

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION

CHEMICAL SCIENCES

CODE:01

2.7.2. Homogenous Equilibrium

At a Glance

Law of mass action, Equilibrium constant (K_p & K_c), Relation between them, various kinds of Homogeneous equilibrium, Van't Hoff's reaction isotherm, Temperature dependence of reaction etc.



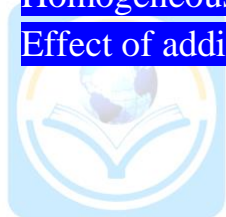
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Key Statements

Basic Key Statements: Law of mass action (2.7.2.1), Equilibrium constant (K_p & K_c) (2.7.2.2), Types of Reversible reaction (2.7.2.4), Significance of the magnitude of equilibrium constant (2.7.2.8), Le-Chatelier's principle (2.7.2.10), Effect of catalyst (2.7.2.15), Temperature dependence of equilibrium constant (2.7.19)

Standard Key Statements: Relation between different equilibrium constants (2.7.2.3), Reaction Quotient (Q) (2.7.2.9), Effect of concentration (2.7.2.11), Effect of volume (2.7.2.12), Effect of pressure (2.7.2.13), Effect of temperature (2.7.2.14),

Advance Key Statements: Case-I: Homogeneous and $\Delta n=0$ (2.7.2.5), Case-II: Homogeneous and $\Delta n>0$ (2.7.2.6), Case-III: Homogeneous and $\Delta n<0$ (2.7.2.7), Effect of addition of inert gas (2.7.2.16)

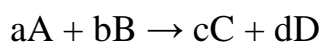


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Key Facts

2.7.2.1. Law of mass action:

According to this law, rate of reaction at a given temperature is directly proportional to the product of active mass of the reactants, raised to the power equal to stoichiometric coefficient of the balance chemical equation at particular instant of reaction.



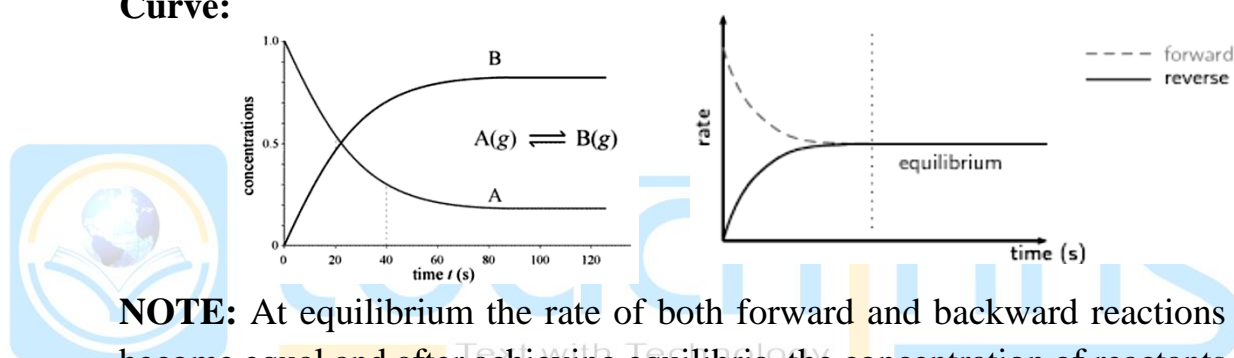
$$\text{Rate of reaction} \propto [A]^a[B]^b$$

$$\text{Rate of reaction} = K[A]^a[B]^b$$

Where K is the rate constant at that temperature.

Unit = $[moles/li]^{1-n} time^{-1}$, where n is the order of the reaction.

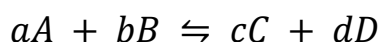
Curve:



NOTE: At equilibrium the rate of both forward and backward reactions become equal and after achieving equilibria, the concentration of reactants and products remains constant as shown in the above figure.

2.7.2.2. Equilibrium constant (K_p & K_c):

Let us consider a reversible reaction



$$\text{The rate of forward reaction} = k_f[A]^a[B]^b$$

$$\text{The rate of backward reaction} = k_b[C]^c[D]^d$$

Equilibrium the rate of the above reaction becomes same i.e.,

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

$$\text{Equilibrium constant, } K = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

2.7.2.3. Relation between different equilibrium constants:

- **Relation between K_p and K_c :**

We know that $P_i = \frac{n_i RT}{V} = C_i RT$, where, C_i is the molar conc. of 'i'.

$$\text{So, } K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} = \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b} (RT)^{\Delta n}, \Delta n = (c + d) - (a + b)$$

$$\text{Hence, } K_p = K_c \times (RT)^{\Delta n} \dots\dots\dots(1)$$

- **Relation between K_p and K_x :**

We know $p_A = x_A \times P$, where p_i is the partial pressure of i with mole fraction x_i .

$$\text{So, } K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} = \frac{(x_C \times P)^c (x_D \times P)^d}{(x_A \times P)^a (x_B \times P)^b} = \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b} (P)^{\Delta n}$$

$$\text{Hence, } K_p = K_x \times (P)^{\Delta n} \dots\dots\dots(2)$$

- **Relation between K_c and K_x :**

Comparing (1) and (2) we have

$$K_c = K_x \times \left(\frac{P}{RT}\right)^{\Delta n}$$

2.7.2.4.

Reversible Reactions

Homogeneous

$$\Delta n=0$$

$$\Delta n>0$$

$$\Delta n<0$$

Heterogeneous

2.7.2.5. Case-I: Homogeneous and $\Delta n=0$

	$2A(g)$	\rightleftharpoons	$B(g)$	+	$C(g)$	n_T
$t = 0$	a		0		0	a
At eqm, t	$a - 2x$		x		x	a
conc.	$\frac{a-2x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$	
mole fraction	$\frac{a-2x}{a}$		$\frac{x}{a}$		$\frac{x}{a}$	
p_i	$\left(\frac{a-2x}{a}\right)P$		$\left(\frac{x}{a}\right)P$		$\left(\frac{x}{a}\right)P$	
So, $K_x = \frac{x^2}{(a-2x)^2}$; $K_P = \frac{x^2}{(a-2x)^2}$; $K_C = \frac{x^2}{(a-2x)^2}$						

2.7.2.6. Case-II: Homogeneous and $\Delta n > 0$

	$A(g)$	\rightleftharpoons	$B(g)$	+	$C(g)$	n_T
$t = 0$	a		0		0	a
At eqm, t	$a - x$		x		x	$a + x$
conc.	$\frac{a-x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$	
mole fraction	$\frac{a-x}{a+x}$		$\frac{x}{a+x}$		$\frac{x}{a+x}$	
p_i	$\left(\frac{a-x}{a+x}\right)P$		$\left(\frac{x}{a+x}\right)P$		$\left(\frac{x}{a+x}\right)P$	
So, $K_x = \frac{x^2}{(a-x)(a+x)}$; $K_P = \frac{x^2}{(a-x)} \frac{1}{V}$; $K_C = \frac{x^2}{(a-x)(a+x)} P$						

2.7.2.7. Case-III: Homogeneous and $\Delta n < 0$

	$A(g)$	+	$B(g)$	\rightleftharpoons	$C(g)$	n_T
$t = 0$	a		b		0	$a + b$
At eqm, t	$a - x$		$b - x$		x	$a + b - x$
conc.	$\frac{a-x}{V}$		$\frac{b-x}{V}$		$\frac{x}{V}$	
mole fraction	$\frac{a-x}{a+b-x}$		$\frac{b-x}{a+b-x}$		$\frac{x}{a+b-x}$	
p_i	$\frac{a-x}{a+b-x} P$		$\frac{b-x}{a+b-x} P$		$\frac{x}{a+b-x} P$	
So, $K_x = \frac{x(a+b-x)}{(a-x)(b-x)}$; $K_P = \frac{x(a+b-x)}{(a-x)(b-x)P}$; $K_C = \frac{xV}{(a-x)(b-x)}$						

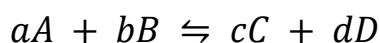
2.7.2.8. Significance of the magnitude of equilibrium constant:

- ✓ Very large value of equilibrium constant suggests that the forward reaction goes to the completion.
- ✓ In a reversible reaction the ratio of the product to reactant remains nearly same only for low equilibrium constant value.

2.7.2.9. Reaction Quotient (Q):

The ration of the concentration of the product to reactant at any instant is the quotient of the reaction.

Let us consider a reversible reaction



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q helps us to predict the direction of the reaction.

- If the reaction in equilibrium then $Q = K$.
- If $Q > K$, that means reverse reaction takes place.
- If $Q < K$, that means forward reaction takes place.

2.7.2.10. Le-Chatelier's principle:

When a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, (1) the system changes to a new equilibrium and (2) this change partly counteracts the applied change.

2.7.2.11. Effect of concentration:

- With increasing the reactant concentration for a reversible reaction, the rate of forward reaction increases i.e., equilibrium shifts towards right.
- Again, with increasing the product concentration for a reversible reaction, the rate of backward reaction increases i.e., equilibrium shifts towards left.

