

Phase Equilibrium

Phase:

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state. Number of phases is denoted by p .

A substance can have solid, liquid and gas phases. A gas or a gaseous mixture, mixture of two completely miscible liquids forms a single phase. A crystal forms a single phase; however, there can be different types of solid phases such as white phosphorus and black phosphorus. A pure liquid in equilibrium with its vapour forms two phases ($p = 2$). A solution of two substances forms a single phase, but a dispersion does not.

Constituent (c):

A constituent of a system is a chemical species (an ion or a molecule) present in the system e.g., a mixture of water and ethanol has two constituents ($c = 2$).

Component (C):

A component is a chemically independent constituent of a system. The number of component (C) in a system is the minimum number of independent species necessary to define the composition of the system. e.g.,

(a) The system containing PCl_5 , PCl_3 and Cl_2 is a two-component system though there are three constituents. Out of the three constituents, only two are components, because the chemical equilibrium is established:

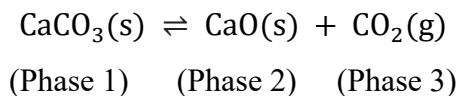


One can alter the number of moles of any two of these chemical individuals arbitrarily; the alternation of the number of moles of the third species is then fixed by the equilibrium constant:

$$K_x = \frac{x_{\text{PCl}_3} x_{\text{Cl}_2}}{x_{\text{PCl}_5}}$$

Consequently, any two of these species are chemically independent, the third is not.

(b) A system where the following equilibrium occurs:



To specify the composition of the gas phase, we need the species CO_2 and to specify the composition of the phase 2 we need the species CaO . However, we do not need an additional

species to specify phase 1 because the alternation in the number of moles of CaCO_3 is fixed by the equilibrium condition:

$$K_x = \frac{x_{\text{CaO}}x_{\text{CO}_2}}{x_{\text{CaCO}_3}}$$

Hence, the system has two components.

Degrees of freedom or variance (F):

The degrees of freedom or variance of a system is defined as the number of independent intensive variables required to define the equilibrium state of a system.

Gibbs Phase Rule

Let us consider a multiphase system at temperature T and pressure P . Let there be p no. of phases, namely $\alpha, \beta, \gamma, \delta$, etc. Let the number of constituents in each phase be c , namely $1, 2, 3, \dots, j, \dots$ and every constituent is present in every phase.

We can specify the composition of a phase by giving the mole fractions of $c - 1$ constituents because $x_1 + x_2 + x_3 + \dots + x_c = 1$ and all mole fractions are known if all except one are specified.

Because there are p phases, the total number of composition variables is $p(c - 1)$. Adding T and P , we have total number of intensive variables:

$$p(c - 1) + 2$$

At equilibrium, the chemical potential of a constituent j must be same in every phase:

$$\mu_{j,\alpha} = \mu_{j,\beta} = \dots$$

for p phases $\alpha, \beta, \gamma, \delta$, etc.

That is, there are $p - 1$ equations to be satisfied for each j . As there are c constituents, the total number of equations is $c(p - 1)$. These $(p - 1)$ equations provide $(p - 1)$ simultaneous relations between T, P and mole fractions as each chemical potential $\mu_{j,\alpha}$ is defined as

$$\mu_{j,\alpha} = \mu_j^\alpha(T, P, x_j^\alpha, \dots, x_c^\alpha)$$

Each of these $c(p - 1)$ equations make one variable dependent. Hence, we have to eliminate $c(p - 1)$ variables. Therefore, the number of independent intensive variables is

$$\begin{aligned} F &= p(c - 1) + 2 - c(p - 1) \\ &= pc - p + 2 - pc + c \\ &= c - p + 2 \end{aligned}$$

$$\boxed{F = c - p + 2}$$

As we have not considered any reaction equilibria, no. of constituent (c) is equal to number of components (C). Thus,

$$\boxed{F = C - p + 2}$$

This is the Gibbs phase rule for a *non-reactive system*.

Phase rule for systems with reactions (reactive system)

Each independent chemical reaction occurring in a system provides one relation between the chemical potentials of each reacting species:

$$\sum_j v_j \mu_j = 0$$

Where v_j 's are the stoichiometric coefficients of the reacting species. Each such relation between μ_j 's can be used to eliminate one variable from T, P and mole fractions. If the number of chemical reactions is r then

$$F = c - p + 2 - r$$

If, besides the ' r ' reaction-equilibrium conditions, there are ' a ' additional restrictions on the molefractions arising from stoichiometry and electroneutrality, then

$$F = c - p + 2 - r - a$$

Since we define the number of independent constituents as number of components, we write

$$\boxed{C = c - r - a}$$

and

$$\boxed{F = C - p + 2}$$

Worked out examples

1. Find the number of degrees of freedom for a system consisting of solid sucrose in equilibrium with an aqueous solution of sucrose.

Solution:

Number of constituents, $c = 2$ (water, sucrose)

Number of phases, $p = 2$ (solution, solid sucrose)

Hence,

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

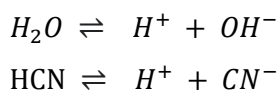
Therefore, Once T, P are specified, the equilibrium mole fraction of sucrose in the saturated solution is fixed.

2. Find F for a system consisting of a liquid solution of methanol and ethanol in equilibrium with a vapour mixture of methanol and ethanol. Give a reasonable choice for the independent intensive variables.
3. For an aqueous solution of the weak acid HCN find the number of components and degrees of freedom.

Solution: The system has five constituents, namely $H_2O, H^+, OH^-, CN^-, HCN$.

Therefore, $c = 5$

The two independent reactions are:



Therefore, $r = 2$

Another additional relation is the electroneutrality condition

$$n_{H^+} = n_{CN^-} + n_{OH^-}$$

So, $a = 1$

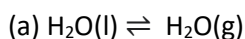
Therefore, $C = c - r - a = 5 - 2 - 1 = 2$

and $p = 1$

Therefore, $F = C - p + 2 = 2 - 1 + 2 = 3$

Choice of variables are T, P and x_{HCN} . The two components are obviously H_2O and HCN.

4. Determine the no. of degrees of freedom in each of the following systems. Suggest the variables that could correspond to these degrees of freedom:



(b) liquid water and water vapour in equilibrium at a pressure of 1 atm.

(c) an aqueous solution of glucose.

Solution

(a) Here,

$$c = 1 \text{ (H}_2\text{O)}$$

$$P = 2$$

$$\text{Therefore, } F = C - p + 2 = 1 - 2 + 2 = 1$$

Only one variable T or P need to be specified.

(b) Since P is held constant, F reduces by one.

$$\text{Therefore, } F = C - p + 1$$

$$\text{Here, } C = 1$$

$$p = 2$$

$$\text{Therefore, } F = 1 - 2 + 1 = 0$$

The system is non-variant.

(c) Here,

$$c = 2 \text{ (H}_2\text{O, C}_6\text{H}_{12}\text{O}_6\text{)}$$

$$P = 1$$

$$\text{Therefore, } F = C - p + 2 = 2 - 1 + 2 = 3$$

Choice of variables are T, P and $x_{\text{C}_6\text{H}_{12}\text{O}_6}$.

5. Give the number of components in the following systems:

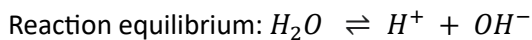
(a) water, allowing for its ionization,

(b) aqueous acetic acid.

Solution:

(a) The constituents: $\text{H}_2\text{O}, \text{H}^+$ and OH^- .

$$\text{Therefore, } c = 3$$



$$\therefore r = 1$$

$$\text{Electroneutrality: } n_{\text{H}^+} = n_{\text{OH}^-}$$

$$\therefore a = 1$$

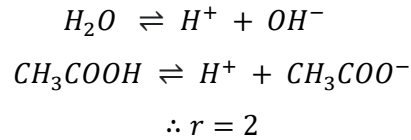
Therefore, no. of components,

$$\begin{aligned} C &= c - r - a \\ &= 3 - 1 - 1 = 1 \end{aligned}$$

(b) Constituents: H_2O , H^+ , OH^- , CH_3COO^- , CH_3COOH .

