinate’ and the ‘extract’.
- The A-rich phase is known as the raffinate and the B-rich phase is known as the extract.
- The ternary liquid–liquid equilibrium diagrams are usually represented on equilateral triangular coordinates.
- On the equilateral triangle the length of the altitude is allowed to represent 100% composition and the length of the perpendiculars from any point to the bases represent the percentages of the three components. The apexes of the triangle represent the pure components A, B, and C and points on the sides represent binary mixtures.
- **Type-I systems** - one pair is partially soluble.
  The pairs A-C and B-C are miscible in all proportions and the pair A-B is miscible only partially.
  Examples: water (A)–chloroform (B)–acetone (C)
  water (A)–benzene (B)–acetic acid (C)
  Liquid C dissolves completely in A and B whereas A and B dissolve only to a limited extent in each other.
- In the region below the mutual solubility curves the two liquid phases exist under equilibrium. The mixture, whose combined composition is represented by point M separates into a raffinate R and an extract E at equilibrium. Thus, RE is a tie line for the system.
- The curve DRPF is the binodal solubility curve, which shows the change in the solubility of A-rich and B-rich phases upon addition of C at a fixed temperature. Any mixture outside this curve will be a homogeneous solution of a single liquid phase. There is one point on the binodal curve P, which will represent the last of the tie lines where the A-rich and B-rich phases become identical. It is known as the plait point. With increase in temperature the mutual solubilities of A and B increase and extraction is not possible under this condition.

- **Type II systems** - two pairs are partially soluble
  Examples: chlorobenzene(A) – water(B) – Methylethylketone(C)
  n-heptane (A) – aniline (B) – methylcyclohexane(C)
Here A and C are completely miscible while A-B and B-C pairs show only limited solubility.

Points D and F represent the mutual solubility of A and B and points H and G those of B and C at the prevailing temperature. Curves DRH and FEG are the ternary solubility curves.

As temperature is increased the mutual solubilities increase and above the critical solution temperature of the binary pair B-C, the system becomes identical to type I system.

9. Write note on azeotropes, high boiling and low boiling azeotropes. Discuss the effect of Temperature for pressure on Azeotropic composition. (May 2012)

- **Azeotropes** are constant boiling mixtures.
- When an azeotrope is boiled, the resulting vapour will have the same composition as the liquid from which it is produced.
- The boiling point of an azeotrope remains constant till the entire liquid is vaporised.
- The azeotropes are formed by solution showing large positive or negative deviation from ideality.
- If the vapour pressures of the constituents of a solution are very close, then any appreciable positive deviation from ideality will lead to a maximum in the vapour pressure curve and negative deviations from ideality under the same conditions leads to a minimum in the vapour pressure curve.
- At the composition at which there exists a maximum or minimum in the vapour pressure curve, the same exists in the boiling point diagrams. The mixture is said to form an azeotrope at this composition under the given temperature and pressure.

- **Minimum-boiling azeotropes.** Solutions showing positive deviation from ideality.
  - In the boiling point diagram, the liquid and vapour curves are tangent at point M, the point of azeotropism at this pressure. The temperature at M is the minimum temperature of boiling for the system.
  - For all mixtures of composition less than M, the equilibrium vapour is richer than the liquid in the more volatile component. For all mixtures richer than M, the vapour is less rich than the liquid in the more volatile component.
  - If solutions either at P or Q are boiled in an open vessel with continuous escape of vapours, and solutions like these cannot be distilled by usual distillation methods.
Examples:
- ethanol–water which forms azeotrope at 89.4% (mol) ethanol at 351.4 K and 101.3 kPa.
- benzene–ethanol (341.2 K and 101.3 kPa, 55% benzene),
- isopropyl ether–isopropyl alcohol (345.1 K and 101.3 kPa, 39.3% alcohol)

**Maximum-boiling azeotropes**
When the total pressure of the system at equilibrium is less than the ideal value, the system is said to exhibit negative deviation from ideality.

- Solution on either side of the azeotrope, if boiled in an open vessel with escape of vapours will ultimately leave a residual liquid of the azeotropic composition in the vessel.
- Maximum-boiling azeotropes are less common than the minimum-boiling type.

Examples:
- Hydrochloric acid–water system forms an azeotrope at 11.1% (mol) HCl at 383 K and 101.3 kPa.
- Chloroform–acetone (337.7 K and 65.5% acetone),

10. Water (1) – hydrazine (2) system forms an azeotrope containing 58.5% (mol) hydrazine at 393 K and 101.3 kPa. Calculate the equilibrium vapour composition for a solution containing 20% (mol) hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of hydrazine at 393 K is 124.76 kPa.
The vapour pressure of water at 393 K = 1.6 × vapour pressure of hydrazine at 393 K = 1.6 × 124.76 = 199.62 kPa.

\[ P_1^s = 199.62 \text{kPa}; \quad P_2^s = 124.76 \text{kPa} \]

For the azeotrope, \( x_1 = 0.415 \) and \( x_2 = 0.585 \)

\[ \gamma_1 = \frac{P}{P_1^s} = \frac{101.3}{199.62} = 0.5075 \quad \gamma_2 = \frac{P}{P_2^s} = \frac{101.3}{124.76} = 0.8120 \]

Using these in Eq. we obtain

\[ A = \ln \gamma_1 \left(1 + \frac{x_1 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = -0.6783 \left(1 + \frac{0.585 \times (-0.2083)}{0.415 \times (-0.6783)}\right)^2 = 1.3927 \]

\[ B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = -0.2083 \left(1 + \frac{0.415 \times (-0.6783)}{0.585 \times (0.2083)}\right) = -2.2822 \]

For the solution containing 20% (mol) hydrazine, \( x_1 = 0.8 \) and \( x_2 = 0.2 \). The activity coefficients are evaluated using Eq.

\[ \ln \gamma_1 = \frac{A x_2^2}{[(A/B) x_1 + x_2]^2} = \frac{-13927 \times 0.2^2}{[0.8(-1.3927)/(-2.2822)+0.2]^2} = 0.1176 \]

\[ \ln \gamma_2 = \frac{B x_1^2}{[x_1 (B/A) x_2]^2} = \frac{-2.2822 \times 0.8^2}{[0.8+0.2(-2.2822)(-1.3927)]^2} = 1.1485 \]

\[ \gamma_1 = 0.8891; \quad \gamma_2 = 0.3171 \]

From Eq, we see that \( y_i P = \gamma_i x_i P_i^s \). That is,

\[ y_1 = \gamma_1 x_1 \frac{P_1^s}{P}, \quad y_2 = \gamma_2 x_2 \frac{P_2^s}{P} \]

To evaluate the vapour compositions using these equations, we should know the vapour pressure values at the new equilibrium temperature. Taking the ratio of the last two equations, we get

\[ \frac{y_2}{y_1} = \frac{1-y_1}{y_1} = \frac{\gamma_2 x_2 P_2^s}{\gamma_1 x_1 P_1^s} = \frac{\gamma_2 x_2}{\gamma_1 x_1} \frac{1}{\alpha_{12}} \]

This can be rearranged to give

\[ y_1 = \frac{1}{1 + \frac{\gamma_2 x_2 P_2^s}{\gamma_1 x_1 P_1^s}} = \frac{1}{1 + \frac{0.3171 \times 0.2 \times 1}{0.8891 \times 0.8 \times 1.6}} = 0.9472 \]

\[ y_2 = 1 - 0.9472 = 0.0528 \]

The composition of the vapour in equilibrium with the liquid containing 20% hydrazine is 5.28% hydrazine and 94.72% water.
UNIT – 3 – CORRELATION AND PREDICTION OF PHASE EQUILIBRIA

PART A

   Activity is the ratio of fugacity to the fugacity in standard state. It is relative fugacity. The concentration of a species to the overall property value is dependent on its activity in the solution.

2. What is co-existence equation? (May/June 2013)
   \[ \frac{dP}{dy_i} = \frac{P(y_i - x_i)}{y_i(1 - y_i)} \]

3. Give the importance of Gibbs-Duhem’s equation. (May/June 2013) (May/June 2014)
   - In the absence of complete experimental data on the properties of the solution, Gibbs Duhem’s equation may be used to calculate additional properties.
   - It can be used to test thermodynamic consistency of experimental data.

   Activity coefficients are a measure of the extent to which the real solution departs from ideality. Activity coefficient of the component \( \gamma_i \) is defined by the following relation:
   \[ \tilde{f}_i = \gamma_i x_i f_i^0 \]

5. What is the effect of pressure on activity coefficients? (DEC 2009) (May/June 2014)
   \[ \left( \frac{\partial \ln \gamma_i}{\partial P} \right)_T = \frac{\gamma_i - \gamma_i^0}{RT} \]

   A plot of \( ln \) versus \( x_1 \) is prepared and if the net area under the curve obtained is zero, then it is assumed that the data is consistent. This is also called as Redlich-Kister method.

7. What do you mean by excess property? (Nov 2011)
   Excess property is defined as the difference between actual property value of a solution and the value it would have as an ideal solution at the same Temperature, pressure and composition.

8. Define Activity coefficient (May/June 2012)
   By definition, activity coefficient is the ratio of activity to the number of moles or mole fractions of component \( i \) in a solution. The numerical value of the activity coefficient is dependent on both the standard state and the units of expression for composition. For an ideal solution, activity coefficient is considered to be unity, i.e., \( \gamma_1 = 1 \). It can be expressed as
   \[ \gamma_i = \frac{a_i}{n_i} = \frac{f_i}{f_i^0} n_i = \frac{f_i}{f_i^0} n_i = \frac{\tilde{f}_i}{f_i^0} x_i \]

9. Discuss the significance of co-existence equation. (Nov/Dec 2012)
   The co-existence equation can be used for testing the consistency of vapor liquid equilibrium data. It can be used to calculate any one of three variables \( P, x \) or \( y \) if experimentally measured values of the other two variables are available. If all the three variables are experimentally determined then the co-existence equation can be used to test the consistency of the measured data.

10. What do you mean by Consistency tests?
    Consistency tests are ways and means of validating experimentally obtained VLE data which are prone to inaccuracies. Almost all these tests are based on Gibbs – Duhem’s equations written in terms of activity coefficients.