2.7.2.12. Effect of volume:

- With increasing volume, i.e., by decreasing the pressure the reaction will shift in that direction for which the change in pressure is been counteracts.
- If volume is increased for
 - ❖ $n > 0$; forward reaction
 - ❖ $n < 0$; backward reaction
 - ❖ $n = 0$; no effect over equilibrium.

2.7.2.13. Effect of pressure:

- On increasing the pressure, the equilibrium will shift itself in that direction in which no of moles of product decreases or vice versa.
- If pressure is increased for
 - ❖ $n > 0$; backward reaction
 - ❖ $n < 0$; forward reaction
 - ❖ $n = 0$; no effect over equilibrium

2.7.2.14. Effect of temperature:

- On increasing the temperature, the equilibrium will shift itself in that direction in which no of moles of product decreases or vice versa.
- If temperature is increased for
 - ❖ exothermic reaction; backward reaction
 - ❖ endothermic reaction; forward reaction

2.7.2.15. Effect of catalyst:

A catalyst increases the rate of both the forward as well the backward reaction for a reversible reaction. That means the equilibrium remains unchanged.

2.7.2.16. Effect of addition of inert gas:

Inert gas can be added in two conditions as followed—

- i. at constant volume:
This does not affect the equilibrium.
- ii. at constant pressure:
For a reaction when;
 - ✓ $n > 0$, forward reaction.
 - ✓ $n < 0$, backward reaction.
 - ✓ $n = 0$, no affect.

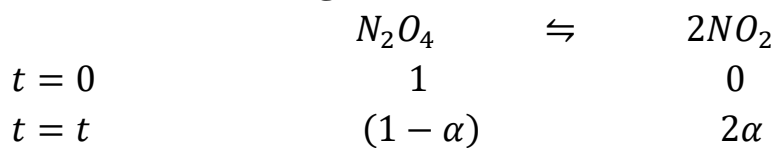
2.7.2.17. Thermodynamic treatment of law of mass of action:

As per thermodynamics, we say that, for the feasibility of any chemical reaction we need to know the value of change in Gibb's free energy (ΔG).

We know for any spontaneous reaction $\Delta G = -ve$

Now, according to Van't Hoff reaction isotherm,

$$\Delta G = -RT \ln K_p$$

2.7.2.18. In form of degree of dissociation:

Total no of moles = $(1 - \alpha) + 2\alpha = (1 + \alpha)$

$$K_p = \frac{(2\alpha)^2}{(1-\alpha^2)} P = \frac{4\alpha^2}{(1-\alpha^2)} P$$

2.7.2.19. Temperature dependence of equilibrium constant:

Using the two famous equation

$$\Delta G = -RT \ln K_p$$

$$\text{And, } \ln K_p = \frac{-\Delta G^0}{RT}$$

We can correlate and say

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^0}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$



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2.7.3. Heterogeneous equilibrium and Phase rule

At a Glance

Phases, Components, degree of freedom, various phase diagrams, eutectic mixture etc.



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Key Statements

Basic Key Statements: Introduction (2.7.3.1), Explanation of various types of equilibrium (2.7.3.2)

Standard Key Statements: Component (C) (2.7.3.3), Degree of freedom (F) (2.7.3.4), First order phase transition (2.7.3.5)

Advance Key Statements: Phase diagram (2.7.3.6), Eutectic Systems (2.7.3.7)



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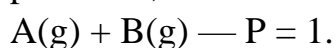
Key Facts

2.7.3.1. Introduction:

Phase is a homogeneous physically distinct and mathematically separable part of a system and dynamic equilibrium with the other parts through the transition of substances.

2.7.3.2. Explanation of various types of equilibrium:

- i. Mixture of gases is always homogeneous and constitutes single phase i.e., $P = 1$



But if is Vander wall force of $\underbrace{A(g)}_{\text{liquify easily}} \gg \underbrace{B(g)}_{\text{liquify hardly}}$

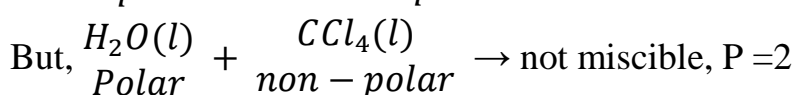
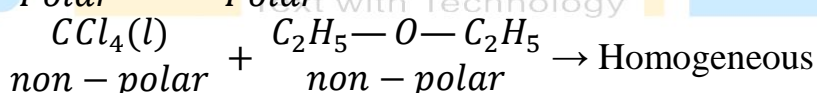
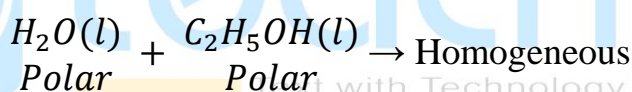
Therefore, $P = 2$

- ii. Colloidal solutions are heterogeneous.

Therefore, $P = \text{number of solute} + \text{solvent}$

- iii. True or aqueous solution is always homogeneous, therefore $P = 1$.

- iv. Two polar solvents or non polar solvent is always homogeneous, $P = 1$.



- v. A gas is constitute of a liquid generally constitutes separate phase
 $SO_2(g) + H_2O(l) \rightarrow P = 2$.

But as the dipole moment of gas increases solubility of gas in water increases, $P = 1$.

- vi. In saturated solution excess solid is in contact with aqua solution, $P = 2$.

e.g., Saturated solution of sugar.

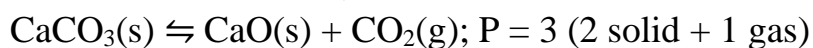
Below saturation only aqueous sugar, $P = 1$.

- vii. In a mixture of solid; $P = \text{number of solids}$

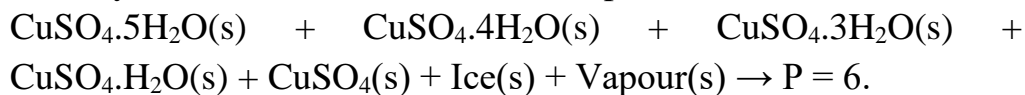
- viii. In an allotropic mixture, $P = \text{number of allotropes}$.

- ix. An alloy is always homogeneous; $P = 1$

- x. In a chemical reaction, P = different chemical substance



- xi. Each hydrate in a solution constitutes a phase.



2.7.3.3. Component (C):

The minimum number of constituents (i.e., molecular species) sufficient for determining the composition of all the phase of the system.

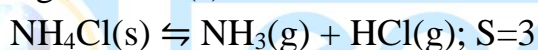
Every substance that can be separated from a system and exist outside of it, is called constituent.

Number of component (C) = Constituent (S) – Equation relating them (R)

If ions are present, then electro neutrality condition (positive ion = negative ion)

$$C = S - (R+1)$$

e.g., $\text{NH}_4\text{Cl}(\text{s})$ is heated in a closed vessel



(a) NH_3 and HCl are present in equimolar ratio $[\text{NH}_3]=[\text{HCl}]$

$$R = 2, \text{ then } C = 3-2=1$$

(b) If in the vessel NH_3 so HCl are present, then $[\text{NH}_3] \neq [\text{HCl}]$

$$R = 1 \text{ i.e., } C = 2.$$

2.7.3.4. Degree of freedom (F):

The minimum number of independent variables, such as temperature, pressure and concentration which are utilised to characterize the system completely.

$$F = C - P + 2$$

2.7.3.5. First order phase transition:

Clapeyron equation is applicable and only one variable temperature or pressure or concentration is used to define a system.

Melting, vaporization, sublimation etc.

- **Melting:**

As heat is absorbed during melting, $\Delta H_f = +ve$

Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta H}{T_f(V_l - V_s)}$, we all know that, $V_l < V_s$ i.e.,

$V_l - V_s = -ve$. Therefore, $\frac{dP}{dT} = -ve$.

Thus on increasing pressure, melting point of ice decreases.

- **Vaporization:**

As heat is absorbed during vaporising, $\Delta H_f = +ve$

Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta H}{T_f(V_g - V_l)}$, we all know that, $V_g \gg V_l$ i.e.,

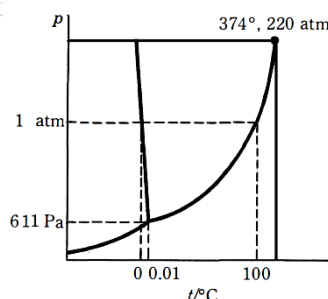
$V_g - V_l = +ve$. Therefore, $\frac{dP}{dT} = +ve$.

Thus on increasing pressure, boiling point of water decreases.