Therefore, $c = 5$

Reactions equilibria:



Electroneutrality:

$$\begin{aligned} n_{\text{H}^+} &= n_{\text{OH}^-} + n_{\text{CH}_3\text{COO}^-} \\ \therefore a &= 1 \end{aligned}$$

Therefore, No. of components,

$$\begin{aligned} C &= c - r - a \\ &= 5 - 2 - 1 = 2 \end{aligned}$$

6. Find F in a system consisting of $\text{CaCO}_3(\text{s})$, $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$, where all the CaO and CO_2 come from the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Solution: Here, $p = 3$ ($\text{CaCO}_3(\text{s})$, $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$)

Constituents, $c = 3$ (CaCO_3 , CaO , CO_2)

No. of reaction equilibrium, $r = 1$

Therefore,

$$C = c - r - a = 3 - 1 - 0 = 2$$

Therefore,

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

7. State the number of components in the following systems:

(a) NaH_2PO_4 in water at equilibrium with water vapour but disregarding the fact that the salt is ionized.

(b) The same, but taking into account the ionization of the salt.

(c) AlCl_3 in water, noting that hydrolysis and precipitation of $\text{Al}(\text{OH})_3$ occur.

Solution:

(a) No. of components, $C = 2$ (NaH_2PO_4 , H_2O)

(b) Constituents present: Na^+ , H_2PO_4^- , H_2O .

Therefore, $c = 3$

Electroneutrality,

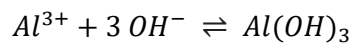
$$n_{\text{Na}^+} = n_{\text{H}_2\text{PO}_4^-}$$

Therefore, No. of components,

$$C = 3 - 1 = 2$$

(c) Constituents present: Al^{3+} , Cl^- , $\text{Al}(\text{OH})_3$, H^+ , H_2O , OH^-

Reaction equilibrium:



electroneutrality:

$$n_{\text{H}^+} + n_{\text{Al}^{3+}} = 3n_{\text{Cl}^-} + n_{\text{OH}^-}$$

Here, $c = 6$; $r = 2$; $a = 1$

Therefore, No. of components,

$$\begin{aligned} C &= c - r - a \\ &= 6 - 2 - 1 = 3 \end{aligned}$$

8. Blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals release their water of hydration when heated. How many phases and components are present in an otherwise empty heated container?

Solution: The constituents (or components): CuSO_4 , H_2O

$$C = 2$$

No of phases, $p = 2$ ($\text{CuSO}_4(\text{s})$ & $\text{H}_2\text{O}(\text{g})$)

9. Ammonium carbonate decomposes when it is heated.

(a) How many components and phases are present when the salt is heated in an otherwise empty container?

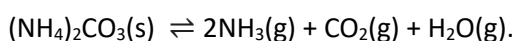
(b) Now suppose that additional ammonia is also present. How many components and phases are present?

Solution:

(a) Constituents present: $(\text{NH}_4)_2\text{CO}_3$, CO_2 , NH_3 , H_2O

$$c = 4$$

Reaction equilibrium:



Therefore, $r = 1$

Stoichiometric relation:

$$p_{NH_3} = 2p_{CO_2}$$

Therefore, $a = 2$

Therefore, No of Component

$$C = c - r - a = 4 - 1 - 2 = 1$$

No of phases, $p = 2$ [(NH₄)₂CO₃(s) and NH₃, CO₂, H₂O(g)]

(b) When additional NH₃ is also present, the relation $p_{NH_3} = 2p_{CO_2}$ will not exist anymore,

Therefore,

$$C = c - r - a = 4 - 1 - 1 = 2$$

10. An aqueous solution of Na₂SO₄ is present at equilibrium with its vapour phase in a closed vessel.

(a) How many phases and components are present?

(b) What is the variance of the system?

Solution:

(a) constituents: Na⁺, SO₄²⁻, H₂O

$$\therefore c = 3$$

Reaction equilibria: Nil

$$r = 0$$

Electroneutrality condition:

$$2n_{Na^+} = n_{SO_4^{2-}}$$

$$\therefore a = 1$$

Therefore, no of components,

$$C = c - r - a = 3 - 0 - 1 = 2$$

No of phases, $p = 2$ (liq & gaseous)

(b) $F = C - P + 2 = 2 - 2 + 2 = 2$

11. A saturated solution of Na₂SO₄, with excess of the solid, is present at equilibrium with its vapour in a closed vessel.

(a) How many phases and components are present?

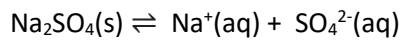
(b) What is the variance of the system?

Solution:

(a) Constituents: Na_2SO_4 , Na^+ , SO_4^{2-} , H_2O

$$c = 4$$

Reaction equilibrium:



$$\therefore r = 1$$

Electroneutrality condition:

$$2n_{\text{Na}^+} = n_{\text{SO}_4^{2-}}$$

$$\therefore a = 1$$

$$C = c - r - a = 4 - 1 - 1 = 2$$

No of phases = 3 (solid (Na_2SO_4), solution, vapour)

$$(b) F = C - P + 2 = 2 - 3 + 2 = 1$$

Conditions for equilibrium between phases:

Following conditions must be satisfied for the existence of equilibrium between various phases in a multiphase system:

1. Thermal equilibrium:

All the phases must be at the same temperature, otherwise there will be flow of heat from one phase to another.

2. Mechanical equilibrium:

All the phases must be under same pressure, otherwise volume of one phase will increase at the expense of another.

3. Chemical equilibrium:

For a system of many phases at equilibrium, the chemical potential of a component j must be same in all the phases.

For the component j present in $\alpha, \beta, \gamma, \delta, \dots$ phases at constant T and P ,

$$\mu_j^\alpha = \mu_j^\beta = \mu_j^\gamma = \mu_j^\delta = \dots$$

Phase Diagram of one-component system

We can represent any intensive state of a one-component system by a point on a two-dimensional P-vs-T diagram, where each point corresponds to a definite T and P . Such a diagram is called a phase diagram.

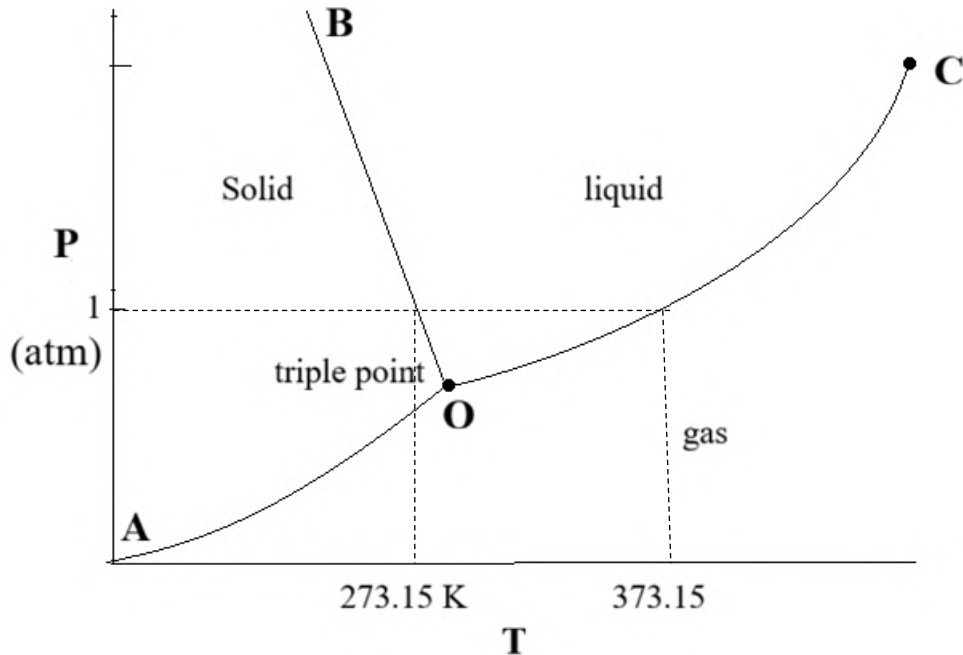
In one-component system (pure substances) $c = 1$, hence $F = 3 - p$, when only one phase is present, $F = 2$ and both P and T can be varied independently without changing the number of phases. A single phase is therefore represented by an area on a P-T diagram.

When two phases are in equilibrium, $F = 1$, and only one of the two variables T and P is sufficient to describe the system; when temperature is set, the pressure cannot vary freely. Therefore, at a given temperature, a liquid has a characteristic vapour pressure. It follows that equilibrium of two phases is represented by a line in the phase diagram.

When three phases are in equilibrium, $F = 0$ and the system is invariant. The equilibrium of three phases is represented by a point on the phase diagram. This point is called *triple point*.

The water system

The phase diagram for H₂O system is shown below:



The diagram is divided into three areas - AOB, BOC and AOC representing solid, liquid and gaseous phase respectively. For a single phase, $p = 1$, hence $F = 2$. Therefore, the two variables P and T must be specified to define the state of the system in each phase.