11. What is the effect of pressure of activity? (May 2014)
    \[ \left( \frac{\partial \ln a}{\partial P} \right) = \frac{\nu}{RT} \]
12. How do you define the activity of a component in a solution?
Activity of a component in a solution is the ratio of the fugacity of the component in the solution to that of the fugacity of the component in standard state.


\[
\ln v_1 = x_1^{\frac{1}{r_{11}}(x_1 G_{11} + x_2 G_{12})} + \frac{r_{11} G_{12}}{(x_1 + x_2 G_{12})}
\]

\[
\ln v_2 = x_2^{\frac{1}{r_{12}}(x_2 G_{12} + x_1 G_{11})} + \frac{r_{12} G_{11}}{(x_1 + x_2 G_{11})}
\]

14. What are UNIQUAC and UNIFAC method?
UNIQUAC is Universal quaci chemical equation and UNIFAC is Universal functional activity coefficient method. These two are local composition models which account for the short range order and non random molecular orientations that result from differences in molecular size and intermolecular sizes.

15. Name local composition models for activity coefficients.
1) Non Random Two Liquid (NRTL) model.
2) UNIQUAC model.
3) UNIFAC model.

16. Which is the most reliable method for testing the consistency of experimental VLE data?
Local composition models are considered as the most reliable method for testing the consistency of experimental VLE data.

17. How can you test the consistency data using partial pressure data?
Using Gibbs-Duhem’s equation.

18. How can you calculate the activity coefficient using Gibbs-Duhem’s equation?

\[
x_1 \frac{\partial \ln v_1}{\partial x_1} = x_2 \frac{\partial \ln v_2}{\partial x_2}
\]

19. How would you estimate the composition of the vapor phase in equilibrium with two immiscible liquid phases?
For immiscible binary systems

\[
y_A = \frac{x_A}{y_B} = \frac{P_A^0}{P_B^0}
\]

The relative proportions of two liquids in the distillate can be calculated remembering that the number of mole of each component present in the vapor phase is proportional to its Vapor Pressure.

20. List out the different tests available for testing the consistency of VLE data of binary system.
(Nov 2015)
Different methods of testing the consistency of VLE data are
(i) Using slope of ln \(\frac{P}{x}\) curves.
(ii) Using data of mid point
(iii) Redlich-Kister method
(iv) Using the coexistence equation.
(v) Using the Partial pressure data.

21. What are activity coefficient equations? Give an example.
Activity coefficients equations are those which relate activity coefficient and concentration of the solution.
Eg: Margules Equation, VanLaar Equation.

22. What is the difference between Activity Composition models and Local composition models?
Activity composition models consider the solution is under investigation is of uniform concentration and it will not take in to consideration the variation in the composition the sample at different points. Whereas the local composition models considered various parameters that will account for the variation in the concentration at different points in the solution.

23. Write down any two activity composition models.
Margules and Van laar models are most used two activity composition models.
24. Explain the importance of $G^E/RT$ term.

$G^E/RT$ is the ratio of energies and is a dimensionless quantity which specifies the ratio of energy deviation from that of the ideal value.

25. What is the effect of Temperature on activity coefficients?

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T = \frac{H_i - H_i^0}{RT^2}$$


$$\ln \gamma_i = -\ln(x_i + x_i \lambda_{12}) + x_i \left[ \frac{\lambda_{12}}{x_i + x_i \lambda_{12}} - \frac{\lambda_{21}}{x_i + x_i \lambda_{21}} \right]$$

$$\ln \gamma_j = -\ln(x_j + x_j \lambda_{12}) + x_j \left[ \frac{\lambda_{21}}{x_j + x_j \lambda_{21}} - \frac{\lambda_{12}}{x_j + x_j \lambda_{12}} \right]$$

27. What is a coexistence equation? (May 2016)

Coexistence equation is used to test the consistency of VLE data.

$$\frac{dP}{dy_i} = \frac{P(y_i - x_i)}{y_i(1 - y_i)}$$


**Margules equation**

$$\ln \gamma_1 = x_1^2 \left[ A_{12} + 2(A_{21} - A_{12})x_1 \right]$$

$$\ln \gamma_2 = x_2^2 \left[ A_{21} + 2(A_{12} - A_{21})x_2 \right]$$

**Van Laar equation**

$$\ln \gamma_1 = \left[ 1 + \frac{A_{12}^e x_1}{A_{21}^e x_2} \right]^{-2}$$

$$\ln \gamma_2 = \left[ 1 + \frac{A_{21}^e x_2}{A_{12}^e x_1} \right]^{-2}$$
PART B

1. For the system n-pentane (1) n-heptane (2), the vapor pressures are given by the Antoine equation \( \ln P = A - \frac{B}{(T - C)} \) where \( P \) is in kPa and \( T \) is in K. The constants are as follows:

<table>
<thead>
<tr>
<th>System</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>13.8183</td>
<td>2477.07</td>
<td>40.00</td>
</tr>
<tr>
<td>n-heptane</td>
<td>13.8587</td>
<td>2911.32</td>
<td>56.56</td>
</tr>
</tbody>
</table>

Assuming that the solution formed is ideal, calculate:

i) The composition of the liquid and vapor in equilibrium at 95 kPa and 336.2 K

ii) The composition of the vapor in equilibrium with a liquid containing 34% (mol) pentane and the equilibrium temperature at \( P = 95 \text{kPa} \).

iii) The total pressure and the vapor composition in equilibrium with a liquid of composition \( x_1 = 0.44 \) at \( T = 333.2 \text{K} \) (May 2013), (Nov 2014)

From Antoine equation, at 336.2 K

\[
\ln P_1^S = 13.8183 - \frac{2477.07}{(T - 40.00)} \\
\ln P_1^S = 13.8183 - \frac{2477.07}{(336.2 - 40.00)} \\
\ln P_1^S = 5.4554 \quad P_1^S = 234.02 \text{ kPa} \\
\ln P_1^S = 13.8587 - \frac{2911.32}{(T - 56.56)} \\
\ln P_1^S = 13.8587 - \frac{2911.32}{(336.2 - 56.56)} \\
\ln P_2^S = 3.4477 \quad P_2^S = 31.43 \text{ kPa} \\

We know that, \( P = P_2^S + (P_1^S - P_2^S) x_1 \)

\[
95 = 31.43 + x_1 (234.02 - 31.43) \\
X_1 = 0.3137
\]

We know that, \( y_1 = x_1 \frac{P_1^S}{P} \) from this we can obtain \( y_1 = 0.7727 \)

i) \( P = P_2^S + (P_1^S - P_2^S) x_1 \)

\[
95 = P_2^S + 0.34 (P_1^S - P_2^S)
\]

Assume \( T = 335 \text{ K} \), by using Antoine equations we get,

\[
P_1^S = 226.207 \text{ kPa} \quad P_2^S = 30.050 \text{ kPa} \]

Thus, \( P_2^S + 0.34 (P_1^S - P_2^S) = 96.743 > 95 \text{ kPa} \)
Assume $T=334$ K, by using Antoine equations we get,

\[ P_1^S = 219.837 \text{ kPa} \quad P_2^S = 28.938 \text{ kPa} \]

Thus, $P_2^S + 0.34 (P_1^S - P_2^S) = 93.844 < 95 \text{ kPa}$

Assume $T=334.7$ K, by using Antoine equations we get,

\[ P_1^S = 224.282 \text{ kPa} \quad P_2^S = 29.713 \text{ kPa} \]

Thus, $P_2^S + 0.34 (P_1^S - P_2^S) = 95.866 > 95 \text{ kPa}$

So

Assume $T=334.6$ K, by using Antoine equations we get, $P_1^S$ & $P_2^S$ at 334.6K, we get $y_1= 0.80$

ii) At 333.2 K we have $P_1^S = 214.842 \text{ kPa} \quad P_2^S = 28.0739 \text{ kPa}$

by using Antoine equations, we know that,

\[ P = P_2^S + (P_1^S - P_2^S)X_1 \]

\[ P=110.25 \text{ kPa} \]

Also, $y_1 = x_1 \frac{P_1^S}{P}$

\[ y_1= 0.8574 \]

2. Explain the following activity coefficient models. (May 2013,2016)

i) Wilson Model

ii) NRTL model

iii) UNIQUAC model

iv) UNIFAC model

Wilson equation

\[
\ln y_1 = - \ln (x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)
\]

\[
\ln y_2 = - \ln (x_2 + \Lambda_{21}x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right)
\]

- Based on the concept of local compositions
- recommended only for liquid systems that are completely miscible, or for partially miscible systems
- 2 adjustable positive parameters $L12$ and $L21$.

\[
\Lambda_{12} = \frac{V_2}{V_1} \exp \left[ - \frac{\lambda_{12} - \lambda_{11}}{RT} \right] = \frac{V_2}{V_1} \exp \left[ - \frac{a_{12}}{RT} \right]
\]

\[
\Lambda_{21} = \frac{V_1}{V_2} \exp \left[ - \frac{\lambda_{12} - \lambda_{22}}{RT} \right] = \frac{V_1}{V_2} \exp \left[ - \frac{a_{21}}{RT} \right]
\]

- The differences in the characteristic energies($aij$) are assumed to be temperature independent
- Wilson equation provides a good representation of VLE of a variety of miscible mixtures
- suitable for solutions of polar or associating components like alcohols in non-polar solvents for which the Margules and van Laar equations are generally inadequate.