2.7.3.6. Phase diagram:

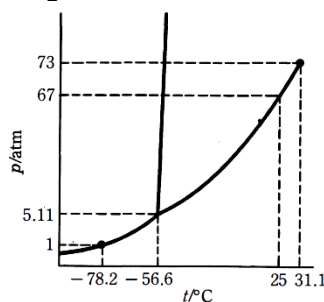
A. One component system:

❖ Phase diagram of H_2O :



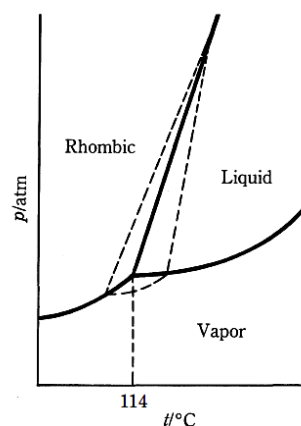
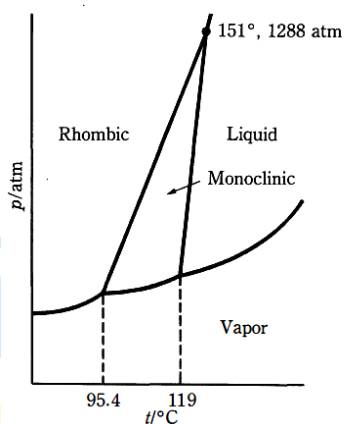
Along the curves, $F = 1 - 2 + 2 = 1$

At the triple point, $F = 1 - 3 + 2 = 0$

❖ Phase diagram of CO₂:

Along the curves, $F = 1 - 2 + 2 = 1$

At the triple point, $F = 1 - 3 + 2 = 0$



❖ Phase diagram of sulphur:

Along the curves, $F = 1 - 2 + 2 = 1$

At the triple point, $F = 1 - 3 + 2 = 0$

Along the curve, $F = 1 - 1 + 2 = 2$

B. Two component system:

For two component system the phase rule becomes $F = C - P + 2 = 4 - P$

The minimum number of phases, P in the system is 1.

So, for two component system,

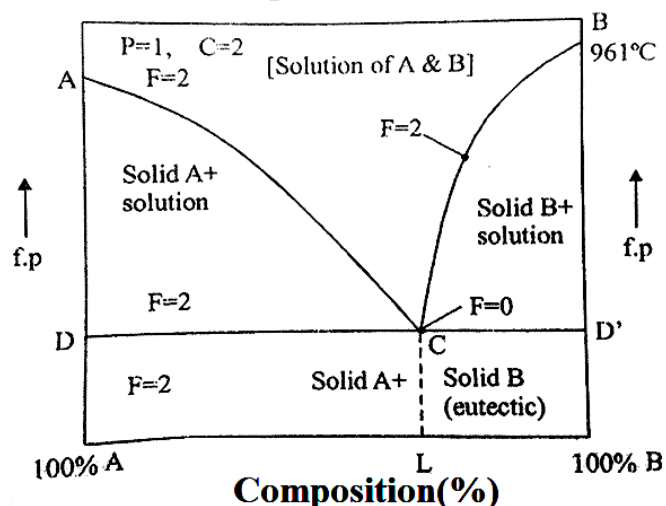
$$F_{max} = 2 - 1 + 2 = 3$$

The maximum number of the degree of freedom, F is 3.

2.7.3.7. Eutectic Systems:

A liquid mixture of two components, which has lowest freezing point (thus easily melt) compared to all other liquid mixtures and on cooling such a mixture, both the components separate out as solid phases.

The temperature at eutectic point is called eutectic temperature (T_E)



Calculation of Eutectic point and composition:

For the two substance, A and B the composition can be expressed:

$$d \ln x_A = \left(\frac{\Delta H_{fus,A}}{RT^2} \right) dT$$

$$d \ln x_B = \left(\frac{\Delta H_{fus,B}}{RT^2} \right) dT$$

By integrating the above two equations using limits, $T=T_{fus}$, $T=T_e$, the eutectic point, to obtain the following equation

$$-\ln(x_A)_e = \frac{\Delta H_{fus,A}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{m,A}} \right)$$

$$-\ln(x_B)_e = \frac{\Delta H_{fus,B}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{m,B}} \right)$$

Using the above two equations, we can calculate the eutectic point, T_e , and composition, $(x_A)_e$ and $(x_B)_e$.

2.7.4. Ideal and Real Gas

At a Glance

Postulates of kinetic theory of gas, three types' velocities, limiting density, vapour density, Maxwell's velocity distribution equation, Molar Heat capacity, Equipartition of energy, viscosity, critical states, Different types of gas equation reveals with critical phenomena.



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Key Statement

Basic Key Points: Postulates of kinetic theory of gas (2.7.4.1), Root mean square (r.m.s) velocity ($C_{r.m.s}$) (2.7.4.2), Average velocity (2.7.4.3), Most probable velocity (2.7.4.4), Limiting density (2.7.4.15), Abnormal vapour density (2.7.4.18), Vander Wall's equation (2.7.4.62), Significance of Vander Waals constant a & b (2.7.4.63/64),

Standard Key Point: Concept of temperature from kinetic theory of gas (2.7.4.8), Maxwell distribution in three dimensional space (2.7.4.26), Principle of Equipartition of energy (2.7.4.34/35/36), Critical temperature of the gas (T_c) (2.7.4.48), Andrew's experiment (2.7.4.53), Dieterici equation (2.7.4.74/75/76/77), Berthelot equation of state (2.7.4.78/79/80)

Advance Key Point: Characteristics features of maximum speed distribution for three dimensions (2.7.4.27), Distribution of kinetic energy (2.7.4.28), Amagat's curve (2.7.4.57), Compressibility factor (2.7.4.59), Reduced equation of state (2.7.4.72),



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Key Facts

2.7.4.1. **Postulates of kinetic theory of gas:** Clausius, Maxwell, Boltzmann and many scientists put forward some postulates regarding behavior of gas molecule. The postulates are-

- All gases consist of large number tiny discrete particle called molecules. All molecules of a particular gas are equal in shape, size and mass.
- Gas molecules are always in random motion. They move in all possible direction in a straight line.
- During motion the gas molecules collide with each other and with the wall of the container.
- Collisions are perfectly elastic in nature.
- Pressure of a gas is due to the collision of the gas molecules on the wall of the container.
- Gas molecules are point masses, their actual volume is negligible in comparison to that the container.
- There is no force of attraction and repulsion between the gas molecules.
- Kinetic energy of a gas is directly proportional to the absolute temperature.

From postulates of kinetic theory, the Kinetic gas equation is

$$PV = \frac{1}{3}mnc^2 = \frac{2}{3}N \times \frac{1}{2}m\overline{c^2} = \frac{2}{3}N\epsilon$$

Where,

$\overline{c^2}$ = mean square velocity

m = mass of each molecule

N = total number of gas molecules

P = pressure of gas

V = volume of gas

ϵ = average translational kinetic energy of a gas molecule.

2.7.4.2. Root mean square (r.m.s) velocity ($C_{r.m.s}$): Average of the square of the velocities of different gas molecules is called mean square velocity. Square root of mean square velocity is called root mean square velocity.

$$C_{r.m.s} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}} \text{ where, } k = \text{Boltzmann Constant} = 1.38 \times 10^{-23}.$$

2.7.4.3. Average velocity (C_a): Average velocity is the simple average of the velocities of different gas molecules.

$$C_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

2.7.4.4. Most probable velocity (C_{mp}): For a particular gas maximum number of molecules move with a particular velocity at particular temperature. This velocity is called most probable velocity of the gas at that temperature.

$$C_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$$

2.7.4.5. Comparison among different velocities:

$$C_{mp} : C_a : C_{rms} = 1 : 1.128 : 1.224$$

$$\text{So, } C_{mp} < C_a < C_{rms}$$

2.7.4.6. Advantage or importance of rms velocity over average velocity:

- In root mean square velocity the direction of the velocities become immaterial as only the squares of their magnitudes are considered.
- Actual kinetic energy of a gas is obtained using root mean square velocity, not by using average velocity.
- The velocity used in the Kinetic gas equation is root mean square velocity.

2.7.4.7. In calculating the average kinetic energy of a molecule one used the formula $E = \frac{1}{2}mc^2$, taking c as the average speed. There is an error.

$$\% \text{ of error} = \frac{\frac{1}{2}mc_{rms}^2 - \frac{1}{2}mc_a^2}{\frac{1}{2}mc_{rms}^2} \times 100 = 15.07$$

2.7.4.8. Concept of temperature from kinetic theory of gas: According to the kinetic theory of gas, temperature is a measure of the average translational kinetic energy.

$$E = \frac{3}{2} nRT$$

For one mole gas $E = 3/2 RT = 3/2 kT$.

If two different ideal gases are at same temperature in absolute scale, they have same average translational kinetic energy.

Thus temperature in absolute scale is the manifestation of the average translational kinetic energy of the molecule.

2.7.4.9. Concept of absolute zero temperature from kinetic theory of a gas: For Kinetic gas equation $PV = \frac{1}{3} mn\overline{c^2}$, it can be proved that total translational kinetic energy of n mole ideal gas $E = 3/2 nRT$ and average translational kinetic energy of a molecule $\epsilon = 3/2 kT$. Hence temperature is a function of translational kinetic energy. Translation of kinetic energy is proportional to temperature in absolute scale. If $T = 0K$, $E = 0$. Therefore absolute zero temperature is the temperature at which the gas molecules are at completely rest.

2.7.4.10. Boyle's law: In a given amount of gas N remains constant. Hence at constant temperature for a given amount of gas, $PV = \text{constant}$.

$$V \propto \frac{1}{P}$$

2.7.4.11. Charle's law: At constant pressure for a given amount of gas,

$$V \propto T$$

2.7.4.12. Ideal gas equation for n mole gas:

$$PV = nRT$$

2.7.4.13. Graham's law of diffusion:

$$r_d \propto \frac{1}{\sqrt{\rho}}$$

ρ = density of the gas

r_d = rate of diffusion.