Along the lines, two phases are in equilibrium. Hence, $F = 1$ along a line. The line OC represents liquid and vapour phases of water in equilibrium. Thus, with the liquid and vapour in equilibrium, we can vary T along the line OC, but once T is fixed then, P the equilibrium vapour pressure is fixed at that T . The boiling point of a liquid at a given pressure P is the temperature at which its equilibrium vapour pressure equals P . The line OC shows how the boiling point of a liquid varies with pressure. From the perspective of vapor pressure, the line OC shows the variation of vapour pressure with temperature. Normal boiling point of water is 373.15 K at 1atm.

The melting point of a solid at a given pressure P is the temperature at which solid and liquid are in equilibrium at pressure P . Line OB is the solid-liquid equilibrium for H₂O and gives the melting point of ice as a function of pressure. Melting point of ice decreases with increase in pressure. Normal T_m of water is 273.15 K at 1 atm.

Along the line OA, there is equilibrium between solid and vapour. The line OA is the vapor pressure curve of the solid. Vapor pressure of a solid goes to zero as $T \rightarrow 0$, so the solid vapor line on a phase diagram intersects the origin at $P = 0, T = 0$.

Point C is the critical point. The temperature and pressure at this point are the critical temperature T_c and pressure P_c . For water, $T_c = 647 \text{ K}$, $P_c = 218 \text{ atm}$. At any temperature above T_c , liquid and vapor phases cannot co-exist in equilibrium i.e. above T_c there is no distinction between liquid and vapor. At the point C, the liquid-vapour line ends.

Point O is the triple point. Here, solid, liquid and vapor phases are in mutual equilibrium and $F = 0$. Since the system is invariant at the triple point, it is established at a definite T and P . The Triple point of water lies at 273.16 K and 611 Pa (0.01°C and 4.585 Torr).

Solid-liquid equilibrium line OB has a negative slope. This means that melting point decreases as the pressure is raised. The reason for this unusual behaviour can be attributed to the decrease in volume that occurs in melting. Hence, as the pressure is increased, it becomes more favourable for the solid to transform into the denser liquid phase.

Phase boundary

Phase diagram of a substance shows the regions of P and T at which its various phases are thermodynamically stable. The boundaries between these regions representing phases of the substance are called phase boundaries. Phase boundaries show the values of P and T at which two phases co-exist in equilibrium. There are three types of phase boundaries:

(i) Solid-liquid phase boundary:

It is a plot of the freezing point at various pressures.

(ii) Liquid-vapour phase boundary:

It is a plot of vapour pressure of the liquid against temperature.

(iii) Solid-vapour phase boundary:

It is a plot of the sublimation vapour pressure against temperature.

Clapeyron Equation: The slopes of the phase boundaries

The condition for equilibrium between two phases, α and β , of a pure substance is

$$\mu_\alpha(T, P) = \mu_\beta(T, P) \dots \dots \dots (1)$$

Slopes of the phase boundaries are given by $\frac{dP}{dT}$. So an expression for $\frac{dP}{dT}$ is the mathematical expression for phase boundary.

If the pressure is changed to a value $P + dP$, the equilibrium temperature will change to $T + dT$, and the value of each μ will change to $\mu + d\mu$. Hence at $T + dT$ and $P + dP$, the equilibrium condition is

$$\mu_{\alpha}(T, P) + d\mu_{\alpha} = \mu_{\beta}(T, P) + d\mu_{\beta} \dots \dots \dots (2)$$

Subtracting equation 1 from equation 2,

$$d\mu_{\alpha} = d\mu_{\beta} \dots \dots \dots (3)$$

Using the fundamental equation,

$$dG = -SdT + VdP$$

we can write,

$$d\mu_{\alpha} = -S_{\alpha,m}dT + V_{\alpha,m}dP \dots \dots \dots (4a)$$

and

$$d\mu_{\beta} = -S_{\beta,m}dT + V_{\beta,m}dP \dots \dots \dots (4b)$$

Using equation 4 in 3,

$$\begin{aligned} -S_{\alpha,m}dT + V_{\alpha,m}dP &= -S_{\beta,m}dT + V_{\beta,m}dP \\ \Rightarrow (S_{\beta,m} - S_{\alpha,m})dT &= (V_{\beta,m} - V_{\alpha,m})dP \end{aligned}$$

If the transformation is written as $\alpha \rightarrow \beta$, then

$$\Delta S_m dT = \Delta V_m dP$$

or

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \dots \dots \dots (5)$$

Equation 5 is called Clapeyron equation. This equation is fundamental to any discussion of the equilibrium between two phases of a pure substance and expresses the qualitative dependence of the equilibrium temperature on pressure.

The liquid-vapour phase boundary: Clausius-Clapeyron equation

For the transformation, liquid \rightarrow vapour at temperature T , the molar entropy change $\Delta_{vap}S$ is given by

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T} \dots \dots \dots (6)$$

where $\Delta_{vap}H$ is the molar enthalpy of vaporization.

Applying Clapeyron equation to liquid-vapour equilibrium we have,

$$\frac{dP}{dT} = \frac{\Delta_{vap}S}{\Delta_{vap}V}$$

where $\Delta_{vap}V$ is the molar volume change that occurs on vaporisation.

Applying equation 6,

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} \dots \dots \dots (7)$$

The enthalpy of vaporization $\Delta_{vap}H$ is positive and $\Delta_{vap}V$ is large and positive. Therefore, dP/dT is positive but it is much smaller than for the solid-liquid boundary.

The molar volume of a gas $V_m(g)$ is much greater than the molar volume of a liquid $V_m(l)$, we can write,

$$\Delta_{vap}V = V_m(g) - V_m(l) \approx V_m(g)$$

Assuming that the vapour behaves ideally,

$$V_m(g) = \frac{RT}{P}$$

we get,

$$\Delta_{vap}V = \frac{RT}{P}$$

After this approximation, equation 7 becomes

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta_{vap}H \cdot P}{RT^2} \\ \Rightarrow \frac{dP}{PdT} &= \frac{\Delta_{vap}H}{RT^2} \\ \Rightarrow \frac{d \ln P}{dT} &= \frac{\Delta_{vap}H}{RT^2} \dots \dots \dots (8) \end{aligned}$$

This equation is known as *Clausius-Clapeyron equation* for the variation of vapour pressure with temperature.

Integrating between limits under the assumption that $\Delta_{vap}H$ is independent of temperature yields

$$\int_{p^*}^p d \ln P = \frac{\Delta_{vap}H}{R} \int_{T^*}^T \frac{dT}{T^2}$$

where p^* is the vapour pressure at T^* and p is the vapour pressure at T .

$$\ln \frac{p}{p^*} = -\frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

This equation gives the curve plotted as the liquid-vapour boundary.

The solid-liquid phase boundary

Melting is accompanied by a molar enthalpy change $\Delta_{fus}H$ and occurs at a temperature T .

Molar entropy change for the change solid \rightarrow liquid is given by

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T} \dots \dots \dots (9)$$

Applying Clapeyron equation to the solid-liquid equilibrium,

$$\frac{dP}{dT} = \frac{\Delta_{fus}S}{\Delta_{fus}V} \dots \dots \dots (10)$$

where $\Delta_{fus}V$ is the molar volume change that occurs on melting.

$\Delta_{fus}V$, enthalpy of fusion is positive and $\Delta_{fus}V$ is usually positive and always small. Hence, dP/dT is usually steep and +ve. It is much greater than the slope of the liquid-vapour boundary.

From equations 9 and 10,

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V} \dots \dots \dots (11)$$

Integrating the expression 11 between the melting temperatures T^* (when the pressure is p^*) and T (when the pressure is p), we get

$$\int_{p^*}^p dp = \frac{\Delta_{fus}H}{\Delta_{fus}V} \int_{T^*}^T \frac{dT}{T}$$

assuming that $\Delta_{fus}H$ and $\Delta_{fus}V$ do not vary with temperature and pressure.

Or,

$$p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T}{T^*}$$

Now, when T is close to T^* , the logarithm can be approximated as:

$$\ln \frac{T}{T^*} = \ln \left(1 + \frac{T - T^*}{T^*} \right) \cong \frac{T - T^*}{T^*}$$

because $\ln(1 + x) \cong x$ when x is small.

So,

$$p = p^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V} \times (T - T^*)$$

This equation is a mathematical expression for solid-liquid phase boundary.