Disadvantages
- It is not suitable for systems showing maxima or minima on the ln g versus $x$ curves.
- Not useful for systems exhibiting limited miscibility.
NRTL Model – Non Random Two Liquid Operation

\[
\ln \gamma_i = x_i^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_i + x_j G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_i + x_j G_{12})^2} \right]
\]

\[
\ln \gamma_j = x_j^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_i + x_j G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_i + x_j G_{21})^2} \right]
\]

The adjustable parameters

\[
G_{ij} = \exp (-a_{ij}RT) \quad G_{ij} = \exp (-a_{ij}RT)
\]

\[
\tau_{12} = \frac{b_{12}}{RT} \quad \tau_{21} = \frac{b_{21}}{RT}
\]

- The constants $b_{12}$ and $b_{21}$ and $a_{12}$ are independent of composition and temperature.
- The parameter $a_{12}$ is related to the non-randomness in the mixture.
- If $a_{12}$ is zero, the mixture is completely random and the NRTL equation reduces to the Margules equation.
- It is found from fitting of experimental data that $a_{12}$ varies from about 0.20 to 0.47. In the absence of the experimental data, the value of $a_{12}$ is arbitrarily set, a typical choice being $a_{12} = 0.3$. When $a_{12}$ is arbitrarily fixed, NRTL equation becomes a two-parameter model.
- NRTL equation is applicable to partially miscible as well as totally miscible systems. For moderately non-ideal systems, it offers no advantage over the van Laar and Margules equations. But, for strongly non-ideal solutions and especially partially miscible systems, the NRTL equations provide a good representation.

UNIQUAC model

- Consists of two parts – combinational and residual
- Combinational part describes the prominent entropic contribution and is determined by the sizes and shape of the molecules and requires only pure component data.
- Residual part - which is due primarily to the intermolecular forces that are responsible for the enthalpy of mixing and depends on the intermolecular forces and involves two adjustable binary parameters.

\[
\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\phi_1}{\phi_2} + \phi_2 \left( l_1 - \frac{\tau_{12}}{\theta_1} \right) - q_1 \ln (\theta'_1 + \theta'_2 \tau_{12})
\]

\[
+ \phi_1 q_1 \left( \frac{\tau_{12}}{\theta'_1 + \theta'_2 \tau_{12}} - \frac{\tau_{21}}{\theta'_2 + \theta'_1 \tau_{21}} \right)
\]

\[
\ln \gamma_2 = \ln \frac{\phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\phi_2}{\phi_1} + \phi_1 \left( l_2 - \frac{\tau_{21}}{\theta_1} \right) - q'_2 \ln (\theta'_2 + \theta'_1 \tau_{21})
\]

\[
+ \phi_2 q_2 \left( \frac{\tau_{21}}{\theta'_2 + \theta'_1 \tau_{21}} - \frac{\tau_{12}}{\theta'_1 + \theta'_2 \tau_{12}} \right)
\]

Where

\[
l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1), \quad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1)
\]
$z$ is the coordination number, $r$, $q$ and $q'$ are pure-component molecular structure constants. The molecular size and surface area are given by $r$ and $q$ respectively. For fluids other than water or lower alcohols, $q = q'$. For alcohols, the surface of interaction $q'$ is smaller than the geometric surface $q$. The adjustable binary parameters $t_{12}$ and $t_{21}$ are related to the characteristic energies $\Delta u$ as follows.

\[
\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right)
\]

\[
\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right)
\]

The segments and area fractions are obtained as follows

\[
\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right)
\]

\[
\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right)
\]

- The UNIQUAC equation satisfies a large number of non-electrolyte mixtures containing non-polar fluids such as hydrocarbons, alcohols, etc., and water, including partially miscible mixtures.
- The main advantages of this equation are its wide applicability and simplicity.

**UNIFAC model**

The activity coefficients are estimated through group contributions. The liquid is treated as a solution of different structural groups from which the molecules are formed, rather than a solution of molecules themselves. This method is based on and similar to the UNIQUAC model.

\[
\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R
\]

3. The following data were reported for the vapor - liquid equilibrium for the ethanol water system at 298 K. Test whether the data are thermodynamically consistent or not.

<table>
<thead>
<tr>
<th>Xi</th>
<th>0.122</th>
<th>0.163</th>
<th>0.226</th>
<th>0.320</th>
<th>0.337</th>
<th>0.437</th>
<th>0.440</th>
<th>0.579</th>
<th>0.830</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yi</td>
<td>0.474</td>
<td>0.531</td>
<td>0.562</td>
<td>0.582</td>
<td>0.589</td>
<td>0.620</td>
<td>0.619</td>
<td>0.685</td>
<td>0.849</td>
</tr>
<tr>
<td>$P$</td>
<td>5.57</td>
<td>6.02</td>
<td>6.38</td>
<td>6.76</td>
<td>6.80</td>
<td>7.02</td>
<td>7.04</td>
<td>7.30</td>
<td>7.78</td>
</tr>
</tbody>
</table>

The vapor pressure of ethanol and water are 7.86 and 3.17 KPa. (MAY 2011), (Nov 2015)

Assuming that the gas phase behaves ideally, the activity coefficients are calculated as, $\gamma_1 = \frac{y_1^P}{x_1P^*}$ and $\gamma_2 = \frac{y_2^P}{x_2P^*}$

Thus the values are calculated and listed below:

<table>
<thead>
<tr>
<th>$X_1$</th>
<th>0.122</th>
<th>0.163</th>
<th>0.226</th>
<th>0.320</th>
<th>0.337</th>
<th>0.437</th>
<th>0.440</th>
<th>0.519</th>
<th>0.830</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>2.95</td>
<td>2.49</td>
<td>2.018</td>
<td>1.56</td>
<td>1.51</td>
<td>1.26</td>
<td>1.26</td>
<td>1.09</td>
<td>1.01</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>1.05</td>
<td>1.06</td>
<td>1.13</td>
<td>1.31</td>
<td>1.33</td>
<td>1.49</td>
<td>1.51</td>
<td>1.72</td>
<td>2.18</td>
</tr>
</tbody>
</table>
\[
\ln(\frac{\gamma_1}{\gamma_2})
\]

\[
= \begin{bmatrix}
0.96 & 0.85 & 0.43 & 0.12 & -0.16 & -0.18 & -0.45 & -0.76
\end{bmatrix}
\]

\[
\ln(\gamma_1 / \gamma_2) \text{ is plotted against } x_1 \text{ and the net area is not equal to zero. Thus, the data doesn’t satisfy Redlich Kister criteria for consistency.}
\]

4. **Water (1) - Hydrazine (2)** system forms an azeotrope containing 58.5 mole% hydrazine at 393K and 101.3KPa. Calculate the equilibrium vapor composition for a solution containing 20 mole% hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapor pressure of hydrazine at 393K is 124.76Kpa. (May 2013, Nov 2012, Nov 2013)

The VP of water at 373 K = 1.6 x VP of hydrazine at 373 K = 1.6 x 124.76 = 199.62 KPa

\[
P_1^S = 199.62 \text{ KPa and } P_2^S = 124.76 \text{ KPa}
\]

\[
x_1 = 0.415 \text{ and } x_2 = 0.585
\]

\[
\gamma_1 = \frac{P_1}{P_1^S} = \frac{101.3}{199.62} = 0.5075 \text{ and } \gamma_2 = \frac{P_2}{P_2^S} = \frac{101.3}{124.76} = 0.812
\]

Substituting in Van Laar equations we get,

\[
\ln \nu_1 = \left[1 + \frac{A_{12}x_1}{A_{21}x_2}\right]^{-2} \quad \ln \nu_2 = \left[1 + \frac{A_{21}x_2}{A_{12}x_1}\right]^{-2}
\]

\[
A = -1.3927 \text{ and } B = -2.2822
\]

Here, \(x_1=0.8\) and \(x_2=0.2\). Substituting these in the following equation,

\[
\ln \gamma_1 = A \frac{x_2^2}{[(A/B)x_1 + x_2]^2}; \quad \ln \gamma_2 = B \frac{x_1^2}{[x_1 + (B/A)x_2]^2}
\]

We get \(\gamma_1=0.8891\) and \(\gamma_2=0.3171\)

Also,

\[
y_1 = \gamma_1 x_1 \frac{P_1^S}{P}, \quad y_2 = \gamma_2 x_2 \frac{P_2^S}{P}
\]

\[
\frac{y_2}{y_1} = \frac{1-y_1}{y_1} = \frac{\gamma_2 x_2 P_2^S}{\gamma_1 x_1 P_1^S} = \frac{\gamma_2 x_2}{\gamma_1 x_1} \frac{1}{\alpha_{12}}
\]

Rearranging, we get,

\[
y_1 = \frac{1}{1 + \frac{\gamma_2 x_2 P_2^S}{\gamma_1 x_1 P_1^S}} = \frac{1}{1 + \frac{0.3171 \times 0.2}{0.8891} \times \frac{1}{1.6}} = 0.9472
\]

\[
y_2 = 1 - 0.9472 = 0.0528
\]
Thus, 5.28% hydrazine and 94.72% water.

5. (i) Explain the criteria for phase equilibrium
(ii) Discuss vapor liquid equilibrium. (MAY 2011)

(i) Consider a closed system consisting of two phases of a binary solution, for example, the vapour and liquid phases of an alcohol–water solution. If the system is in thermodynamic equilibrium, mass, temperature and pressure are uniform throughout. We know that, ‘Clausius inequality’,

\[ dS \geq \frac{dQ}{T} \]
\[ dQ = dU + dW \]
\[ TdS \geq dU + dW \]
\[ dU \leq TdS - dW \]
\[ dU \leq TdS - PDV \]

**Constant U and V** - For an isolated system, dQ=0, dW=0 and thus dU=0. Also the volume is constant. dV=0. Thus

\[ dS_{U,V} \geq 0 \]

Thus, the entropy must be maximum at equilibrium.