2.7.4.14. Dalton's law of partial pressure:

$$P = P_A + P_B + P_C$$

Where, P_A , P_B , P_C are partial pressure of A, B, C gas respectively.

2.7.4.15. **Limiting density:** The ratio of density and pressure of a gas remaining at pressure very close to zero is called limiting density of the gas.

$$\text{So, limiting density} = \left(\frac{\rho}{P} \right)_{P \rightarrow 0}$$

2.7.4.16. **Relation between normal density and limiting density of gas:**

$$\text{Limiting density} = \text{normal density} \times \frac{PV}{P_0V_0}$$

Where,

P = pressure of a gas

V = volume of a gas

P₀ = extremely low pressure

V₀ = volume of the gas at extremely low pressure

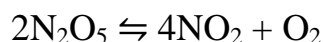
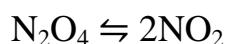
2.7.4.17. **Vapour Density:** The ratio of the weight of a given volume gas or vapour of a substance to that of the same volume of hydrogen measured under similar conditions of temperature and pressure is called the vapour density of the gas or the substance.

2.7.4.18. **Abnormal vapour density:** We know vapour density (D) is half of molecular weight (M/2) and it does not depend on temperature.

But there are some substances of which observed densities are different from the theoretical value and the observed value changes with the change of temperature at constant pressure. Vapour density of such substances is known as abnormal vapour density.

Abnormal vapour density is due to either dissociation or association of the substances.

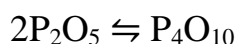
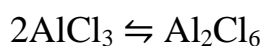
Due to thermal dissociation of N₂O₄, NH₄Cl, PCl₅, N₂O₄ etc. observed vapour density of these substances is less than actual value.



Due to dissociation of the above substance total number of moles increases. So, at constant pressure during dissociation volume increases. As a result density as well as vapour density of the substance decreases. With increasing temperature dissociation increases. Therefore vapour density

decreases with increasing temperature and it will be the minimum after complete dissociation of the substance. Therefore observed density of a substance depends on degree of dissociation (α).

For substances like aluminium chloride, Phosphorus pentoxide etc. observed vapour density is higher than theoretical value. It is due to association of the above substances.



Due to association total number of moles decreases, therefore volume decreases at constant pressure. As a result density as well as density increases. Here observed people density depends on degree of association (β).

2.7.4.19. Relation between observed vapour density and degree of dissociation:

$$\alpha = \frac{D_0 - D}{D(n - 1)}$$

D_0 = vapour density of pure substance

D = experimental vapour density

2.7.4.20. Relation between observed vapour density and degree of association:

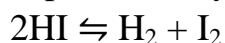
$$\beta = \frac{D_0 - D}{D\left(\frac{1}{n} - 1\right)}$$

D_0 = vapour density of pure substance

D = experimental vapour density

2.7.4.21. Dissociation of a substance does not always show abnormal vapour density.

In many cases during dissociation number of moles does not change. Therefore volume remains unchanged. So density as well as vapour density will remain unchanged.



2.7.4.22. Distribution of molecular speed: The gaseous state of matter is the most chaotic state where the molecules are always in random motion. The speed of a molecule of a gas changes continuously as a result of collision with other molecules. Thus it is not possible to maintain the speed of an individual molecule; rather one must consider the statistical average of the speeds of the whole collection of gas molecules. It shows range of velocities from 0 to infinity. This is actually distribution of molecular speed.

2.7.4.23. Assumption for Maxwell's law of distribution of molecular speed:

- All the basic assumptions of kinetic theory are considered to be valid.
- Gas is supposed to be perfectly isotropic in nature.
- Gas is supposed to be free from any external force field, so that number density is same everywhere.
- Gas is supposed to be in the steady state i.e., number of molecules moving with a given velocity is constant though a particular molecule may change its velocity.

2.7.4.24. Maxwell's velocity in one dimensional distribution:

$$F(u) = \frac{1}{n} \frac{dn_u}{du} = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mu^2/kT}$$

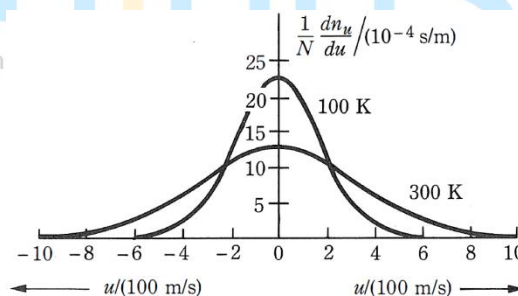


Figure x component distribution in nitrogen.

2.7.4.25. Maxwell's velocity for Speed distribution in two dimension:

$$\frac{1}{n} \frac{dn_c}{dc} = 2\pi \left(\frac{m}{2\pi kT} \right) c e^{-mc^2/kT}$$

2.7.4.26. Maxwell distribution in three dimensional space:

$$\frac{1}{n} \frac{dn_c}{dc} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2/kT}$$

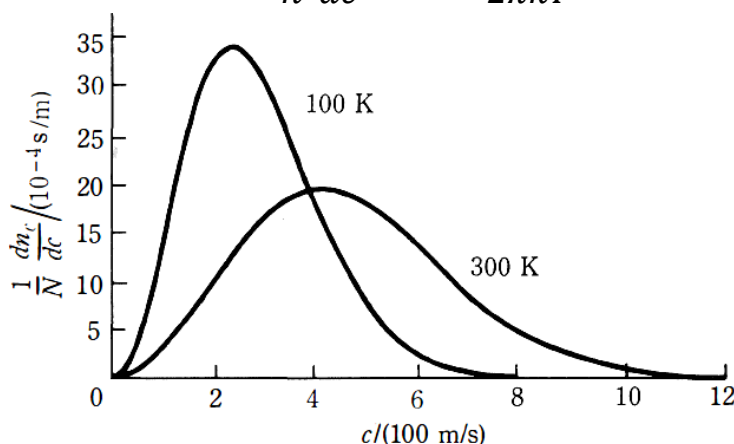


Figure Maxwell distribution for nitrogen at two temperatures.

dn_c = number of molecules moving between narrow speed range c and $c + dc$

n = total number of molecules

dn_c/n = fraction of total number of molecules moving between narrow speed range c and $c + dc$.

$\frac{1}{n} \frac{dn_c}{dc}$ represent the probability of finding the molecules for unit speed width in the narrow speed range c and $c + dc$ and is called the speed distribution function.

m = mass of each molecule

k = Boltzmann constant

T = temperature of gas in absolute scale.

2.7.4.27. Characteristics features of maximum speed distribution for three dimension:

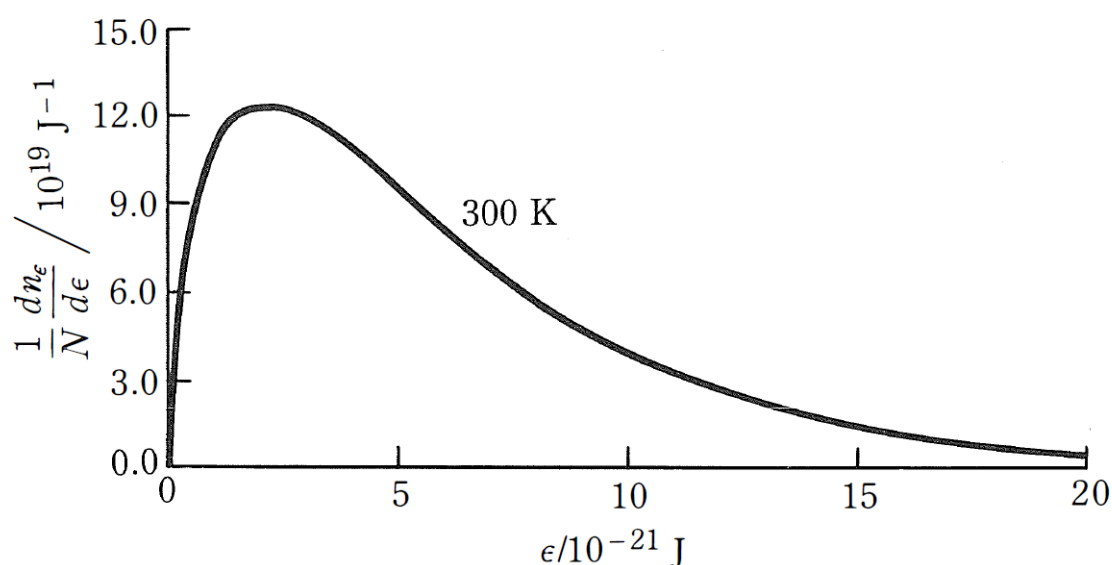
- No molecules of a gas are as completely rest or at infinite velocity as $\frac{1}{n} \frac{dn_c}{dc} = 0$, when $c = 0$ or ∞ .
- The curve has maxima. The velocity corresponding to the peak represent the velocity possessed by maximum number of molecules. This velocity is called most probable velocity.
- Total area under the curve is always equal to unity.