Worked out examples

1. Vapour pressure of water at 95°C and 100°C are 634 and 760 mm, respectively. Calculate molar enthalpy of vaporization of water between 95°C and 100°C.

Solution: Applying

$$\ln \frac{p}{p^*} = -\frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

Here, $p = 760 \text{ mm}$

$$p^* = 634 \text{ mm}$$

$$T = 373 \text{ K}$$

$$T^* = 368 \text{ K}$$

$$\begin{aligned} \therefore \ln \frac{760 \text{ mm}}{634 \text{ mm}} &= -\frac{\Delta_{vap}H}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{368 \text{ K} - 373 \text{ K}}{368 \text{ K} \times 373 \text{ K}} \right) \\ \Rightarrow \Delta_{vap}H &= \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 137264 \text{ K}}{5} \times 2.303 \log 1.1987 \\ \Rightarrow \Delta_{vap}H &= 525642.6 \text{ J mol}^{-1} \times 0.0787 \\ \Rightarrow \Delta_{vap}H &= 41373.6 \text{ J mol}^{-1} = 41.373 \text{ kJ mol}^{-1} \end{aligned}$$

2. The vapour pressure of water at 100°C is 760 mm. What will be the vapour pressure at 95°C? Molar enthalpy of vaporization of water at the temperature range 95°C to 100°C is 41.27 kJ mol⁻¹.

Solution: Applying

$$\ln \frac{p}{p^*} = -\frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

Here, $p = 760 \text{ mm}$

$$p^* = ?$$

$$T = 373 \text{ K}$$

$$T^* = 368 \text{ K}$$

$$\Delta_{vap}H = 41.27 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \therefore \ln \frac{760 \text{ mm}}{p^*} &= -\frac{41270 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{368 \text{ K} - 373 \text{ K}}{368 \text{ K} \times 373 \text{ K}} \right) \\ \Rightarrow \ln \frac{760 \text{ mm}}{p^*} &= \frac{206350}{1141212.9} \\ \Rightarrow \ln \frac{760 \text{ mm}}{p^*} &= 0.1808 \end{aligned}$$

$$\Rightarrow \log 760 - \log p^* = \frac{0.1808}{2.303}$$

$$\Rightarrow \log p^* = 2.8808 - 0.0785 = 2.8023$$

$$\Rightarrow p^* = \text{Antilog}(2.8023) \text{ mm} = 634.3 \text{ mm}$$

3. Ether boils at 33.5°C at one atmospheric pressure. At what temperature will it boil at a pressure of 750 mm, given that the enthalpy of vaporization of ether is 369.86 Jg⁻¹.

Solution: Applying

$$\ln \frac{p}{p^*} = -\frac{\Delta_{vap}H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$$

Here, $p = 760 \text{ mm}$

$$p^* = 750 \text{ mm}$$

$$T = 33.5 + 273 = 306.5 \text{ K}$$

$$T^* = ?$$

$$\therefore \log \frac{760 \text{ mm}}{750 \text{ mm}} = -\frac{(369.86 \text{ Jg}^{-1}) \times (74 \text{ g mol}^{-1})}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{T^* - 373 \text{ K}}{T^* \times 373 \text{ K}} \right)$$

$$\Rightarrow 0.0057 = 1429.4 \left(\frac{T^* - 373 \text{ K}}{T^* \times 373 \text{ K}} \right)$$

$$\Rightarrow 0.0057 = 1429.4 \left(\frac{T^* - 373 \text{ K}}{T^* \times 373 \text{ K}} \right)$$

$$\Rightarrow 0.0057 \times 373 \times T^* = 1429.4(T^* - 373)$$

$$\Rightarrow 2.1261T^* = 1429.4 T^* - 533166.2$$

$$\Rightarrow 1427.2739 T^* = 533166.2$$

$$\Rightarrow T^* = 373.6 \text{ K}$$

Two-component systems

For a two-component system, the phase rule becomes, $F = C - p + 2 = 4 - p$. Since the minimum number of phases in any system is 1, the maximum number of degrees of freedom is 3. Thus. Three variables would be necessary to describe a system. Since three variables are difficult to plot, it is customary to hold one of them constant. For example, P is kept constant on a diagram of temperature plotted against concentration.

For two-component systems having solid-liquid equilibria, the following cases are important:

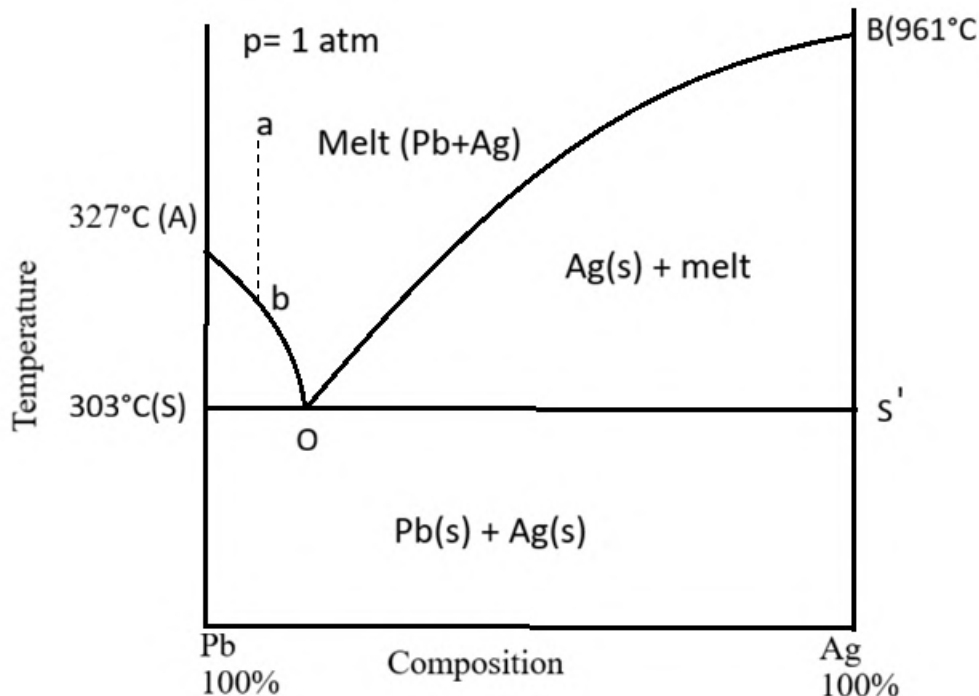
- (i) Two-component system showing eutectic
- (ii) Two-component system showing congruent melting points
- (iii) Two-component system showing incongruent melting points
- (iv) Two-component system forming solid solutions.

Two-component system showing eutectic

Such a system can be discussed taking Pb-Ag system as an example.

This is the extracted text from the images provided, transcribed exactly as written:

Keeping the pressure constant at 1 atm, the temperature versus composition diagram for this system is shown below:



A (327°C) is the melting point of pure Pb and B (961°C) is that of pure Ag. On addition of Ag, melting point of Pb decreases along the curve AO. Therefore, AO is called the melting point curve of Pb. Again, on addition of Pb, melting point of Ag decreases along the curve BO i.e., BO is the melting point curve for Ag. The system along AO and BO has two phases and is consequently monovariant:

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

The curve AO represents the equilibrium between Pb(s) and melt, and curve BO represents equilibrium between Ag(s) and melt.

Above AOB (liquidus curve) there exists only liquid phase, and below SOS' (solidus curve) it's only solid phase. In the area AOS, Pb(s) and melt and inside BOS', Ag(s) and melt are present.

At the point O, the three phases Pb(s), Ag(s) and their melt are in equilibrium. At this point, temperature 303°C and composition (2.6% Ag, 97.4% Pb) are fixed. This is called the Eutectic point. The corresponding temperature and composition are called eutectic temperature and eutectic composition, respectively. At this point, three phases are in equilibrium, therefore $F = 0$. It means that without changing the no of phases (p), it is impossible to vary the other parameters (T, x_i).

The desilverisation of lead by Pattinson's process is based on the fact that when a molten lead–silver alloy is cooled, pure lead crystallizes out first while silver remains in the liquid. Initially, the alloy is heated above its melting point to form a uniform liquid, and then it is slowly cooled. Let us consider the point 'a' in the figure. The temperature of the melt falls along the line ab. As soon as the point 'b' is reached, lead begins to separate out and is removed. This makes the remaining liquid richer in silver. With continued cooling the system shifts along the line bO. Lead continues to separate out and with the removal of lead crystals the silver concentration in the melt gradually increases from a very small amount (about 0.1% or less) to a higher value (around 2.6%) when the eutectic point O is reached. Thus, this process helps in concentrating silver in the alloy.