**Constant T and V** - We know that, \( A = U - TS \) and \( U = A + TS \)

\[ dU = dA + TdS + SDT \]

Also, \( dU \leq TdS - PDV \) and thus, \( dA \leq -PDV - SDT \)

At constant temperature and volume, we get

\[ dA_{T,V} \leq 0 \]

Thus, the Helmholtz free energy must be minimum at equilibrium

**Constant T and V** - We know that, \( G = H - TS \) and \( H = U + PV \)

Therefore, \( G = U + PV - TS \)

\[ dG = dU + PDV + VdP - TdS - SDT \]
\[ dU = dG - PDV - VdP + TdS + SDT \]
Also, $dU \leq TdS - PdV$ Thus, $dG \leq VdP - SdT$

Therefore,

$$dG_{T,P} \leq 0$$

Thus, the free energy must be minimum at equilibrium.

ii) **The vapour-liquid equilibrium** (VLE) data are essential for many engineering calculations. The conditions of equilibrium require that the fugacity of a component in the liquid phase be equal to that in the vapour phase. That is,

$$\tilde{f}_i^L = \tilde{f}_i^V \quad \text{for } i = 1, 2, 3, \ldots, C$$

Also, for the vapour phase

$$\tilde{f}_i^V = \gamma_i^V \phi_i^V f_i^V$$

The fugacity of a component in gas mixture can be written as

$$\tilde{f}_i^V = y_i \phi_i^V P$$

Where $\phi_i$ is the fugacity coefficient. For the liquid phase,

$$\tilde{f}_i^L = x_i \gamma_i^L \phi_i^L f_i^0$$

Also, rearranging using activity coefficient

$$\tilde{f}_i^L = x_i \phi_i^L P$$

Equating the fugacities of the vapour and the liquid phase,

$$y_i \phi_i^V P = x_i \phi_i^L P$$

Rearranging,

$$y_i \phi_i^V P = \gamma_i^L x_i \phi_i^L f_i^0$$

This is called the activity coefficient approach. Using this, the VLE problem can be solved by dividing them into the following grouping for convenience.

**Case 1: IDEAL GAS – PHASE, IDEAL LIQUID SOLUTION:**
For ideal gases, the fugacity coefficient is equal to 1 and for ideal solutions the activity coefficient is 1 and the fugacity at low pressure, is equal to saturation pressure of pure liquid. Then,

\[ y_i P = x_i P^S_i \]

**Case 2: LOW – PRESSURE VLE PROBLEMS:**
If the pressure is low enough that the assumption of ideal gas behaviour for the gas phase would not introduce any significant errors in practical calculations. The above equation can be modified as follows.

\[ y_i P = \gamma_i^L x_i P^S_i \]

**Case 3: HIGH – PRESSURE VLE PROBLEMS:**
The fugacity and activity coefficient are complex functions of temperature, pressure and compositions and can be written as

\[ \phi_i^V = F'(T, P, y_1, y_2, ..., y_{n-1}) \]

\[ \gamma_i^L = F''(T, P, x_1, x_2, ..., x_{n-1}) \]

Also, we know that,

\[ RT = \ln VdP \]

\[ \ln \frac{f^0_i}{\phi^S_i P^S_i} = \frac{V_i}{RT} (P - P^S_i) \]

the volume does not change appreciably with pressure, we get,

\[ f^0_i = \phi^S_i P^S_i \exp \left[ \frac{V_i (P - P^S_i)}{RT} \right] \]

Therefore, substituting we get,

\[ y_i \phi^V_i = \gamma_i^L x_i \phi^S_i P^S_i \exp \left[ \frac{V_i (P - P^S_i)}{RT} \right] \]

This is the general equation for vapour – liquid equilibria. The exponential in the above equation is known as the **poynting correction** and it is approximately unity when pressure is low.
UNIT 4 – CHEMICAL REACTION EQUILIBRIA

PART A

   At equilibrium the total Gibbs Energy at $G'$ is minimum. Its differential is zero at equilibrium.

2. Explain the term “Reaction co-ordinate” (May 2011, Nov 2014)
   The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced. It is denoted by $\varepsilon$.

3. Define Standard Free Energy and how it is related to equilibrium constant? (May 2011)
   Standard free energy is the change in the energy content observed in the system before and after the reaction.
   \[ \Delta G = -RT \ln K \]

   The equilibrium constant defined in terms of activities of reactants and products is independent of pressure.

5. Explain the activities of reactants and products.
   The activities of reactants and products correspondingly decides the rate of forward and backward reactions and hence the overall rate.

6. What reaction conditions affect the equilibrium conversion in chemical reactions? (May/June 2013)
   Temperature and activities of the reactants and products affects the equilibrium conversion in chemical reaction.

7. Write a note on the choice of Standard State in the study of Chemical reactions. (May 2014)
   The temperature in the standard state is the same as that of the reaction, and the pressure of 1 bar (or std 1 atm) is used.
   For gases the std state chosen is the pure component at the temperature of the reaction and at unit fugacity.

8. Explain Equilibrium constant
   Equilibrium constant for a reaction is the ratio of product of activities of all products raised to their stoichiometric coefficients to that of the product of all activities raised to their stoichiometric coefficients.

9. What are the various methods to compute equilibrium constant?
   Equilibrium constant can be computed from experimental data using std. heat of reaction or employing thermal data.

10. What are the applications of equilibrium constant?
    Equilibrium constant is the most necessary data for the design of reactor systems.

11. What is the effect of temperature on equilibrium constant?
    \[ \ln \frac{K}{K_1} = - \frac{\Delta H^o}{R} \left[ \frac{1}{T} - \frac{1}{T_1} \right] \]
12. What is meant by Set of Primary reactions?
Primary reactions are first step of intermediate reactions that altogether constitutes, microscopically observed overall chemical reaction.

13. What is the relation between $K_a$, $K_y$, and $K_\phi$?
$K = K_a K_y P^\nu$

14. What are Single and Multiple reactions?
The reactants reacting in only one manner and yielding specific products are called single reactions. The reactants reacting in different ways yielding different types of products are called multiple reactions.

15. Is the Gibbs free energy change of a chemical reaction related to the work done by the system? Give an example.
The Gibbs free energy change of a chemical reaction is related to temperature.

16. Explain the term “Equilibrium Conversion”
Equilibrium conversion is the conversion obtained in the reactor system with its $\Delta G$ minimum.

17. What are Homogeneous and Heterogeneous reactions?
Homogeneous reactions are those in which all the chemicals involved in a reaction are in the same physical phase. If not they are called Heterogeneous reactions.

18. What is the effect of Pressure on the Degree of conversion at equilibrium, for a gas phase reaction?
Though the equilibrium constant is unaffected by pressure it does affect the equilibrium composition in gas phase reactions according to the Le chtellier’s principle.

19. How does the addition of Inert gases affect the degree of conversion on chemical reaction? (Nov 2015)
$$\Pi_i^w = \frac{K}{K_\phi} \left( \frac{N}{P} \right)^\omega$$
Inert affects the equilibrium conversion as per the above equation. The presence of inerts will decrease conversion if reaction is accompanied by a decrease in the number of moles and inerts present in the system will have no influence on the degree conversion if $\gamma$ is zero.

20. Write the relation between Equilibrium constant and standard free energy change.
$$\Delta G = -RT \ln K$$

21. What do you mean by the term “feasibility of a reaction”
Feasibility of a reaction is indicated the numerical figure obtained by adding the standard free energy of all the chemicals involved in the chemical reaction. If the value is negative then the reaction is thermodynamically feasible and if the value is negative then the reaction is thermodynamically not feasible.
22. How will you estimate the standard heat of reaction at temperature \( T \) given the standard heat of reaction? 
By considering the energy requirements for decreasing the reacting system to the reference standard temperature and energy requirements for increasing the reacting system to the original temperature Standard heat of reaction at temperature \( T \) is determined. 

23. What is the effect of Pressure on Equilibrium composition? 
Pressure affects the equilibrium composition is gas phase reactions. According to Le Chatelier’s principle when pressure is applied the system responds in such a way as to minimize the effect of increase in pressure. 

24. List out the factors affecting Equilibrium Conversion 
The reaction conditions that influence the extent of reaction under equilibrium are Temperature, Pressure, and presence of inert materials, presence of Excess reactants and presence of the products of the reaction in the initial mixture. 

25. In what type of reactions, is the equilibrium constant independent of temperature? 
For the reactions in which the heat of reaction is negligible then their equilibrium constant is independent of temperature. 

26. Explain the term “Reaction co-ordinate” ?What is its significance in chemical reaction. (Nov 2015) 
The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced. It is denoted by \( \epsilon \).
1. **What is the effect of temperature on equilibrium constant? Define van’t Hoff equation (Nov 2015)(May 2016)**

   The effect of temperature on equilibrium constant is quantitatively expressed by equation, which is developed below. The relationship of equilibrium constant to the energy of reaction is given by

   \[ \Delta G^0 = -RT \ln K \]  

   The standard state is identified by specifying pressure (or fugacity), but the temperature is always the same as that of the reaction equilibrium. \( \Delta G^0 \) and hence K will vary with this temperature.

   For a single species the effect of temperature on its free energy is predicted by Git equation

   \[ \left( \frac{\partial (G^0/T)}{\partial T} \right)_p = -\frac{H^0}{T^2} \]  

   For the substance in its standard state,

   \[ \left( \frac{d (G^0/T)}{dT} \right)_p = -\frac{H^0}{T^2} \]

   The partial derivative notation is dropped from the above equation, as the energy, by virtue of the definition of the standard state, depends on the equilibrium but not on the equilibrium pressure. Multiplying the above equation by \( v_i \) and sums species present in the system, we get

   \[ \left( \frac{d \sum v_i C_i^0 T}{dT} \right)_p = \sum v_i H_i^0 \]

   The standard free energy of the reaction and standard heat of reaction are related to the energy and enthalpy of individual species respectively as given below.

   \[ \Delta G^0 = \sum v_i G_i^0, \quad \Delta H^0 = \sum v_i H_i^0 \]

   Using these in Eq. 3 and dividing both sides by R, we get

   \[ \left( \frac{d (\Delta G^0/RT)}{dT} \right)_p = -\frac{\Delta H^0}{RT^2} \]  

   Substitute Eq. 3 into Eq. 4 we get

   \[ \frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \]  

   Equation 5 known as van’t Hoff equation, predicts the effect of temperature on the constants and hence on the equilibrium yield. \( \Delta H^0 \) in Eq. 5 is the standard heat of if is apparent that if \( \Delta H^0 \) is negative, i.e. if the reaction is exothermic, the equilibrium eases as the reaction temperature increases. Alternatively, for an endothermic reaction, the equilibrium constant will increases with increase in temperature.