- Maxwell's velocity distribution plot depends on temperature and the molecular weight of gas.
- For a particular gas, the increase of temperature has different effects on the probability of finding molecules at low and high speed range. The probability of finding the molecules in the lower speed range decreases while that in the higher speed range increases with the increase of temperature. Therefore with increasing temperature the curve flattens, the most probable velocity increases but number of molecules with most probable velocity decreases.
- At a given temperature, the speed distribution curve flattens as molecular mass of gas decreases. Therefore for lighter gas the curve flattens compare to heavier gas; most probable velocity for gas molecules will be more.
So the speed distribution curve for heavier molecules runs below the curve for lighter molecules at higher speed.

2.7.4.28. Distribution of kinetic energy:

$$\frac{1}{n} \frac{dn_{\epsilon}}{d\epsilon} = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT} \right)^{3/2} \epsilon^{1/2} e^{-\epsilon/kT}$$

$\frac{1}{n} \frac{dn_{\epsilon}}{d\epsilon}$ represent the probability of finding the molecules per unit energy gap



moving with kinetic energy ranging between ϵ to $\epsilon + d\epsilon$.

2.7.4.29. Barometric distribution law: Due to gravitational force number density of the gas in the atmosphere decreases with increase in height. The equations which explain the variation of pressure of gas in atmosphere with height is known as Barometric distribution law.

$$P = P_0 e^{-\frac{Mgh}{RT}}$$

P = pressure of the gas in atmosphere at height h .

P_0 = pressure at ground level.

M = Molar mass.

The equation shows that the pressure decreases with increasing height. It also indicates that P/P_0 value at particular height is larger at higher temperature than at lower temperature. At infinite temperature the pressure is same everywhere in the column of atmosphere.

The equation also shows that decreases with increasing height and P/P_0 value at a particular height is larger for lighter gas compare to heavier gas.

Therefore relative amount of the lighter gases are higher at upper atmosphere.

2.7.4.30. Molar heat capacity at constant volume (C_v): The amount of heat required to raise the temperature of one mole gas by 1 degree at constant volume is known as molar heat capacity at constant volume.

C_v = increase in translational kinetic energy + increase in intramolecular energy

$$= \frac{3}{2}R + a$$

2.7.4.31. Molar heat capacity at constant pressure (C_p): The amount of heat required to raise the temperature of one mole gas by 1 degree at constant pressure is known as heat capacity at constant pressure.

C_p = increase in translational kinetic energy + increase in intramolecular energy + mechanical work done due to increase in volume

$$= \left[\frac{3}{2}R(T + 1) - \frac{3}{2}RT \right] + a + R$$

$$= \frac{3}{2}R + a + R$$

$$= \frac{5}{2}R + a$$

2.7.4.32. Molar heat capacity at constant pressure is greater than molar heat capacity at constant volume

$$C_p - C_v = R$$

2.7.4.33. Heat capacity ratio (γ) = $C_p/C_v = (5/2R+a)/(3/2R+a)$

For a monoatomic gas there is not rotational and vibrational energy. So, $a = 0$.

Hence for monoatomic gas $\gamma = (5/2R)/(3/2R) = 5/3 = 1.66$

As atomicity of the molecules increases, intramolecular energy (a) increases, hence the value of γ decreases.

At room temperature, the experimental value of γ for diatomic molecule ≈ 1.40 . At very high temperature experimental value is 1.285.

Values of heat capacities or γ obtained from principle of equipartition of energy are called high temperature limiting value.

2.7.4.34. Principle of Equipartition of energy:

The total energy of a molecule is equally distributed among the different degrees of freedom and the amount of energy being associated with each degree of freedom being equal to $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per mole.

Degrees of freedom are the total number of independent quadratic terms required to express the total energy of a molecule.

2.7.4.35. For n atomic molecule total degrees of freedom = $3n$.

Among those,

Translational degrees of freedom = 3

Rotational degrees of freedom = 2 for linear molecule and 3 for Non linear molecule.

Vibrational degrees of freedom = $(3n - 5)$ for linear molecule and $(3n - 6)$ for Non linear molecule.

2.7.4.36. Calculation of molar heat capacity values of a diatomic molecule:

For diatomic molecule degrees of freedom = $3n = 3 \times 2 = 6$

Among them,

Translational degree of freedom = 3

Rotational degrees of freedom = 2

Vibrational degrees of freedom = $6 - (3 + 2) = 1$

Total energy $E/\text{mole} = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}} = (3 \times \frac{1}{2}RT) + (2 \times \frac{1}{2}RT) + (2 \times \frac{1}{2} \times RT) = 7/2RT$

So, $\left(\frac{dE}{dT}\right)_V = 7/2R$

$C_p = C_v + R = 9/2R$

Heat capacity ratio (γ) = $C_p/C_v = 9/7 = 1.285$

2.7.4.37. To activate the vibrational degree of freedom N_2 require more energy than Cl_2 . At ordinary temperature the energy is sufficient for Cl_2 but not sufficient for N_2 . So that, energy per mole for N_2 is always found to be less than that of Cl_2 at ordinary temperature. Therefore, C_v value for N_2 is less than that of Cl_2 at ordinary temperature.

2.7.4.38. Wall collision frequency (Z_w) = $\frac{1}{4}nC_a$

n = number of molecules per cc

C_a = average velocity of the molecules

2.7.4.39. Number density (n) = $PN_0/RT = P/kT$

2.7.4.40. Graham's law of effusion:

Rate of effusion $\propto \frac{1}{\sqrt{M}}$

2.7.4.41. Collision frequency (Z) = $\frac{1}{\sqrt{2}}\pi\sigma^2C_aN^2$

2.7.4.42. Free path and mean free path: The path travelled by a molecule between two successive collisions is called free path. Average of all such free paths executed in one second is called mean free path (l).

Mean free path (l/λ) = $\frac{1}{\sqrt{2}\pi\sigma^2n}$

2.7.4.43. Three body collisions: Two body collisions occurs frequency in gaseous system but the occurrence of three body collision in gaseous system is rare.

$Z_{111}/Z_{11} = 1 : 1000$

2.7.4.44. **Binary collision (Z)** $\propto P^2$ when T constant

$Z \propto 1/T^{3/2}$ when P constant

2.7.4.45. **Mean free path (l)** $\propto T$, when P constant

$l \propto 1/P$, when T constant

2.7.4.46. **Viscosity and coefficient of viscosity:** The resistance to flow exhibited by a fluid is known as viscosity. Viscosity is due to internal friction between layers of earth as they pass over each other moving with different velocities.

$$f = -\eta \cdot A \cdot \frac{dV}{dR}$$

η is proportionality constant, called the coefficient of viscosity.

Coefficient of viscosity defines as the internal friction between the layers of fluid of unit area of constant and velocity gradient is also unit.

Dimension of η : $ML^{-1}T^{-1}$

Unit of η :

C.G.S unit \rightarrow poise (dyne.sec.cm⁻²)

S.I unit \rightarrow pas (Newton.sec.m⁻²)

1 pas = 10 poise.

2.7.4.47. **Relation between mean free path and coefficient of viscosity of a gas:**

$$\eta = \frac{1}{3} \rho C_a \lambda$$

This relation does not valid at extremely low pressure.

At a particular pressure, $\eta \propto \sqrt{T}$.

According to Champman,

$$\eta = \frac{1}{2} \rho C_a \lambda$$

2.7.4.48. **Critical temperature of the gas (T_c):** For every gas there is a temperature above which liquification is impossible whatever the pressure be. The limiting temperature above which liquification is impossible is called the critical temperature of the gas.

$$T_c = \frac{8a}{27Rb}$$

2.7.4.49. **Critical pressure of the gas (P_C):** The minimum pressure necessary to liquefy a gas at the critical temperature is called the critical pressure.

$$P_C = \frac{a}{27b^2}$$

2.7.4.50. **Critical volume of the gas (V_C):** The volume occupied by one gram mole of a gas at the critical temperature and pressure is called the critical volume.

$$V_C = 3b$$

2.7.4.51. **Critical state:** A substance remaining at critical temperature and critical pressure is called at critical state.

2.7.4.52. **Critical coefficient of gas:**

$$\frac{RT_C}{P_C V_C} = \frac{8}{3}, \text{ a constant quantity.}$$

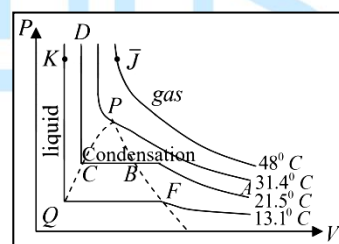
So, $\frac{RT_C}{P_C V_C}$, it is constant for any gas, known as critical coefficient of gas.

Compressibility factor at critical state

$$Z_C = \frac{P_C V_C}{RT_C} = \frac{3}{8}$$

2.7.4.53. **Andrew's experiment:**

From A to B, CO_2 behaves as a gas. At point B, the liquification of the gas just starts. The gas condenses at constant pressure from B to C, so that liquid and vapour phase co-exist. At C, the gas is completely in the liquid phase. From C to D, the slope is very steep since a liquid is almost incompressible.