Some important concepts and definitions

Eutectic mixture:

A eutectic mixture of the components A and B have a definite composition and a sharp melting point or a sharp freezing point. A solid eutectic mixture melts entirely at one temperature. A liquid eutectic mixture freezes at a single temperature, without previously depositing solid A or B.

When a liquid eutectic mixture of A and B freezes, it gives a solid eutectic mixture (of A and B) of same composition. When a solid eutectic mixture of A and B melts, it gives a liquid eutectic mixture (of A and B) of same composition.

Eutectic mixture versus Chemical Compound:

Though a eutectic mixture, like a chemical compound, has a sharp melting point and on melting gives a liquid of same composition, it is not a compound. Because —

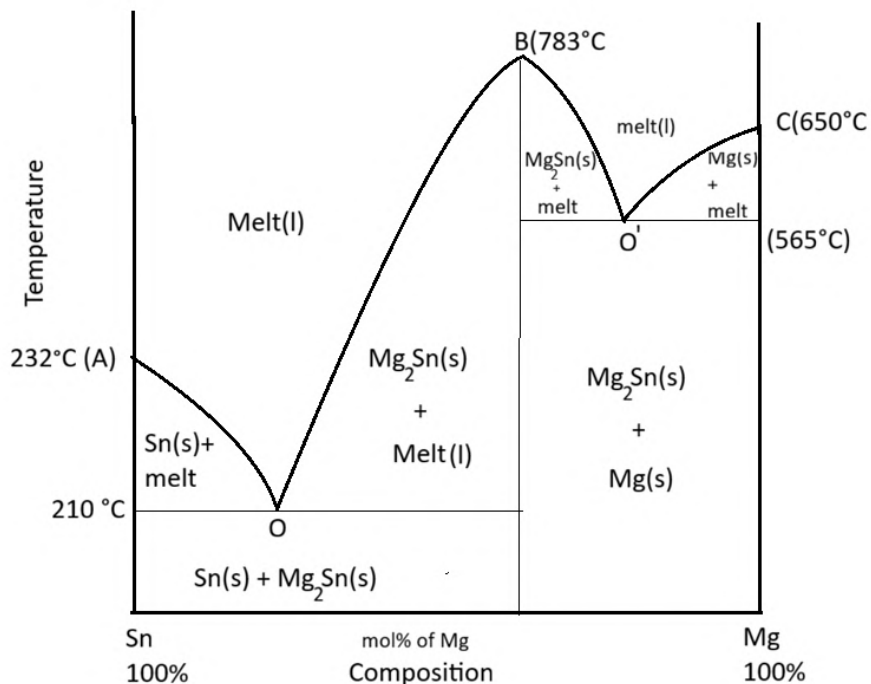
- (i) the components are not present in stoichiometric proportions.
- (ii) the mixture is heterogeneous as revealed under a microscope.

Eutectic mixture versus Solid solution:

A solid solution is a homogeneous mixture of two components whereas a eutectic mixture is heterogeneous in nature. A eutectic solid of A and B is an intimate mixture of crystals of B and crystals of A.

Two-component system showing congruent melting point

Some two-component systems may form stable compound at a certain temperature and composition. A compound is said to have a "congruent melting point" if it melts to give a liquid having the same composition as that of the solid compound. e.g. the system consisting of Sn and Mg exemplifies system showing the formation of a congruent melting compound:



There are two eutectic points in the diagram — O and O'. The first one due to Sn - Mg₂Sn system and the second one due to Mg₂Sn - Mg system. The highest point B indicates the formation of compound Mg₂Sn having a melting point 783°C. The curve AO is the melting point curve of Sn in presence of Mg. Melting

point of Sn decreases with increase in the amount of Mg. CO' is the melting point curve of Mg in presence of Sn. Curve BO and BO' are the melting point curves for Mg₂Sn in presence of Mg and Sn respectively. The compound Mg₂Sn has a congruent melting point. The liquid phase obtained at this temperature has the same composition as that in the solid phase (Mg: Sn \equiv 2: 1 in the liquid phase).

A system showing incongruent melting point

When a compound formed by the chemical combination of the components does not have sufficient stability up to its normal melting point, it decomposes before the normal melting point is reached. Such a phase transition results in a melt and a new solid phase with a composition different from that of the compound. Such a compound is said to possess an incongruent melting point. The temperature at which the decomposition occurs is known as the peritectic point or meritectic point. At the peritectic point, the compound undergoes the reaction



The new solid phase obtained at the peritectic point may be solid A or solid B or some compound different from the original compound.

At the peritectic point $p = 3$, therefore $F = 3 - p = 0$ i.e., all the variables are fixed.

Phase diagram of a system showing incongruent melting point:

Such a system is exemplified by Na-K system (See figure in the next page).

The compound Na₂K has an incongruent melting point. This is stable only in the solid state.

Let us consider a liquid at a₁ which is cooled:

(i) a₁ to a₂: Some Na(s) is deposited, and the remaining liquid is richer in K.

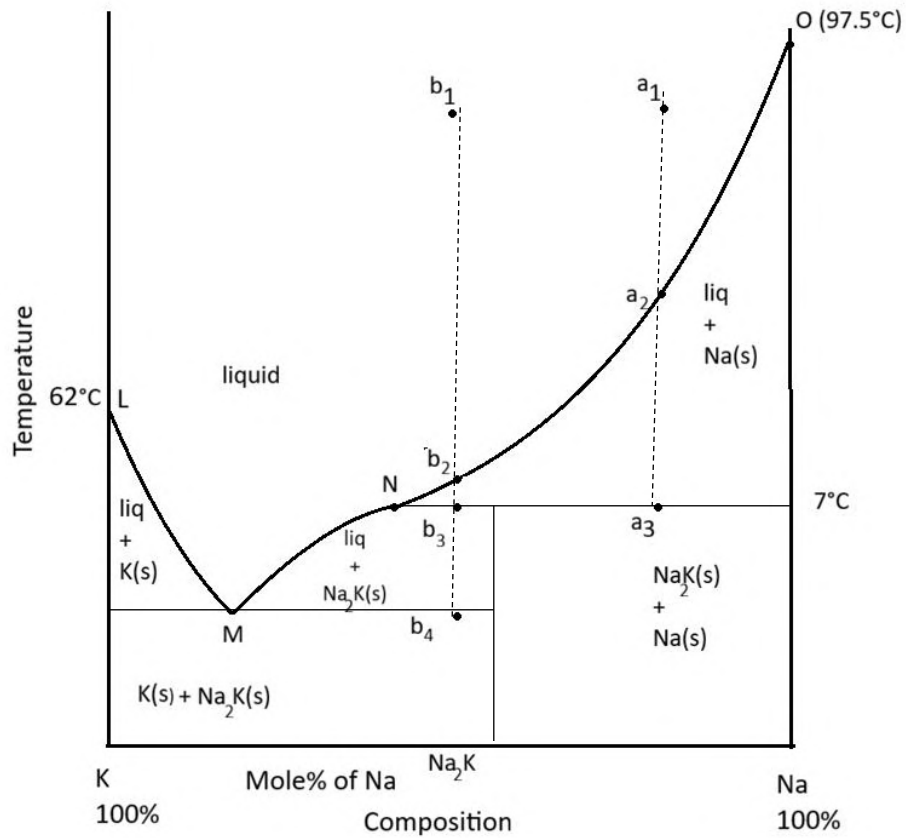
(ii) a₂ to just below a₃: The sample is now entirely solid, and consists of Na(s) and Na₂K(s).

Now let us consider the isopleth at b₁:

(i) b₁ to b₂: at b₂ Na(s) begins to deposit.

(ii) b₂ to b₃: at b₃ a reaction occurs to form Na₂K, at this stage liquid Na/K mixture is in equilibrium with Na₂K(s). At b₄ solid K exists in equilibrium with solid Na₂K.

Thus, no liquid Na₂K forms at any stage because it is too unstable to exist as a liquid. This behaviour is an example of incongruent melting.