   If \( \Delta H^0 \), the standard heat of reaction, is constant, Eq. 5 on integration yields

   \[ \ln \frac{K}{K_1} = \frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) \]

   And \( K_1 \) are the equilibrium constant values at temperatures \( T \) and \( T_1 \) respectively. Equation (6) can be used to evaluate the equilibrium constant with good results over small temperature ranges. Equation is exact if \( \Delta H^0 \) is independent of temperature. A reasonably accurate method of interpolation or extrapolation of equilibrium constant is provided by plotting \( \ln K \) versus reciprocal temperature, which leads to a straight line according to Eq. (6).

2. **The standard heat of formation and standard free energy of formation of ammonia at 298 K are \(-46,100 \text{ J/mol} \) and \(-16,500 \text{ J/mol} \) respectively. Calculate the equilibrium constant for the reaction. (MAY 2011,NOV 2016)**
The standard free energy of reaction is estimated from Equation

$$\Delta G^0 = \sum_{\text{Products}} |v_i| \Delta G_{i,j}^0 - \sum_{\text{Reactants}} |v_i| \Delta G_{i,j}^0$$

The second summation yields zero as the free energy of formation of the elements are zero

$$\Delta G^0 = \sum_{\text{products}} |v_i| \Delta G_{i,j}^0 = 2 \times -16,500 = -33,000 \text{J/mol}$$

Using Equation

$$\ln K = \frac{\Delta G^0}{RT} = \frac{33,000}{8.314 \times 298} = 13.3195$$

Therefore,

$$K \text{ at 298 K} = 6.0895 \times 10^5$$

The standard heat of reaction at 298 K = 2 \times -46,100 = -92,200 J/mol. This is assumed constant within the temperature range involved. Now use Equation to evaluate the equilibrium constant.

$$\ln \frac{K}{K_i} = \frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T_i} \right)$$

$$\ln \frac{K}{6.0895 \times 10^5} = -92,200 \left( \frac{1}{500} - \frac{1}{298} \right) = -15.0344$$

Therefore, the equilibrium constant at 500 K = 0.18

3. Explain reaction coordinate. What are the criteria of chemical reaction equilibrium? (MAY 2011)

- Also called extent of reaction
- It is denoted by $\varepsilon$
- The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced.
- Change in the extent of reaction $d\varepsilon$ is the same for each component, whereas the changes in the number of moles are different for different species taking part in the reaction.

$$\frac{dn_i}{v_i} = d\varepsilon$$

$$dn_i = v_i \ d\varepsilon$$

Before the reaction starts, $\varepsilon = 0$

Criteria for chemical reaction equilibrium

At constant temperature and pressure, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy. Stated mathematically, the total Gibbs free energy is

$$dG_{T,P} = 0$$

There is no change in the Gibbs free energy of the system, provided the change is taking place at constant temperature and pressure.

Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given temperature and pressure.

$$aA + bB \rightarrow lL + mM$$

The free energy change of the process in term of chemical potential, is given by
Also,

\[ dG^t_{T, p} = \sum \mu_i \, dn_i \]

\[ dG^t_{T, p} = \mu_L \, dn_L + \mu_M \, dn_M + \mu_A \, dn_A + \mu_B \, dn_B \]

\[ dn_i = v_i \, d\varepsilon \]

Then,

\[ dG^t_{T, p} = (v_L \mu_L + v_M \mu_M + v_A \mu_A + v_B \mu_B) \, d\varepsilon \]

\[ = (l \mu_L + m \mu_M - a \mu_A - b \mu_B) \, d\varepsilon \]

where \(-a, -b, l, m\) are stoichiometric constants \(\varepsilon\) is the extent of the reaction. For an infinitesimal change in a reacting system,

\[ dG^t_{T, p} = \sum \mu_i v_i \, d\varepsilon \]

Since the process is at equilibrium,

\[ dG^t_{T, p} = \sum \mu_i v_i \, d\varepsilon = 0 \]

\[ \sum \mu_i v_i = 0 \]

This is the criterion of equilibrium for chemical reactions.

Since the reaction proceeds in the direction of decreasing Gibbs free energy \(G\), the forward reaction \((A \rightarrow B)\) takes place if \(mA > mB\) and the backward reaction \((A \rightarrow B)\) proceeds if \(mA < mB\). When \(mA = mB\), the slope of the curve is zero. This occurs at the minimum of the curve and corresponds to the position of chemical equilibrium.

4. Derive the expression relating equilibrium constant and standard free energy change from the fundamentals of thermodynamics. Develop the expression giving the reaction equilibrium constant \((K)\) in terms of the reactants and products in the case of a homogeneous chemical reaction. (May 2012)

Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given temperature and pressure.

\[ aA + bB \rightarrow lL + mM \]

The criterion of equilibrium for the above chemical reaction can be written as,

\[ (l m_L + m m_M) - (a m_A + b m_B) = 0 \]

The chemical potential and fugacity are related as

\[ \mu_i = RT \ln \tilde{f_i} + C \]
At standard state,

\[ \mu_i^0 = RT \ln f_i^0 + C \]

Combining the above two equation we get,

\[ \mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_i^0} = \mu_i^0 + RT \ln a_i \]

Writing the above equation for all 4 species and substituting in

\[(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0\]

We get,

\[ (l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = 0 \]

\[ (l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} \]

\[ \Sigma \mu_i^0 v_i = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_R^b} \]

Using the definition of \( K \) and \( \Delta G^0 \), we arrive at

\[ \Delta G^0 = -RT \ln K \]

5. Show that the equilibrium constant in the decomposition of calcium carbonate into \( CO_2 \) and lime is equal to the partial pressure of \( CO_2 \). Explain how would you estimate the decomposition pressure? What would happen if the \( CO_2 \) pressure is reduced below this value? (May 2013)

The overall reaction can be represented as

\[ CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \]

The equilibrium constant for the reaction is

\[ K = \frac{a_{CO_2} a_{CaO}}{a_{CaCO_3}} \]

The activities of the solid components present at equilibrium are close to unity provided the pressure is moderate and both solids are present at equilibrium. Since the standard state for gases is the ideal gas state at 1 bar, the standard state fugacity is equal to unity and therefore, the activity of \( CO_2 \) in the equilibrium mixture is equal to its fugacity. But fugacity of a component is equal to its partial pressures at low temperature, then

\[ K = \frac{1}{p_{CO_2}} \]

This is the equilibrium partial pressure exerted by \( CO_2 \) and its value depends only on temperature. If the partial pressure is lowered below this equilibrium value, \( CaCO_3 \) will decompose and will eventually disappear.

When two or more reactions occur simultaneously, the number of moles of each component changes because of several reactions. Equations can be modified as

\[ d_{n_i} = \sum_j v_{i,j} \varepsilon_j \]

Here, \( v_{i,j} \) is the stoichiometric number of species \( I \) in the \( j \)th reaction and \( \varepsilon_j \) is the extent of this reaction. When the equation is modified to hold multiple reactions, the number of moles of \( I \) after the reaction is,

\[ n_i = n_{i_0} + \sum_j v_{i,j} \varepsilon_j \]

The total number of moles is obtained by summing the number of moles of individual species.

\[ n = \sum_i n_{i_0} + \sum_i \sum_j v_{i,j} \varepsilon_j = n_{i_0} + \sum_j \left( \sum_i v_{i,j} \right) \varepsilon_j \]

If

\[ \sum_i v_{i,j} = v_j \]

Then,

\[ n = n_{i_0} + \sum_j v_j \varepsilon_j \]

The mole fraction of component \( I \) in the mixture is

\[ y_i = \frac{n_i}{n} = \frac{n_{i_0} + \sum_j v_{i,j} \varepsilon_j}{n_{i_0} + \sum_j v_j \varepsilon_j} \]

7. A gas mixture containing 3 mol CO\(_2\), 5 mol H\(_2\) and 1 mol water is undergoing the following reactions

CO\(_2\)+3H\(_2\) → CH\(_3\)OH+H\(_2\)O

CO\(_2\)+3H\(_2\) → CO+H\(_2\)O

Develop expressions for the mole fraction of the species in terms of the extent of reaction. (MAY 2017)

The total moles initially present,

\[ n_0 = 3 + 5 + 1 = 9 \]

For the first reaction, For the second reaction,

\[ V_1 = -1 \cdot 3 + 1 + 1 = -2 \]
\[ V_2 = -1 \cdot 1 + 1 + 1 = 0 \]

The mole fractions are calculated using Equation

\[ y_1 = \frac{3 + (-1) \times \varepsilon_1 + (-1) \times \varepsilon_2}{9 + (-2) \times \varepsilon_1 + (0) \times \varepsilon_2} = \frac{3 - \varepsilon_1 - \varepsilon_2}{9 - 2 \varepsilon_1} \]
Similarly,

\[ y_{H_2} = \frac{5 - 3e_1 - e_2}{9 - 2e_1}, \quad y_{CH_4OH} = \frac{e_1}{9 - 2e_1} \]

\[ y_{H_2O} = \frac{1 + e_1 + e_2}{9 - 2e_1}, \quad y_{CO} = \frac{e_2}{9 - 2e_1} \]

8. n-Butane is isomerised to i-butane by the action of catalyst at moderate temperatures. It is found that the equilibrium is attained at the following composition.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Mol %, n-butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>317</td>
<td>31.00</td>
</tr>
<tr>
<td>391</td>
<td>43.00</td>
</tr>
</tbody>
</table>

Assuming that activities are equal to the mole fractions, calculate the standard free energy of the reaction at 317 K and average value of heat of reaction over this temperature range. (NOV 2016)

Since activities are equal to mole fractions

\[ K = \frac{y_{ib}}{y_{nb}} \]

where \(y_{ib}\) is the mole fraction of i-butane and \(y_{nb}\) of n-butane in equilibrium mixture. Therefore,

At 317 K, \( K = \frac{0.69}{0.31} = 2.2258 \)

At 391 K, \( K = \frac{0.57}{0.43} = 1.3255 \)

Also,

\[ \Delta G^0 = -RT \ln K \]

\[ \Delta G_{317}^0 = -8.314 \times 317 \ln 2.2258 = -2108.74 \text{ J/mol} \]

\[ \Delta G_{391}^0 = -8.314 \times 391 \ln 1.3255 = -916.03 \text{ J/mol} \]