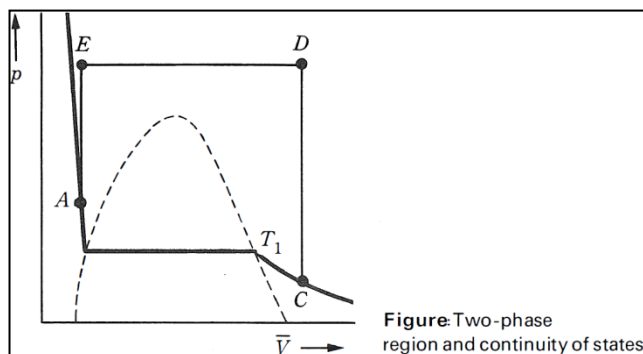


Conclusion: The temperature at which it becomes possible to liquefy a gas under compression is known as critical temperature (T_C) [In Andrews' experiment) $T_C = 48^\circ\text{C}$], corresponding pressure and volume is known as critical pressure [P_C] and critical volume [V_C].

A gas can be liquified only if it is cooled upto or below its characteristic critical temperature.

There exist a continuity of liquid and gaseous states, i.e. they are two distinct stages of a continuous physical phenomenon.

2.7.4.54. Continuity of state: It is always possible to make a sharp distinction between states of the system in which one phase is present and states in which two phases coexist in equilibrium, that is, between those points on and under the "dome" and those outside the "dome." However, it should be noted that there is no dividing line between the liquid states and the gaseous states. The fact that it is not always possible to distinguish between a liquid and a gas is the principle of continuity of states.



2.7.4.55. Coefficient of thermal expansion:

Coefficient of thermal expansion (α) is given by,

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P$$

i.e., increase in volume per unit volume due to increase in temperature at constant pressure.

For ideal gas, $\alpha = 1/T$

So, at a particular temperature α for all gases should be same, if they behave ideally. But actually α is different for different gas. So the equation $PV = nRT$ is not obeyed by the gas i.e., the gas is not ideal.

2.7.4.56. Coefficient of compressibility: The coefficient of compressibility (β) of a gas is given by,

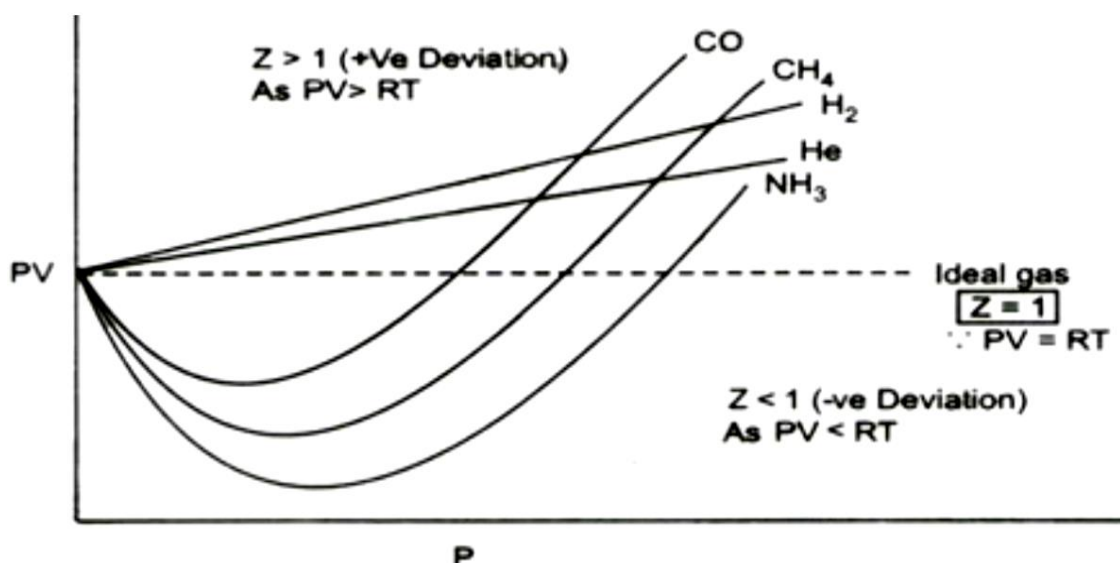
$$\beta = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$$

i.e., decrease in volume per unit volume due to unit increase in pressure at constant temperature.

For ideal gas, $\beta = 1/P$

So, at a particular pressure β for all gases should be same, if they behave ideally. But actually β is different for different gas. So, the equation $PV = nRT$ is not obeyed by the gas i.e., the gas is not ideal.

2.7.4.57. Amagat's curve:



Graph showing deviation of gases from ideal gas

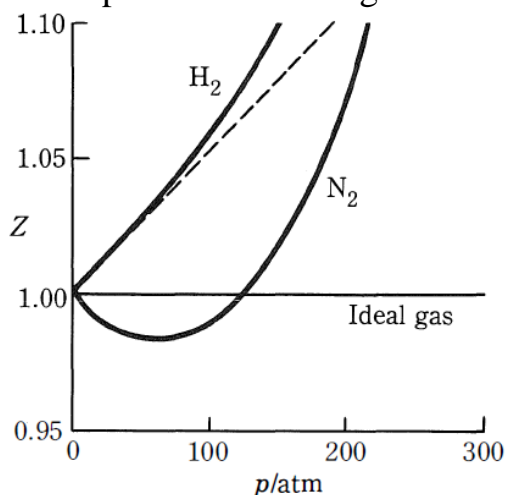
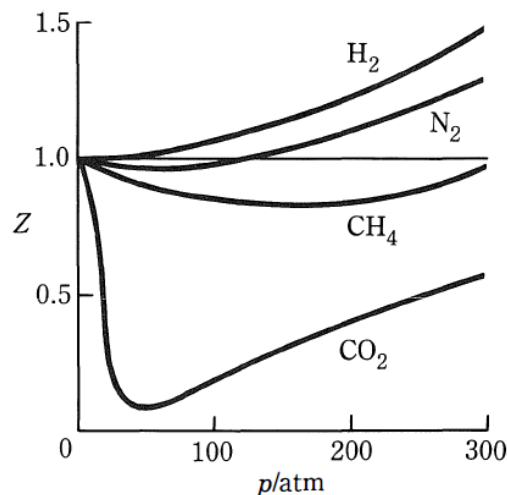
2.7.4.58. **Boyle temperature:** For every gas there is a characteristic temperature at which the gas obeys Boyle's law i.e., PV vs P curve runs parallel to P axis for an appreciable range (0 to moderate value) of pressure. This temperature is called Boyle's temperature.

At Boyle's temperature (T_B), $\frac{d(PV)}{dP} = 0$; $T_B = \frac{a}{Rb}$

2.7.4.59. **Compressibility factor (deviation from ideal behaviour):** A more convenient way of showing the deviation from ideality is in terms of compressibility factor, denoted by Z. Compressibility factor is defined as the ratio of observed volume to the ideal volume.

$$Z = \frac{V_{obs}}{V_{ideal}} = \frac{V_{obs}}{nRT/P} = \frac{PV_{obs}}{nRT}$$

Z vs P plot for different gases

Plot of Z versus p for H_2 , N_2 , and ideal gas at 0°C .Plot of Z versus p for several gases at 0°C .

- For an ideal gas $Z = 1$ and is independent of temperature and pressure.
- At very low pressure Z is approximately equal to 1 for different gases.
- As pressure increases, the compressibility factor for H_2 and He increases gradually.
- For gases like N_2 , CH_4 , CO_2 etc. with increasing pressure Z decreases in the lower pressure region, passes through a minimum and then Z increases at higher pressure region.
- When $Z > 1$ the gas is less compressible compare to ideal gas and cannot be liquefied.
- The gas is more compressible compare to ideal gas and can be liquefied if $Z < 1$.

2.7.4.60. **The expression of Z for a Vander Waals gas in terms of a , b , P and T :**

$$Z = 1 + \frac{P}{RT} \left(b - \frac{a}{RT} \right) + \frac{abP^2}{R^3T^3}$$

2.7.4.61. Reason for deviation from ideal behaviour: The ideal gas laws derived from the kinetic theory of gas are based upon two important assumptions.

- The volume occupied by the gas molecule is negligible in comparison to the total volume occupied by the gas.
- The molecules do not exert any force of attraction on each other.

The observed deviation from ideal behaviour appears to be a consequence of the failure of these assumptions. It is because neither of these assumptions can be regarded as applicable to real gases.

2.7.4.62. Vander Wall's equation for n mole of gas:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Where,

a = It measures the force of attraction between the molecules.

b = co-volume or excluded volume per mole.

2.7.4.63. Significance of Vander Waals constant a:

Value of 'a' of a gas gives the idea about the force of attraction between the molecules. If 'a' is high, the force of attraction among the molecules is also high and the gas can be easily liquefied.

Unit: atm.lit²/mole²

S.I unit: Pascal.met⁶/mole² i.e., Nm⁴mole⁻²

Dimension: ML⁵mole⁻¹

2.7.4.64. Significance of Van-der Waals constant b:

'b' is the excluded volume or co-volume of a gas per mole. The value of 'b' gives the idea about the volume occupied by the gas molecule. If r is the radius of a molecule,

$$b = 4N \times \frac{4}{3}\pi r^3$$

b is also known as repulsion factor.