Eutectic point versus Peritectic point:

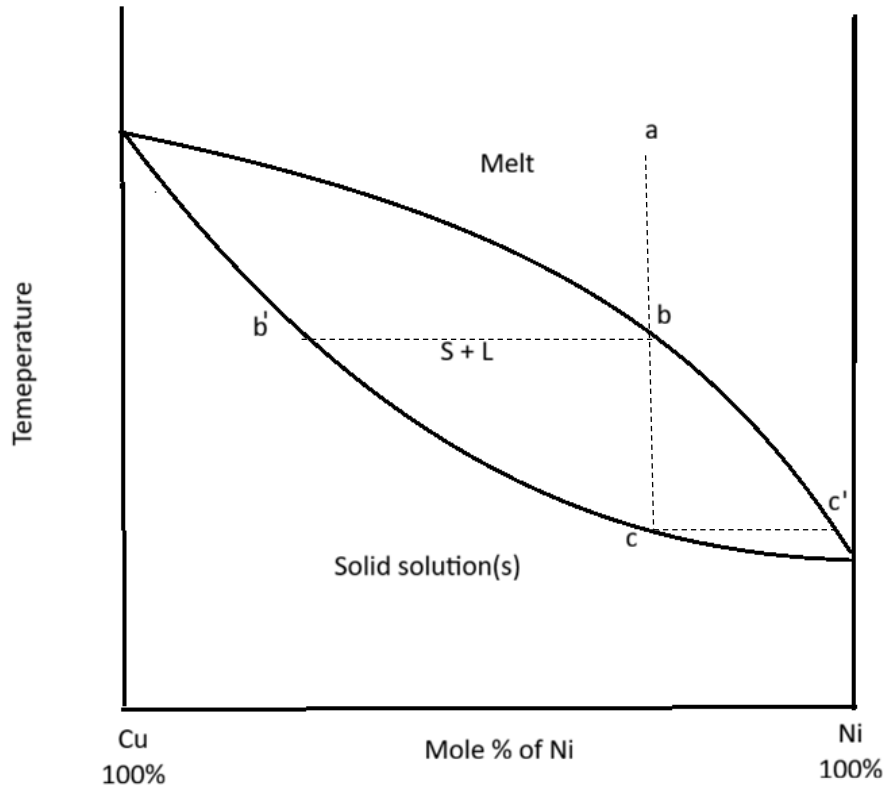
At the eutectic point when a solid eutectic mixture of A and B melts, it gives a liquid eutectic mixture of same composition.

At the peritectic point when a chemical compound formed by chemical combination of A and B decomposes, it yields a new solid phase and a melt with a composition different from that of the compound.

System showing solid solution (complete miscibility in the solid state)

When crystal lattices of the two solid components are identical, they are capable of yielding a series of homogeneous mixtures called solid solutions.

Example of a completely miscible system in the solid state is the Cu - Ni system. The phase diagram for the system is depicted below:



The upper curve is the liquidus curve above which only liquid phase is present. The lower curve is the solidus curve below which only the solid phase is present. The area covered by the two curves represents a two-phase system (S+L).

When a melt of composition 'x' is cooled from point 'a', at 'b' a solid solution of composition b' begins to crystallize out from the melt. Lowering of temperature separates more and more of solid solution and between 'b' and 'c' two phases, solid solution and melt exist. At 'c' the solid solution is in equilibrium with a melt of composition c'. Below c, the entire mass solidifies yielding a homogeneous solid solution of Cu and Ni.

A solid solution can have any composition but a solid compound is formed in a definite and fixed ratio of the components.

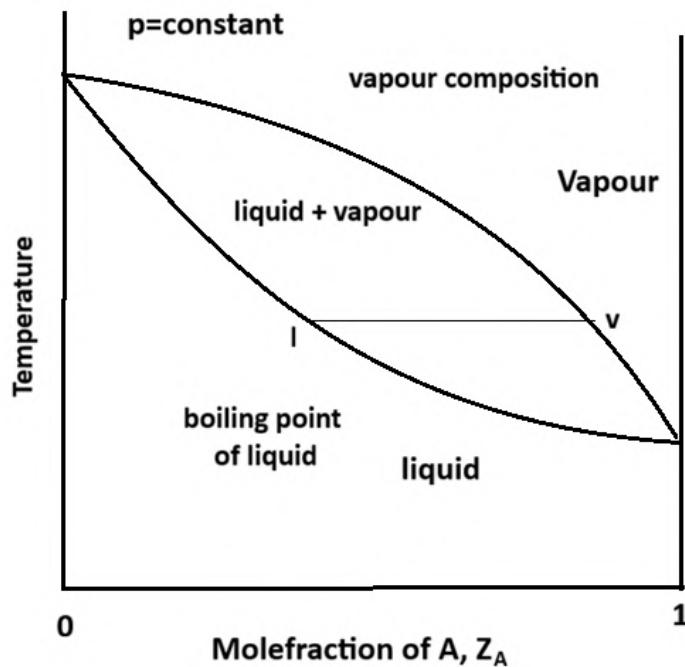
In a solid solution, atoms of one constituent enter the crystal lattice of the other and are uniformly distributed throughout the entire lattice.

In a solid mixture, on the other hand, distribution of components is heterogeneous and each component retains its characteristic crystal structure.

Temperature-Composition Diagram and fractional distillation of binary miscible liquids forming ideal solution

Temperature - Composition diagram:

Temperature composition diagram is a phase diagram in which the phase boundaries show the composition of the phases that are in equilibrium at various temperatures at a given pressure. A typical temperature - composition diagram having liquid-vapour equilibrium is shown below:

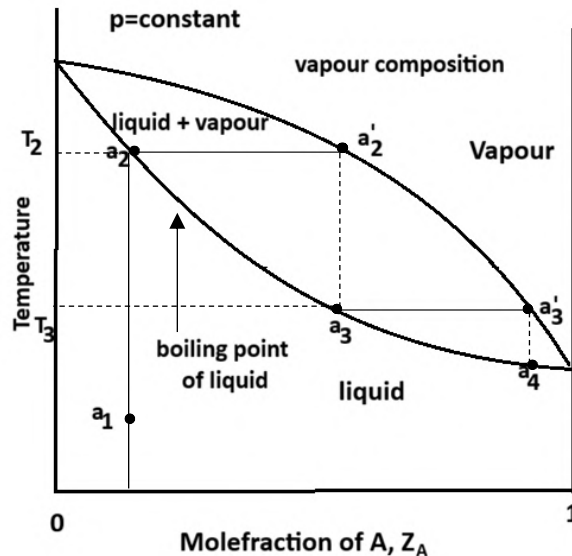


This is a plot of boiling point vs compositions for the ideal solution of two liquids A and B at constant pressure. Z_A is the mole fraction of A in the entire system (liquid+vapour).

The lower curve describes the liquid composition; upper curve describes the vapour composition. The liquid region lies below the lower curve, since under a constant pressure the liquid is stable at low temperatures. The points lying above the upper curve represents systems with gaseous states. The points in the middle region describe states in which liquid and vapour co-exist in equilibrium. The tie-line lv connects the composition of vapour and the composition of liquid that coexist at that temperature. Lower curve gives the boiling point of liquid at different compositions.

Fractional Distillation

Let us consider the fractional distillation of a liquid mixture of two volatile components A and B producing an ideal solution. Temperature-composition diagram for the mixture is:



Let us start with a liquid of composition a_1 which is heated. It boils when temperature reaches T_2 . Then the liquid has composition a_2 (the same as a_1) and the vapour has the composition a'_2 which is present only as a trace. The vapour is richer in more volatile component A, the component with the lower boiling point. In distillation, the vapour is withdrawn and condensed. The vapour of composition a'_2 if condensed gives a liquid of composition a_3 which is richer in the more volatile component A than the original liquid. In fractional distillation, the boiling and condensation cycle is repeated successively, i.e. liquid of composition a_3 is heated again. The phase diagram shows that this mixture boils at T_3 and yields a vapour of composition a'_3 which is even richer in the more volatile component A. That vapour is drawn off, and it condenses to a liquid of composition a_4 . The cycle is repeated until almost pure A is obtained.