Also,

\[ \ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R} \left( \frac{1}{T^2} - \frac{1}{T^1} \right) \]

\[ \ln \frac{2.2258}{1.3255} = -\frac{\Delta H^0}{8.314} \left( \frac{1}{317} - \frac{1}{391} \right) \]

Therefore,

\[ \Delta H^0 = -7218.02 \text{ J/mol} \]

9. Estimate the standard free energy change and equilibrium constant at 700 K for the reaction

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \rightarrow 2\text{NH}_3 (g) \]

Given that the standard heat of formation and standard free energy of formation of ammonia at 298 K to be -46,100 J/mol and -16,500 J/mol respectively. The specific heat (J/mol K) data are given below as function of temperature (K): (DEC 2016)
The standard heat of reaction and standard free energy of reaction at 298 K were estimated in Example
\[ \Delta H^0 = -92,200 \text{ J/mol}; \quad \Delta G^0 = -33,000 \text{ J/mol} \]
Also,
\[ \Delta \alpha = 2 \times 29.75 - 27.27 - 3 \times 27.01 = -48.8 \]
\[ \Delta \beta = (2 \times 25.11 - 49.3 - 3 \times 3.51) \times 10^{-3} = 34.76 \times 10^{-3} \]
\[ \Delta H = -7.9201 \times 10^4 \]
By equation,
\[ -33,000 = \Delta H' - \Delta \alpha T \ln \frac{T \Delta \beta}{2} - ART \]
\[ = 7.9201 \times 10^4 + 48.8 \times 298 \times \ln 298 - 17.38 \times 10^3 \times 298^2 - A \times 8.314 \times 298 \]
\[ -2105 - 2477.57A \]
Therefore, \( A = 14.169 \). Substitute \( \Delta H' \) and \( A \) into Equation, we get
\[ \ln K = \frac{79,201}{RT} + \frac{48.8}{R} \ln T + \frac{17.38 \times 10^3}{R} T + 14.169 \]
\[ \Delta G^0 = -79,201 + 48.8 \ln T - 17.38 \times 10^3 T^2 - 14.169RT \]
Putting \( T = 700 \text{ K} \) in the above equation, we get
\( K = 1 \times 10^{-4} \)
\[ \Delta G^0 = 53,607 \text{ J/mol} \]

10. In the synthesis of ammonia, stoichiometric amounts of nitrogen and hydrogen are sent to a reactor where the following reaction occurs

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

The equilibrium constant for the reaction at 675 K may be taken equal to \( 2 \times 10^{-4} \).

(a) Determine the per cent conversion of nitrogen to ammonia at 675 K and 20 bar.
(b) What would be the conversion at 675 K and 200 bar?

Basis: 1 mol nitrogen and 3 mol hydrogen are in the reactant mixture. Let \( \varepsilon \) be the extent of reaction. Then the number of moles of various species at equilibrium is calculated by
\[ n_i = n_{i0} = V_i \varepsilon \]
Thus the moles of nitrogen, hydrogen and ammonia are \( 1 - \varepsilon \), \( 3 - 3\varepsilon \) and \( 2\varepsilon \). Total moles at equilibrium is \( 4 - 2\varepsilon \). The moles fractions of nitrogen, hydrogen and ammonia are, respectively
\[
\frac{1 - \varepsilon}{4 - 2\varepsilon'} \quad \frac{3(1 - \varepsilon)}{4 - 2\varepsilon'} \quad \frac{2\varepsilon}{4 - 2\varepsilon}
\]

The sum of stoichiometric numbers, \( v = 2 - 1 - 3 = -2 \). Equation gives

\[
K_y = \frac{K}{K_y} P^v = K P^2
\]

In arriving at this result ideal behaviour is assumed, so that \( K_y = 1 \)

Thus we have the necessary relation connecting the equilibrium composition and pressure.

\[
\frac{\left[\frac{2\varepsilon}{(4 - 2\varepsilon)}\right]^2}{\left[\frac{(1 - \varepsilon)}{(4 - 2\varepsilon)}\right] \left[\frac{3(1 - \varepsilon)}{(4 - 2\varepsilon)}\right]^3} = 2 \times 10^{-4} P^2
\]

\[
\frac{4\varepsilon^2 (4 - 2\varepsilon)^2}{27 (1 - \varepsilon)^4} = 2 \times 10^{-4} P^2
\]

\[
\frac{\varepsilon (4 - 2\varepsilon)}{(1 - \varepsilon)^2} = 3.6742 \times 10^{-2} P
\]

When \( P = 20 \) bar

\[
\frac{\varepsilon (4 - 2\varepsilon)}{(1 - \varepsilon)^2} = 0.73485
\]

\[
2.73485\varepsilon^2 - 5.4697\varepsilon + 0.73485 = 0
\]

Solving this, \( \varepsilon = 0.1448 \). Fractional conversion of nitrogen,

\[
\varepsilon = 0.1448
\]

That is, conversion of nitrogen = 14.48%.

When \( P = 200 \) bar

\[
\frac{\varepsilon (4 - 2\varepsilon)}{(1 - \varepsilon)^2} = 7.3485
\]

\[
9.3485\varepsilon^2 - 18.697\varepsilon + 7.3485 = 0
\]

Therefore, \( \varepsilon = 0.5375 \). So, conversion of nitrogen = 53.75%.
UNIT – 5 – REFRIGERATION AND LIQUEFACTION

PART A

A heat engine is a energy conversion devise, which converts heat energy into work. A heat pump is a thermodynamic system operating in a cycle that removes heat from a low temperature body and delivers it to a high temperature body. External work is required to accomplish this.

2. What do you mean by capacity of a refrigerator? (May/June 2013, Nov/Dec 2012)
The refrigerator capacity determines the rate of circulation of the refrigerant, which in turn, decides the design and size of the various units such as condenser, compressor, evaporator, and the expansion devices. The capacity is sometimes measured in ton of refrigeration. One ton is defined as the heat of absorption at the rate of 12000 BTU per hour. This rate corresponds to the rate of heat removal that is required to freeze 1 ton of water in a day originally at 273 K. One ton of refrigeration rate of 12600 KJ/h in SI units.

3. Why the efficiency of actual refrigeration cycles is less than Carnot’s cycle? (May/June 2013)
The COP of real refrigeration cycles is always less than the carnot efficiency. It is usually about 0.6 times the Carnot efficiency for a simple refrigeration cycle, but can be as high as 0.9 times the carnot efficiency if complex cycles are used. If the temperature range is too large then it may be more economical to use a cascaded refrigeration system, in which a low- temperature cycle rejects heat to a higher temperature cycle that rejects heat to cooling water or ambient air.

4. What is joule-Thomson effect? (May/June 2012)
When a compressed gas below its temperature of inversion is expanded through a fine orifice or nozzle, it gets cooled. This phenomenon is known as joule-Thomson effect.

5. Why is throttling used in practical refrigerators in place of turbine? (May/June 2012)

![Diagram of refrigeration cycle]

Domestic compressor refrigerators usually operate on a rankine cycle. The actual device—whose schematic diagram is shown in figure operates almost in an identical cycle to the rankine engine, except for its reverse direction. The most striking difference is the throttling valve between states E and D in place of the turbine. (The throttling valve may be small orifice on a plate, a porous ceramic filter, or a capillary within the tube. The gas expands across the throttle and its pressure drops.) The reason for this change is clear from the T-S diagram; the liquid expanding from state D partly evaporates. This would lead to the technical problems mentioned above in the operation of the turbine, and the liquid part of the mixture would produce much less work while expanding than the vapour. In this case, it is
not worth recycling; it will take the form of losses. Another difference is that, having reversed the direction of the engine cycle, it is not the liquid to be pumped but the vapor to be compressed.

6. What are the limitations of refrigeration system operating in a Carnot cycle? (Nov/Dec 2012)
A refrigeration machine operating on the Carnot cycle cannot be achieved in practice. Carnot cycle demands reversible operation, and it is difficult to eliminate all irreversibility in an actual operation. Isothermal heat interactions at the heat absorption and the heat rejection stages, which proceed at very slow rates necessities large heat transfer areas. A temperature difference between the refrigerant and the reservoirs in the heat absorption and heat injection stages is necessary, in order to have a finite rate of heat transfer. If the heat absorption is achieved by the evaporation of a refrigerant then the possibility of input stream to the compressor containing liquid cannot be overruled. This may lead to severe corrosion problems in the compressor. Apart from these, the work output of an expansion engine or a turbine used for reversible expansion is normally very small whereas their costs are prohibitively high.

7. Explain one ton of refrigeration (Dec 2009)(Nov 2015)
One ton of refrigeration is defined as the heat absorption at the rate of 12000BTU per hour. This rate corresponds to the rate of heat removal that is required to freeze one ton of water in a day originally at 273 K. One ton of refrigeration is equal to a refrigeration rate of 12660 KJ/hr in SI units.

COP, the Coefficient of Performance is the ratio of desired effect to the work input. Refrigeration capacity determines the rate of circulation of the refrigerant and is measured in ton of refrigeration.

\[
COP = \frac{Q_c}{W}
\]

9. Explain the principle of Refrigeration
Refrigeration is the continuous absorption of heat at a low temperature level, usually accomplished by evaporation of a liquid in a steady state flow process. The vapor formed is returned to its original state by either compression and condensing or absorbing by a liquid of low volatility, from which it is subsequently evaporated at higher pressure.

10. What are the requirements for a good refrigerant?
Toxicity, Flammability, cost, corrosion properties and vapor pressure in relation to temperature are of greater importance in the choice of refrigerant.

11. Name few refrigerants and their relative advantages.
Halogenated hydrocarbons like Freon – 12, Genetron, Mafron are non toxic, non flammable and non explosive refrigerants. Less halogenated hydrocarbon are preferred but refrigerants like Ammonia, Carbon dioxide are eco friendly.
12. **Name different components of an air-refrigeration cycle.**
Refrigerator, Compressor, Water cooler and expansion engine are different components of an air refrigeration cycle.

13. **Define compressor efficiency**
Compressor efficiency is defined as the ratio of isentropic work to the actual work required for compression.

14. **Why is throttling used in practical refrigerators in place of turbine?**
Flow through a partly closed valve is known as throttling process, this results in the partial vaporization of the liquid accompanied with reduction in pressure.