Unit: lit/mole

S.I unit: m³mole⁻¹

Dimension: L³mol⁻¹

If the value of 'a' and 'b' of a gas is high, then its deviation from ideal behaviour is also high.

2.7.4.65. **A real gas in a given container tends to behave more ideal as the temperature is raised.** As temperature increases velocity of the gas molecules as well as volume of the gas increases. So, with increasing temperature force of attraction between the molecules i.e., the value of 'a' diminished. Therefore, a real gas behaves more ideally as the temperature is raised.

2.7.4.66. **Condition for ideal behaviour of a gas:**

- Extremely low pressure
- Extremely high temperature

2.7.4.67. **Virial form of Vander Walls' equation:**

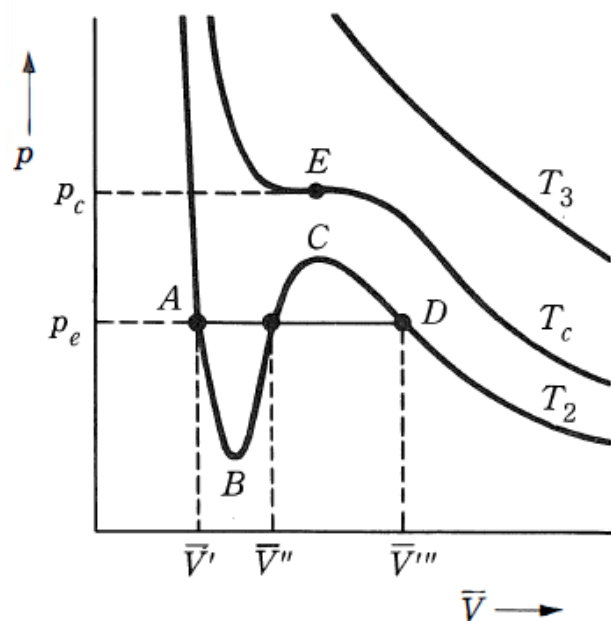
$$PV = nRT \left[1 + \left(nb - \frac{na}{RT} \right) \frac{1}{V} + n^2 b^2 \frac{1}{V^2} + \dots \right]$$

Where, 2nd virial $B = \left(nb - \frac{na}{RT} \right)$ and 3rd virial $C = n^2 b^2$.

2.7.4.68. **The value of critical constants from Vander Waals equation:**

$$T_c = \frac{8a}{27Rb}; P_c = \frac{a}{27b^2}; V_c = 3b$$

2.7.4.69. **P vs V curve from Vander walls equation:**



Isotherms of the van der Waals gas.

2.7.4.70. Demerits of Vander Waals equation:

- Vander Waals constants 'a' and 'b' are not strictly constants. Their value change slightly with temperature.
- Plot of P vs V according to Vander Waals equation does not coincide with the experimental plot below the critical temperature.
- Critical volume calculated from Vander Waals equation is 3b, but its experimental value is 2b.
- The value of $RT_c/P_c V_c = 2.66$ obtained from Vander Waals equation, but its exact value is 3.69.

2.7.4.71. Equation of state: The equation which gives the relation between the temperature, pressure, volume and number of moles of a gas is called equation of state.

2.7.4.72. Reduced equation of state: Gaseous equation containing only the reduced parameters is called the reduced equation of state. It is so called as from this equation we get the idea about the state of the gas.

Reduced parameter is obtained by dividing normal parameter by critical temperature.

Reduced equation of state since that gas dependent parameters (a and b) are removed. But these parameters are not actually removed, they remain in hidden form. It is because reduced parameter depends on critical parameter and critical parameter depends on gas dependent parameters.

The reduced equation of state for Vander Waals equation is,

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$

2.7.4.73. Utility or importance or significance of reduced equation of state:

- Reduced equation of state does not contain any gas dependent term like 'a' and 'b'. So, this equation is applicable to all gases.
- According to reduced equation of state if same moles of two gases have the same values of reduced pressure and reduced temperature, they will have the same reduced volume. This is known as **law of corresponding state**.

2.7.4.74. **Dieterici equation of state:**

$$P = \frac{nRT}{V - nb} \cdot e^{-\frac{na}{RTV}}$$

2.7.4.75. **Virial form of Dieterici equation:**

$$PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right)$$

$$\text{Where, 2}^{\text{nd}} \text{ virial } B = \left(b - \frac{a}{RT} \right); \text{ 3}^{\text{rd}} \text{ virial } C = \left(b^2 - \frac{ab}{RT} + \frac{a^2}{2R^2T^2} \right)$$

2.7.4.76. **Critical constants from Dieterici equation:**

$$T_C = \frac{a}{4Rb}; P_C = \frac{a}{4Rb^2} e^{-2}; V_C = 2b$$

2.7.4.77. **Dieterici Reduced equation of state:**

$$\pi = \frac{\theta}{2\phi - 1} e^{2\left(1 - \frac{1}{\theta\phi}\right)}$$

2.7.4.78. **Berthelot equation of state:**

$$\left(P + \frac{n^2 a}{TV^2} \right) (V - nb) = nRT$$

2.7.4.79. **Virial form of Berthelot equation:**

$$PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right)$$

Where,

$$\text{2}^{\text{nd}} \text{ virial } B = b - \frac{a}{RT^2}; \text{ 3}^{\text{rd}} \text{ virial } C = b^2$$

2.7.4.80. **Critical constants from Berthelot equation:**

$$T_C = \frac{8a}{27Rb}; P_C = \frac{a}{27Rb^2}; V_C = 3b$$

2.7.5. Dilute Solution and Colligative Properties

At a Glance

Colligative property, their types, and also in details for the study of Colligative properties individually.



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Key Statements

Basic Key Statements: Colligative property (2.7.5.1), Ideal and real solution (2.7.5.6)

Standard Key Statements: Relative lowering of Vapour pressure (2.7.5.2), Elevation of Boiling point (2.7.5.3), Depression of Freezing point (2.7.5.4), Osmotic pressure (2.7.5.5)

Advance Key Statements: Abnormal Colligative property (2.7.5.7), Van't Hoff's factor (2.7.5.8)



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Key Facts

2.7.5.1. Colligative property:

The properties of a solution which depends only upon the number of solute particle present in it.

Mainly four are of them-

- ❖ Relative lowering of Vapour pressure.
- ❖ Elevation of Boiling point.
- ❖ Depression of Freezing point.
- ❖ Osmotic pressure.

2.7.5.2. Relative lowering of Vapour pressure:

Due to the presence of solute particle (assuming to be non-volatile) in solution, the vapour pressure decreases as the area of vapourization decreases.

Relative lowering of vapour pressure is represented as $\frac{P^0 - P}{P^0}$, where, P^0 is the vapour pressure of pure solvent and P is that solution.

Roult's law: For a solution containing non-volatile, non-dissociative, non-associative the relative lowering of vapour pressure of the solution is equal to the mole fraction of the solute.

Mathematically: $\frac{P^0 - P}{P^0} = x_2$

1 is for solvent

$$\text{Now, } \frac{P^0 - P}{P^0} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

2 is for solute

i.e., $M_2 = \left(\frac{P^0}{P^0 - P} \right) \frac{w_2 \times M_1}{w_1}$. Using this equation we can easily calculate the molecular weight of any unknown solute.

2.7.5.3. Elevation of Boiling point:

On addition of solute to any volatile solute results to increase in boiling point as higher temperature is required for identical vapour pressure of the upper layer of the solution with the atmospheric pressure.

Roult's law: For a solution containing non-volatile, non-dissociative, non-associative the elevation of boiling point of the solution is directly proportional to the molal concentration of the solution.

Mathematically: $\Delta T_b \propto m$ i.e., $\Delta T_b = K_b \times m = K_b \times \frac{w_2 \times 1000}{w_1 \times M_2}$

Where, K_b is called molal elevation constant or ebullioscopic constant
 $= \frac{RT_b^2}{1000l_v}$.

2.7.5.4. Depression of Freezing point:

On addition of solute to any volatile solvent results to decrease in freezing point as lower temperature is required for identical vapour pressure of the upper layer of the solution with the atmospheric pressure.

Roult's law: For a solution containing non-volatile, non-dissociative, non-associative the depression of freezing point of the solution is directly proportional to the molal concentration of the solution.

Mathematically: $\Delta T_f \propto m$ i.e., $\Delta T_f = K_f \times m = K_f \times \frac{w_2 \times 1000}{w_1 \times M_2}$

Where, K_f is called molal depression constant or cryoscopic constant
 $= \frac{RT_f^2}{1000l_f}$.

2.7.5.5. Osmotic pressure:

The external minimum amount of pressure needed to stop the osmosis process is called osmotic pressure.

According to Van't Hoff's law of osmotic pressure,

$\pi \propto C$ and $\pi \propto T$ i.e., $\pi \propto CT$ i.e., $\pi = CRT$. Where, C is molar concentration of the solution.