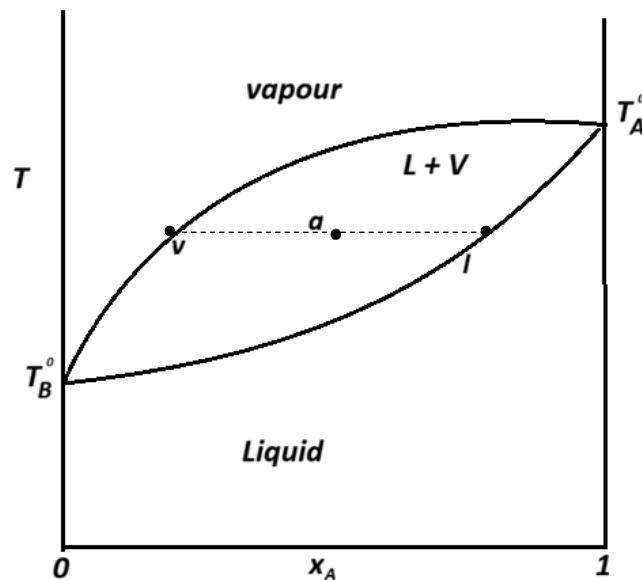
Lever rule

In a two-component temperature-composition phase diagram, the Lever Rule is used to determine the relative amounts of liquid and vapour phases present at any point within the two-phase (L + V) region. For a given point a on the diagram, a horizontal tie line is drawn through it, intersecting the liquid equilibrium curve at l and the vapour equilibrium curve at v . The ratio of the number of moles of liquid phase to that of vapour phase is given by

$$\frac{n_{\text{liquid}}}{n_{\text{vapour}}} = \frac{\text{length } av}{\text{length } al}$$

This is called the Lever rule.

where av is the segment from the point to the vapour curve and al is the segment from the point to the liquid curve.



Temperature-Composition Diagram and fractional distillation of binary miscible liquids forming non-ideal solution

Azeotropes

In case of some liquid pair systems, boiling point reaches a maximum for a certain composition. The liquid and vapour phases at this point have the same composition and boil at a constant temperature. Such a constant boiling mixture without change in composition is called an azeotrope.

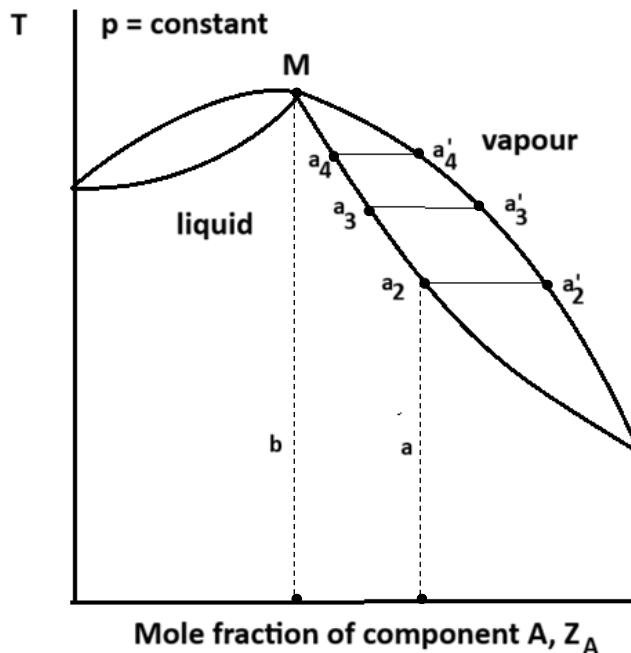
In case of some other liquid pair systems, boiling point takes a minimum value for certain composition. The mixture with the lowest boiling point also represents an azeotropic mixture. Accordingly, two types of azeotropes are found —

- high boiling azeotrope
- low boiling azeotropes.

These are represented in the following diagrams:

(i) High-boiling azeotrope

In the temperature-composition diagram, the point *M* represents the azeotropic mixture. This has the highest boiling point than any other mixture. One example of high boiling azeotrope is HCl/H₂O at 80% by mass of water and boils at 108.6°C.

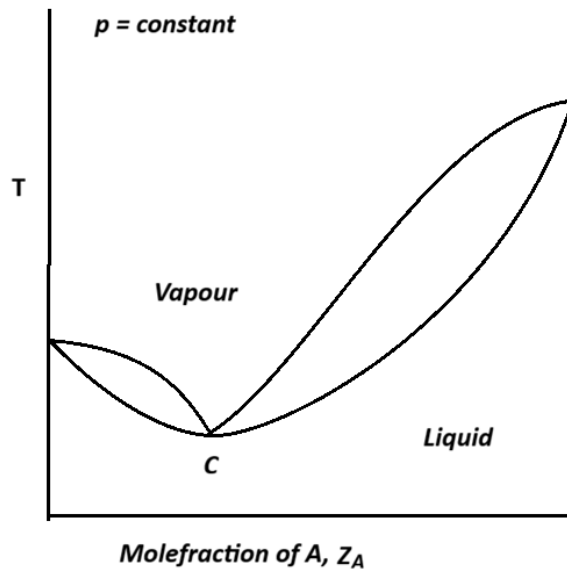


Let us consider a liquid of composition *a*. The vapour (at *a'*₂) of the boiling mixture (at *a*₂) is richer in A. If the vapour is removed and condensed, then the remaining liquid will move to a composition that is richer in the other component (say B), such as represented by *a*₃, and the vapour in equilibrium with this mixture has composition *a'*₃. If that vapour is removed, then the composition of boiling liquid shifts to a point such as *a*₄ and the composition of the vapour shifts to *a'*₄. Hence, as evaporation proceeds the

composition of the remaining liquid shifts towards the other component B as A is drawn off. When so much A has been evaporated that the liquid has reached the composition b, the vapour has the same composition as the liquid. Evaporation thus occurs without change of composition. The mixture is said to form an azeotrope. When the azeotropic composition has been reached, distillation can't separate the two liquids because the condensate has the same composition as the azeotropic liquid.

(ii) Low boiling azeotrope:

In the temperature - composition diagram, point C represents the azeotropic mixture. It has a lower boiling point than any other composition of the mixture. An example is ethanol/water, which boils unchanged when the water content is 4%, and the temperature is 78°C.



Q. Is an azeotrope a mixture or chemical compound?

Ans: An azeotrope although distills unchanged in its composition at a definite temperature, it is not a true chemical compound. Because, the composition of the azeotrope depends on pressure. When the azeotrope is distilled under changed pressure, its composition also changes indicating that it is a mixture and not a chemical compound.

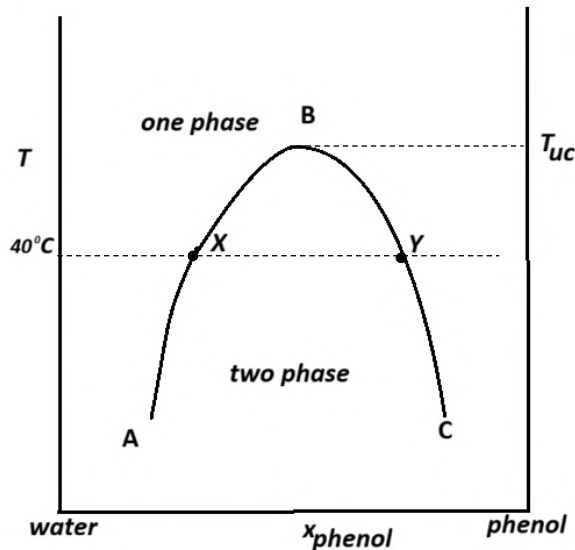
Liquid-Liquid Equilibria

Partially miscible liquids

Partially miscible liquids are those that do not mix in all proportions at all temperatures. e.g. if we add some phenol to water, first phenol will be dissolved in water but as the amount of added phenol increases, phenol will form a separate layer. In fact, the water layer will contain dissolved phenol and the phenol layer will also have appreciable amount of dissolved water. Thus, when two partially miscible liquids A and B are brought together in appreciable amounts, we have two saturated solutions in two phases — one of A in B and another of B in A — at equilibrium. These two solutions are described as conjugate solutions.

Type I: Systems having upper critical solution temperature

This type of system can be illustrated by taking phenol and water as example. Mutual solubility of phenol and water is shown in a temperature - composition diagram:



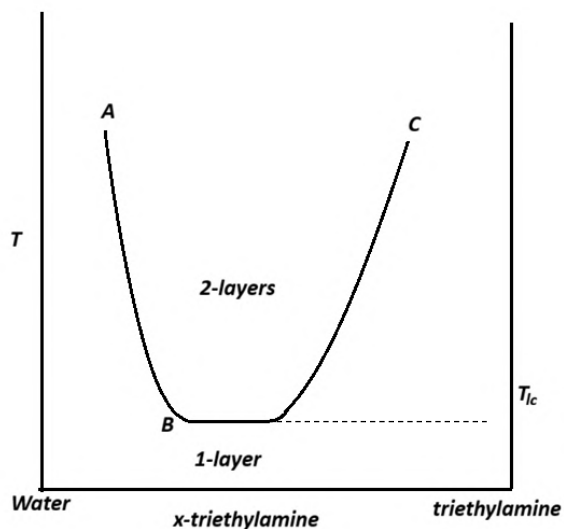
AB gives the percentage of phenol dissolved in water at different temperatures. CB is the solubility curve for water in phenol. In both the case solubility increases with increase in temperature. The two solubility curves meet at a point B. Mutual solubility of the two liquids increases with increase in temperature. Upper critical solution temperature (T_{uc}) is the temperature above which two liquids form a single phase at all proportions i.e. they become completely miscible. For water phenol system this temperature is 65.85°C . The mutual solubility of two liquids increases with rise in temperature because the molecules gain more kinetic energy and move more freely. At lower temperatures, molecules of each liquid prefer

to stay close to their own kind due to stronger intermolecular attractions, so the liquids remain only partially miscible and form two separate layers. As the temperature increases, the increased thermal motion reduces the effect of these attractions and promotes mixing. The upper critical solution temperature (UCST) is the temperature above which the two liquids become completely miscible in all proportions, forming a single homogeneous phase. In the Water–Phenol system, above 65.85°C the increased molecular motion overcomes the tendency of like molecules to remain together, resulting in complete mixing.