15. **What is a vapor-compression refrigeration cycle?**
In vapor compression cycle, the vapor formed due to the absorption of heat in the refrigerated area, is compressed using a compressor followed by condensing and returning it to its original state.

16. **What is meant by absorption refrigeration?**
An absorption refrigeration unit uses the heat absorbed from a high temperature source directly for achieving the necessary refrigeration.

17. **What are the various Liquefaction processes?**
   1). Linde process.
   2). Claude Process.

18. **Name various methods with which liquefaction can be accomplished.**
   1). Vaporization of liquid.
   2). Joule Thomson expansion.
   3). Expansion of gas in an engine delivering external work.

19. **Define Joule-Thomson expansion**
Joule Thomson expansion is a steady state flow process across a restriction

20. **Explain Linde liquefaction process**
The Linde process for gas liquefaction works on the joule Thomson expansion, and gases with positive joule Thomson co efficient are liquefied using Linde’s Process.

21. **Explain Claude liquefaction process**
The Claude process for gas liquefaction utilizes isentropic expansion of a compressed gas in which an expansion turbine is used in place of a throttle valve.

22. **Define Cycle efficiency**
Cycle efficiency is the ratio of reversible work for the process to that of theoretical

23. **Define Practical efficiency**
Practical efficiency is the ratio of theoretical work for an ideal operation to that of the actual work for the cycle.
24. **What is an Air standard diesel dual cycle?**
In diesel engines the temperature at the end of compression, exceeds the final ignition temperature and the combustion of fuel occur spontaneously.

25. **What are Otto and Diesel cycles?**
Otto and Diesel cycles are the two important air standard cycles used for the analysis of internal combustion engines.

26. **What is the advantage of Claude liquefaction process over Linde Liquefaction process?**
Claude process in more efficient in the sense some amount of work is derived from the cooling vapors, by replacing the throttle valve by an expander.

27. **What are the factors that are to be considered for selecting a refrigerant?**
Toxicity, Flammability, cost, corrosion properties and vapor pressure in relation to temperature are of greater importance in the choice of refrigerant.

28. **What are the methods to accomplish cooling?**
Cooling of Vapors and there by liquefaction can be obtained (i) by heat exchange at constant pressure. (ii). by an expansion process for which work is obtained (iii) by a throttling process.
PART B

1. Discuss the desirable properties of refrigerant in detail. (May /June 2014)

   - Boiling temperature: it is necessary that the operating pressure be maintained above atmospheric to avoid air and moisture leaks into the system. The normal boiling point of the refrigerant should, therefore, be lower than the desired temperature levels in the refrigerator.
   - Freezing point: the freezing point of the refrigerant should be well below the minimum temperature at which the system is opened.
   - Critical temperature and pressure: the critical temperature and pressure of the refrigerant should be above the operating system temperature and pressure. If the operating temperature is above the critical temperature, it is impossible to condense the gas by compressing it to high.
   - Condenser and evaporator pressures: the condenser pressure should not be very high. If pressure is very high, the cost of equipment and the cost of operation would be excessive. If the evaporator pressure is excessively low, the compression ratio would be abnormally high. If the refrigerant has sub atmospheric vapor pressures at the temperature in the refrigerator coil, the possibility of contamination by leaks cannot be overruled.
   - Specific volume: specific volume of the vapor determines the size of the compressor. Low suction volumes are desirable for reciprocating compressors and high suction volumes for centrifugal compressors.
   - Latent heat: a high latent heat of vaporization of the refrigerant is desired, because it results in high refrigerant effect per unit weight of the refrigerant and low rate of circulation of the refrigerant.
   - Specific heat of liquid: If the specific heat of the refrigerant liquid is unduly high, large quantity of heat would have to be removed to cool the hot liquid entering the evaporator to bring its temperature down to the saturation valve. Therefore, low specific heat of the liquid refrigerant is preferred.
   - Molecular weight: molecular weight of the refrigerant affects the compressor size because the specific volume of the vapor is directly related to it. A high molecular weight refrigerant gives high specific volumes for the vapor, which is preferred for centrifugal compressors, whereas for reciprocating compressors a low molecular weight for the refrigerant is advantageous.
   - Safety aspects: refrigerants are grouped according to toxicity and flammability. Halogenated hydrocarbons are relatively nonflammable, nontoxic and nonexplosive. These belong to group 1. Group 2 refrigerants are either toxic or flammable. Examples are methyl chloride and sulphur dioxide.
   - Other desirable properties: normally, a refrigerant would be in use for a very long period. Consequently, the chemical stability of the refrigerant is another important criterion in the choice of a proper refrigerant. They should also be non-corrosive, should have low viscosity and high thermal conductivity,
2. Explain the Air-refrigeration cycle in detail with a neat flow diagram. (May 2012) (Nov 2013)

- Working fluid – air
- Air does not undergo any phase change
- Air is compressed adiabatically to pressure \( P_1 \) and temperature \( T_1 \) in the compressor (AB)
- It is then cooled at constant pressure in the cooler (BC)

![Diagram of Air Cycle](image)

- Air is then expanded in the turbine to pressure \( P_2 \), which is equal to the pressure at compressor intake (CD)
- The air leaving the turbine is passed through a refrigerator, where it absorbs heat at constant pressure \( P_2 \)(DA)
- The gas leaving the refrigerator enters the compressor and the cycle is repeated.

Let the rate of air circulation be \( \dot{m} \). Assume that the heat capacity of air remains constant during the cycle. Then, heat absorbed is

\[
Q_2 = \dot{m} C_p (T_A - T_D)
\]

and the heat rejected is

\[
Q_1 = \dot{m} C_p (T_B - T_C)
\]

The net work required is

\[
W = Q_1 - Q_2 = \dot{m} C_p [(T_B - T_C) - (T_A - T_D)]
\]

The coefficient of performance of an air-refrigeration machine is

\[
COP = \frac{Q_2}{W} = \frac{T_A - T_D}{(T_B - T_C) - (T_A - T_D)}
\]
For an adiabatic process

\[
\frac{T_B}{T_A} = \left(\frac{P_1}{P_2}\right)^{(\gamma-1)\gamma} = \frac{T_C}{T_D}
\]

\[
T_B - T_C = (T_A - T_D) \left(\frac{P_1}{P_2}\right)^{(\gamma-1)\gamma}
\]

Substituting in the COP equation, we get

\[
\text{COP} = \frac{1}{\left(\frac{P_1}{P_2}\right)^{(\gamma-1)\gamma} - 1} = \frac{T_A}{T_B - T_A}
\]

- **Advantage** – air is available at no cost
- **Disadvantages:**
  i. Low efficiencies
  ii. Large heat transfer surfaces required
  iii. Large quantity of air is to be handled

3. **Explain with neat sketch of Vapor - Compression refrigeration process.** (May 2011) (Nov 2013,2016)

During this cycle, the fluid is evaporated in the refrigerator for absorbing heat at a constant temperature. The vapors are then compressed to a higher pressure. These vapors at a higher pressure are taken to a condenser whereby condensation the heat is rejected at some higher constant temperature. The cycle is completed by bringing the fluid to its original state through an expansion step. The compression and expansion process are made reversible as much as possible by taking care to eliminate irreversibility.

(a) The expansion step is carried in two ways. By using an expansion engine shown in Figure which operates more or less reversibly. When drawn on a T – S diagram (Figure) the cycle resembles a Carnot cycle with a little difference of cooling of superheated vapor to saturation temperature before the commencement of condensation step.

![Diagram of Vapor Compression Refrigeration Process](image-url)
(b) The expansion may also be carried out by using an expansion valve which makes the expansion step of cycle isenthalpic and consequently an irreversible process. The expansion valve is used, being less expensive as compared to expansion engines, in household refrigerators and air conditioners.

**Performance parameters**

i. **Coefficient of Performance**

\[
\text{COP} = \frac{Q_2}{W} = \frac{H_A - H_D}{H_B - H_A}
\]

ii. **Carnot’s Coefficient of Performance**

\[
\beta_{\text{max}} = \frac{T_C}{T_H - T_C}
\]

This equation represents the maximum theoretical coefficient of performance of any refrigeration cycle operating between cold and hot regions at \( T_C \) and \( T_H \), respectively.

**Features of Actual Vapor-Compression Cycle**

- Heat transfers between refrigerant and cold and warm regions are not reversible.
  - Refrigerant temperature in evaporator is less than \( T_C \).
  - Refrigerant temperature in condenser is greater than \( T_H \).
  - Irreversible heat transfers have negative effect on performance.

- The COP decreases – primarily due to increasing compressor work input – as the temperature of the refrigerant passing through the evaporator is reduced relative to the temperature of the cold region, \( T_C \).
- temperature of the refrigerant passing through the condenser is increased relative to the temperature of the warm region, $T_H$.

Irreversibility during the compression process are suggested by dashed line from state 1 to 2.
- An increase in specific entropy accompanies an adiabatic irreversible compression process. The work input for compression process 1-2 is greater than for the counterpart isentropic compression process 1-2s.
- Since process 4-1, and thus the refrigeration capacity, is the same for cycles 1-2-3-4-1 and 1-2s-3-4-1, cycle 1-2-3-4-1 has the lower COP.