2.7.5.6. Ideal and real solution.

The conditions which have a solution has to keep in for the ideality is

- ✓ $\Delta_{mix}H$ of the solution should be zero.
- ✓ $\Delta_{mix}V$ of the solution should be zero.
- ✓ The solution should obey Roult's law.

2.7.5.7. Abnormal Colligative property:

In practice the theoretical Colligative properties does not reaches to the practical one. This is abnormal Colligative property.

2.7.5.8. Van't Hoff's factor:

To correlate the theoretical value with the practical one, Van't Hoff introduce a new term called Van't Hoff's factor.

Van't Hoff's factor, i = $\frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$.

Previous Year Question Analysis**NET JUNE 2016**

Q. An ideal gas is composed of particles of mass M in thermal equilibrium at a temperature T in one container. Another container contains ideal gas particles of mass $2M$ at a temperature $2T$. The correct statement about the two gases is

- (a) average kinetic energy and average speed will be same in the two cases
- (b) both the averages will be doubled in the second case
- (c) only the average kinetic energy will be doubled in the second case
- (d) only the average speed will be doubled in the second case

Ans. Average velocity, $C_{av} = \sqrt{\frac{8RT}{\pi M}}$ i.e., $C_{av} \propto \sqrt{\frac{T}{M}}$

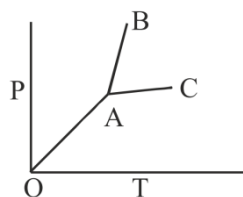
Average kinetic energy, $\bar{\epsilon} = \frac{3}{2} RT$ i.e., $\bar{\epsilon} \propto T$

Correct option is (c)



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Q. Phase diagram of a compound is shown below



The slopes of the lines OA, AC and AB are $\tan \frac{\pi}{4}$, $\tan \frac{\pi}{6}$ and $\tan \frac{\pi}{3}$, respectively.

If melting point and ΔH of melting are 300K and 3kJmol^{-1} respectively, the change in the volume on melting is

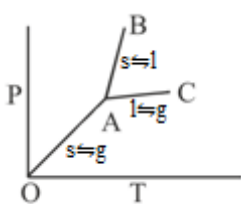
- (a) $10 \tan \frac{\pi}{3}$ (b) $10 \tan \frac{\pi}{4}$ (c) $10 \cot \frac{\pi}{3}$ (d) $10 \cot \frac{\pi}{4}$

Ans. $\Delta H_{\text{melt}} = 3\text{kJ}.\text{mol}^{-1} = 3000\text{J}.\text{mol}^{-1}$

Using Claypeyron equation, $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$



For



So,

ABC we have $\frac{dP}{dT} = \tan \frac{\pi}{3} = \frac{\Delta H}{T\Delta V}$

$$\Delta V = \frac{\Delta H}{T(\tan \frac{\pi}{3})} = 10 \cot \frac{\pi}{3}$$

Correct option is (c).

NET DEC 2016

Q. Triple point pressure of substances A, B, C and D are 0.2, 0.5, 0.8 and 1.2 bar, respectively. The substance which sublimates under standard conditions on increasing temperature is

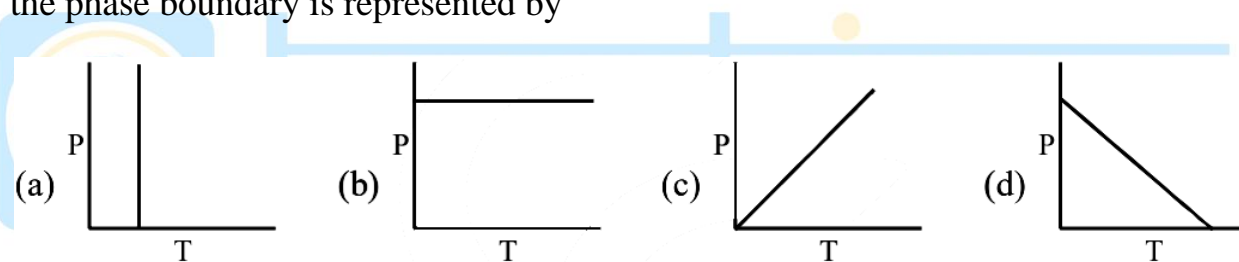
- (a) A (b) B (c) C (d) D

Ans. Standard condition means the pressure is 1 bar

Now for the substance for which the triple point pressure too high compare to standard condition will be sublimate first.

Correct option is (d).

Q. The volume change in a phase transition is zero. From this, we may infer that the phase boundary is represented by

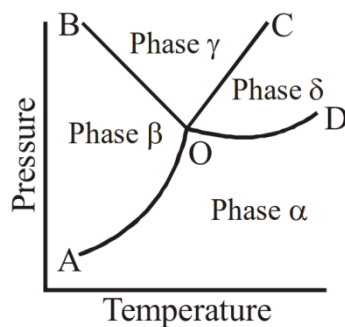


Ans. Claypeyron equation, $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$, if $\Delta V = 0$, then slope, $\frac{dP}{dT} = \infty$

Therefore, $\tan \theta = \infty$, i. e., $\theta = \frac{\pi}{2}$.

Correct option is (a).

Q. A one-component system with the associated phase diagram (see the figure) is not possible because



- (a) OB has a negative slope (b) OC has a positive slope
- (c) Both OB and OC are linear (d) OB, OC and OD cannot all coexist, given OA

Correct option is (d).

Q. A phase transition process is always

- (a) isothermal – isoentropic (b) isochoric – isothermal
(c) isobaric – isochoric (d) isothermal – isobaric

Ans. During phase transition entropy and volume always changes, it is not possible to make them constant.

Correct option is (d).

Q. The fugacity of a real gas is less than the pressure (P) of an ideal gas at the same temperature (T) only when (T_b is the Boyle temperature of the real gas)

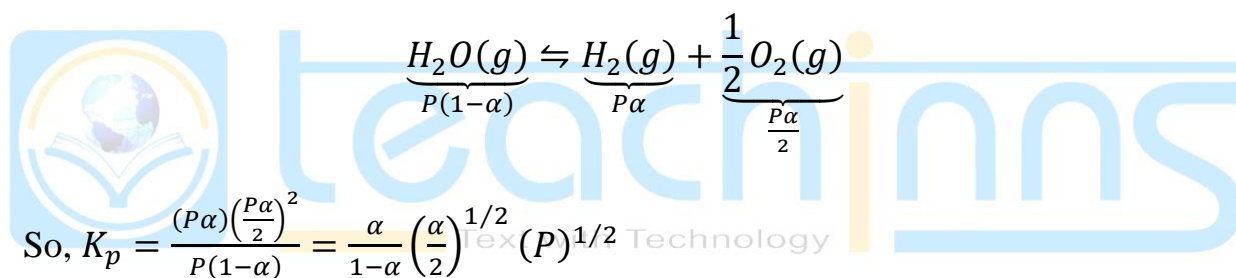
- (a) high P, $T < T_b$ (b) low, P, $T < T_b$
 (c) high P, $T > T_b$ (d) low P, $T > T_b$

Ans. Fugacity of any gas is less than P when attractive forces are dominant. It happens at low and when $T < T_b$.

Q. For the reaction $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$, the equilibrium constant K_p depends on the degree of dissociation α ($\alpha \ll 1$) and total pressure P as

- (a) $K_p \propto \alpha^2 P$ (b) $K_p \propto \alpha^{3/2} P^{1/2}$ (c) $K_p \propto \alpha^{3/2} P^{1/2}$ (d) $K_p \propto \alpha P^2$

Ans.



$$\text{So, } P_T = \left[P(1-\alpha) + P\alpha + \frac{P\alpha}{2} \right] = P + \frac{P\alpha}{2} \text{ i.e., } P = \frac{P_T}{\left(1+\frac{\alpha}{2}\right)}$$

$$\text{Now, } K_p = \frac{\alpha^{3/2}}{\sqrt{2}(1-\alpha)} \frac{P_T^{1/2}}{\left(1+\frac{\alpha}{2}\right)^{1/2}}. \text{ Now, } \alpha \ll 1, \text{ So, } (1-\alpha) \cong 1 \text{ and } \left(1+\frac{\alpha}{2}\right) \cong 1$$

$$\text{So, } K_p = \frac{\alpha^{3/2}}{\sqrt{2}} P_T^{1/2} \text{ i.e., } K_p \propto \alpha^{3/2} P^{1/2}.$$

Correct option is (b).

NET JUNE 2018

Q. Origin of the colligative properties of a dilute solution is

- (a) Volatility of solute molecule (b) Interaction of solute – solvent molecules
(c) Zero enthalpy of mixing (d) Entropy of mixing

Ans. Origin of the colligative properties of a dilute solution is entropy of mixing

Correct option is (d).

Q. In the phase diagram of water, the solid – liquid boundary has a negative slope. The reason for this unusual behavior can be traced to decrease in

- (a) Density of the system on melting (b) Volume of the system on melting
(c) Entropy of the system on melting (d) Enthalpy of the system on melting

Ans. $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$. Now for the transition $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$, we have $\Delta V = -ve$

$\frac{dP}{dT} < 0$. **Correct option is (b).**