At a temperature (say 40°C), point X represents the composition of phenol in water and point Y represents the composition of water in phenol. At points X and Y, completely miscible and homogeneous system will result. Between X and Y, all mixtures yield two layers of compositions X and Y, while a point on the left of X or on the right of Y will correspond to a homogeneous solution. Any point under the curve ABC represents a heterogeneous system while the points outside the dome shaped area (covered by ABC) give a homogeneous solution.

Type II: Systems having lower critical solution temperature

There are liquid pairs in which mutual solubility decreases with increase of temperature. Such a system can be illustrated by taking triethylamine - water system, the mutual solubility curve of which is shown below:

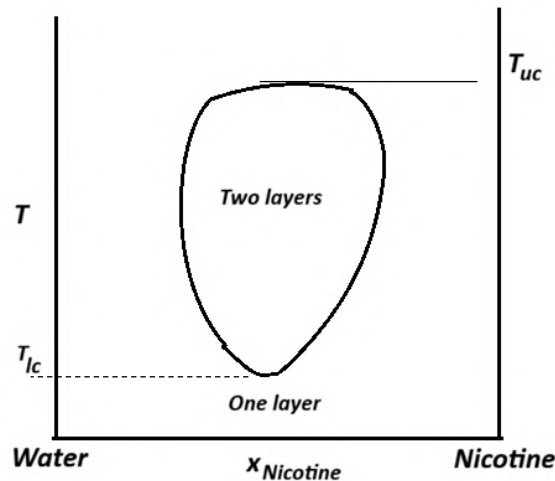


AB is the solubility curve of triethylamine in water; CB is the solubility curve of water in triethylamine. In both cases, mutual solubility decreases with increase in temperature. For such systems, there exists a lower critical solution temperature (T_{lc}) or lower consolute temperature. For triethylamine - water system $T_{lc} = 18.5$. T_{lc} is the temperature below which the two liquids completely mix in all proportions and above

which they form two phases. In this case, at low temperatures, the two components are more miscible because they form a weak complex; at higher temperatures, the complex break-up and the two components are less miscible.

Type III: Systems having both upper and lower critical solution temperatures

There are some substances which exhibit both upper and lower consolute temperatures. Nicotine - water system is an example of this type. Mutual solubility curve for this system is shown below:



Within the enclosed area, liquids are partially miscible while outside the enclosed area, they are completely miscible. The upper critical solution temperature T_{uc} is 210°C and lower critical solution temperature is 61°C.

Fractional distillation of immiscible liquids

When two liquids do not mix with each other (immiscible), each one behaves independently. Both liquids produce their own vapour, and the total vapour pressure (P) above the mixture is just the sum of the vapour pressures of the two liquids. Thus,

$$P = p_A^\circ + p_B^\circ$$

where p_A° and p_B° are the vapour pressures of the pure liquids A and B respectively.

Boiling happens when this total vapour pressure becomes equal to atmospheric pressure. Since the pressures add up, the mixture reaches this point at a temperature lower than the boiling point of either liquid alone. So, the mixture boils at a lower temperature. Again, since the total vapour pressure is constant and independent of the amounts of the components, it follows that the boiling point of the mixture will remain constant as long as the two liquids are present together.

During boiling, both liquids vaporize together. The amount of each liquid in the vapour (and hence in the distillate) depends on their vapour pressures—higher vapour pressure means more of that component in the vapour. If n_A and n_B are the number of moles of the components A and B in the vapour phase at the boiling point, then

$$\frac{n_A}{n_B} = \frac{p_A^\circ}{p_B^\circ}$$

If w_A and w_B represent the actual masses of the two components in the distillate and M_A and M_B are their respective molar masses, then the above equation may be written as

$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B}$$

Thus, the masses of the liquids in the distillate will be in the ratio of their vapour pressures and molar masses. The above principle is made use of in the process of steam distillation. It is used in the purification of organic compounds which have high boiling points. The compounds must be immiscible or nearly so in water.

Problem

An immiscible mixture of water and quinoline boils at 98.9°C under a pressure of 740 torr. The distillate contains 77.9 g of quinoline and 1 kg of water. At the given boiling point, the vapour pressure of quinoline is 7.96 torr. Calculate the molar mass of quinoline.

Solution

Let water and quinoline be denoted by W and Q, respectively.

$$p_Q^\circ = 7.96 \text{ Torr}$$

$$P = p_W^\circ + p_Q^\circ$$

$$\therefore p_W^\circ = P - p_Q^\circ = 740 - 7.96 = 732.04 \text{ Torr}$$

$$\therefore \frac{w_W}{w_Q} = \frac{n_W M_W}{n_Q M_Q}$$

$$\therefore M_Q = \frac{w_Q n_W}{w_W n_Q} M_W = \frac{77.9 \text{ g} \times 732.04 \text{ Torr} \times 18 \text{ gmol}^{-1}}{1000 \text{ g} \times 7.96 \text{ Torr}} = 129 \text{ gmol}^{-1}$$

Nernst Distribution Law

Statement

When a solute is added to a system of two immiscible liquids in contact, it distributes itself between the two phases such that, at a constant temperature, the ratio of its concentrations in the two solvents remains constant, provided the solute exists in the same molecular form in both solvents.

$$\frac{c_1}{c_2} = K_D$$

where

c_1 = concentration of solute in solvent 1

c_2 = concentration of solute in solvent 2

K_D = distribution (or partition) coefficient

Explanation with Example

If iodine is shaken with carbon disulphide (CS_2) and water, it distributes between the two layers. At a fixed temperature, the ratio of iodine concentration in CS_2 to that in water remains constant, regardless of the total amount of iodine added.

Conditions for Validity

The law holds true only under certain conditions:

1. Temperature must be constant.
2. Same molecular state: The solute should not associate or dissociate in either solvent
3. Dilute solutions: The solutions should be sufficiently dilute.
4. Immiscible solvents: The two liquids must be completely or nearly immiscible.

Thermodynamic Derivation:

Let us suppose that a solute A is present in two immiscible solvents 1 and 2 in contact with each other. Also suppose that its chemical potential in solvent 1 is μ_1 and in solvent 2 is μ_2 . When two phases are in equilibrium, their chemical potentials will be equal to one another, i.e.,

$$\mu_1 = \mu_2$$

Since

$$\mu = \mu^\circ + RT \ln a$$

Therefore,

$$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad \text{for Phase 1}$$

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \quad \text{for Phase 2}$$

Hence,

$$\mu_1^\circ + RT \ln a_1 = \mu_2^\circ + RT \ln a_2$$

or

$$RT \ln \frac{a_1}{a_2} = \mu_2^\circ - \mu_1^\circ$$

Now, at constant temperature, the standard chemical potentials μ_1° and μ_2° are constant. Since R is also a constant (being the gas constant), it follows that at constant temperature

$$\frac{a_1}{a_2} = \text{constant}$$

Since the solutions are dilute, they behave ideally and hence Henry's law, according to which activity is proportional to mole fraction, is obeyed in each phase.

$$\frac{a_1}{a_2} = \frac{k_1 x_1}{k_2 x_2} = \text{constant}$$

where x_1 and x_2 are the mole fractions of the solute in the two phases and k_1 and k_2 are the Henry's law constants for the solute in the two phases. Therefore, at constant temperature

$$\frac{x_1}{x_2} = \text{constant}$$

Further, since the solutions are dilute, the ratio of the mole fractions is almost the same as the ratio of the concentrations. Hence,

$$\frac{x_1}{x_2} = \frac{c_1}{c_2} = \text{constant} = K_D$$

This is the Nernst distribution law.