**Isentropic Compressor Efficiency**

- The isentropic compressor efficiency is the ratio of the minimum theoretical work input to the actual work input, each per unit of mass flowing:

$$\eta_c = \frac{(-W_{cv}/m)_s}{(-W_{cv}/m)} = \frac{h_{2s} - h_1}{\bar{h}_2 - h_1}$$


Another form of refrigeration that becomes economically attractive when there is a source of inexpensive heat energy at a temperature of 100 to 200°C is absorption refrigeration, where the refrigerant is absorbed by a transport medium and compressed in liquid form. The most widely used absorption refrigeration system is the ammonia-water system, where ammonia serves as the refrigerant and water as the transport medium. The work input to the pump is usually very small, and the COP of absorption refrigeration systems is defined as

$$COP_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Cooling effect}}{\text{Work input}} = \frac{Q_L}{Q_{gen} + W_{pump,in}} \approx \frac{Q_L}{Q_{gen}}$$

- Absorption refrigeration systems (ARS) involve the absorption of a refrigerant by a transport medium.
• The most widely used system is the ammonia–water system, where ammonia (NH₃) serves as the refrigerant and water (H₂O) as the transport medium.
• Other systems include water–lithium bromide and water–lithium chloride systems, where water serves as the refrigerant. These systems are limited to applications such as A-C where the minimum temperature is above the freezing point of water.
• Compared with vapor-compression systems, ARS have one major advantage: A liquid is compressed instead of a vapor and as a result the work input is very small (on the order of one percent of the heat supplied to the generator) and often neglected in the cycle analysis.
• ARS are often classified as heat-driven systems.
• ARS are much more expensive than the vapor-compression refrigeration systems. They are more complex and occupy more space, they are much less efficient thus requiring much larger cooling towers to reject the waste heat, and they are more difficult to service since they are less common.
• Therefore, ARS should be considered only when the unit cost of thermal energy is low and is projected to remain low relative to electricity.
• ARS are primarily used in large commercial and industrial installations.

For a refrigeration rate of \( Q_2 \) kJ/h, the minimum work required when the refrigerator and the condenser are at temperatures \( T_2 \) and \( T_1 \) respectively is given by

\[
W = Q_2 \frac{T_1 - T_2}{T_2}
\]
In order to deliver a work equal to $W$, a heat engine operating between a high-temperature source at $T_3$ and the surroundings at $T_1$ should absorb a quantity of heat $Q_3$, where

$$Q_3 = W \frac{T_3}{T_3 - T_1}$$

Substituting we get,

$$Q_3 = Q_2 \frac{T_1 - T_2}{T_2} \frac{T_3}{T_3 - T_1}$$

$$\frac{Q_2}{Q_3} = \frac{T_3 - T_1}{T_3} \frac{T_2}{T_1 - T_2}$$

The above ratio is the refrigeration obtainer per unit quantity of high temperature heat. It is the efficiency if the cycle.

5) With necessary diagram explain the Claude liquefaction system. (MAY 2010, Nov 2012)
   - It is expansion of gas in an engine which delivers external work
   - Utilizes isentropic expansion of compressed gas
An energy balance around the heat exchanger, turbine, and the separator gives
\[ xH_C = (1-x)H_A + xH_F + W_S \]
where
\[ WS \]
is the work delivered by the turbine. If the turbine operates adiabatically, the shaft work \( W_S \) is equal to the decrease in enthalpy of the gas during expansion.
\[ W_S = H_D - H_E \]

The thermodynamic efficiency of the process is defined as the ratio of the minimum reversible work for the given process to the actual work. This can be evaluated as the product of two other efficiencies, viz., the cycle efficiency and practical efficiency.

\[
\text{Cycle efficiency} = \frac{\text{Reversible work for the process}}{\text{Theoretical work for ideal operation}}
\]
\[
\text{Practical efficiency} = \frac{\text{Theoretical work for ideal operation}}{\text{Actual work for the cycle}}
\]

6) Give a comparative study between vapor compression and vapor absorption system.
(MAY 2010, Nov 2012)

<table>
<thead>
<tr>
<th>S.no</th>
<th>Aspect</th>
<th>Vapor Absorption System</th>
<th>Vapor Compression System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Quality of the Energy Input</td>
<td>Low grade energy sources are more than capable of running a vapor absorption system. These sources can be waste heat from furnaces, exhaust steam etc. Solar power can also be used for running it.</td>
<td>Vapor compression system needs high grade energy. It needs electrical or mechanical energy for operating compressor which is an essential part of VC refrigeration system.</td>
</tr>
<tr>
<td>2</td>
<td>Moving part in the system</td>
<td>The only moving part of Vapor absorption refrigeration system is</td>
<td>In Vapor compression the moving part is the compressor which</td>
</tr>
</tbody>
</table>
the pump. operated by electric motor or engine

<table>
<thead>
<tr>
<th></th>
<th>Effect of Evaporator pressure</th>
<th>Very little effect is seen in the refrigeration capacity with the lowering evaporator pressure.</th>
<th>The refrigerating effect or refrigeration capacity decreases with the lowering evaporator pressure.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Workability at Load varying load</td>
<td>Load Variation does not have any effect on the performance of the vapor absorption system</td>
<td>Vapor compression system does not work well at partial load. The performance is very poor.</td>
</tr>
<tr>
<td></td>
<td>Evaporator exit</td>
<td>In vapor absorption system, if the liquid refrigerant leaves the evaporator, the refrigerating effect is reduced but the system functions well without any problem.</td>
<td>Liquid refrigerant entering compressor is not desirable in Vapor compression system. It could damage the compressor. So the refrigerant is superheated before leaving the evaporator.</td>
</tr>
<tr>
<td></td>
<td>Lowest temperature</td>
<td>When water is used as refrigeration the temperature attained is above 0 degree Celsius</td>
<td>-150 degree Celsius or even lower can be achieved with the cascading system.</td>
</tr>
<tr>
<td></td>
<td>Coefficient of Performance</td>
<td>The COP of absorption refrigeration system is poor.</td>
<td>The COP of Vapor compression system is very good.</td>
</tr>
<tr>
<td></td>
<td>Capacity</td>
<td>Capacity above 1000 TR is easily achievable.</td>
<td>It is difficult to capacity above 1000 TR with single compression system.</td>
</tr>
<tr>
<td></td>
<td>Refrigerant</td>
<td>Ammonia or water can be used as refrigerant with a proper absorber.</td>
<td>Hydrocarbons, Chlorofluorocarbons and Hydrochlorofluorocarbons are used as refrigerations.</td>
</tr>
</tbody>
</table>

7) **Write about Carnot cycle with T-S diagram and discuss its limitation. (May 2011)**

**Carnot cycle.** The carnot cycle is an ideal cycle consisting of two isothermal processes during which Q₂ is absorbed at the lower temperature T₂ and the heat Q₁ is rejected at higher temperature T₁ and two adiabatics, the result of which is the addition of the network W to the system. The carnot cycle (on T-S) is shown in Figure **Fig. Carnot cycle.**
• Idealized thermodynamic cycle consisting of four reversible processes (any substance):
  - Reversible isothermal expansion (1-2, $T_H=$constant)
  - Reversible adiabatic expansion (2-3, $Q=0$, $T_H \rightarrow T_L$)
  - Reversible isothermal compression (3-4, $T_L=$constant)
  - Reversible adiabatic compression (4-1, $Q=0$, $T_L \rightarrow T_H$)

• Work done by gas = $\int PdV$, area under the process curve 1-2-3.

**The Carnot Principles**

- The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs. $\eta_{irrev} < \eta_{rev}$
- The efficiencies of all reversible heat engines operating between the same two reservoirs are the same. $(\eta_{rev})_A = (\eta_{rev})_B$
- Both can be demonstrated using the second law (K-P statement and C-statement). Therefore, the Carnot heat engine defines the maximum efficiency any practical heat engine can reach up to.
- Thermal efficiency $\eta_{th}=\frac{W_{net}}{Q_H}=1-(\frac{Q_L}{Q_H})=f(T_L,T_H)$ and it can be shown that $\eta_{th}=1-(\frac{Q_L}{Q_H})=1-(T_L/T_H)$. This is called the Carnot efficiency.
- For a typical steam power plant operating between $T_H=800$ K (boiler) and $T_L=300$ K(cooling tower), the maximum achievable efficiency is 62.5%.
8) A vapor compression refrigeration system with ammonia as the working fluid is to operate between 266 K and 300 K. Determine the following.
(i) COP given that the enthalpy of saturated vapor at 266 K = 656 KJ/Kg and the enthalpy of superheated vapor leaving the compressor is 724 KJ/Kg, enthalpy of saturated liquid at 300 K is 144 KJ/Kg.
(ii) COP if a temperature approach of 5 K is necessary in the evaporator and condenser, and the efficiency of the compressor is 75%. Enthalpy of saturated vapor entering the condenser is 758 KJ/Kg, enthalpy saturated liquid at 305 K is 159 KJ/Kg.
(iii) The COP of an ideal Carnot refrigerator. (MAY 2011, MAY 2017)

(a) \( H_A = 656, \ H_B = 724, \) and \( H_C = H_D = 144. \)

\[
\text{COP} = \frac{H_A - H_D}{H_B - H_A} = \frac{656 - 144}{724 - 656} = 7.53
\]

(b) \( H_A = 652, \ H_B = 758, \) and \( H_C = H_D = 159, \) then

\[
\text{COP} = \frac{H_A - H_D}{H_B - H_A} \times \eta = \frac{652 - 159}{(758 - 652) \times 1/0.75} = 3.49
\]

(c) For Carnot cycle, COP is given by

\[
\text{COP} = \frac{T_2}{T_1 - T_2} = \frac{266}{300 - 266} = 7.8
\]

9) An air-refrigeration machine rated at 10ton is used to maintain the temperature of a cold room at 261K, when the cooling water is available at 293K. The machine operates between pressures of 1.013bar and 4.052bar. Assume a 5-K approach in the cooler and refrigerator. If the specific heat of air may be taken as 1.008 KJ / Kg K and \( \gamma = 1.4, \) calculate the COP and air circulation rate. (JUNE 2013)

The temperature of the air leaving the refrigerator is

\[
T_A (= T_2) = 261 - 5 = 256 \ K
\]

The temperature of the air leaving the cooler is

\[
T_C (= T_1) = 293 + 5 = 298 \ K
\]

\[
T_B = T_A \left( \frac{P_1}{P_2} \right)^{(\gamma - 1)/\gamma} = 256(4)^{0.4/1.4} = 380.4 \ K
\]

Similarly, \( T_D = 200.5 \ K \)

\[
\text{COP} = \frac{T_A}{T_B - T_A}
\]
COP = \frac{256}{(380.4 - 256)} = 2.06

Considering energy balance in the refrigerator, we get

\dot{m}C_{p}(T_{A} - T_{D}) = 10 \times 12660

\dot{m} = \frac{10 \times 12660}{1.008 \times (256 - 200.5)} = 2263 \text{ kg/h}