QP 03726 Dt- 16/04/2018

Q.1	Α		Select the correct option (MCQ) and complete the following sentences.	(12)
		i]	The van- der Waal's constant 'a' is introduced to account for intermolecular	
		-	forces .	
		ii]	Inversion temperature can be expressed as $T_i = 2a/Rb$	
		-	· · · <u>-</u>	
		iii]	For the reaction, $C_2H_{4(\alpha)} + H_{2(\alpha)}$, $\Rightarrow C_2H_{6(\alpha)}K_n < Kc$	
		-	, 2 (6) 2(6) <u>-</u>	
		iv]	At constant temperature and pressure, the criterion for spontaneity is $\Delta G < 0$	
		-		
	В		State whether the following statements are True or False	(3)
		i]	The free path is the distance travelled by the molecule before collision True	
	С		Match the followings	(5)
			Column A Column B	
			Average mean velocity $\sqrt{\frac{\sigma \kappa T}{\pi M}}$	
			Gibbs free energy $G = H - TS$	

Q.2A

i] Causes for Deviation from Ideal Behaviourmarks

 The volume occupied by the molecules themselves is negligibly small as compared to the total volume occupied by the gas. The molecules of the gas occupies a certain volume, since gases can be liquefied and solidified at low temperatures and high pressures.

When the temperature of a gas is decreased, the thermal energy of the molecule is also get decreased and when the pressure is increased, the molecules are brought closer to one another as a results the forces of attraction gets increased amongst them.

Both these factors favour the liquefaction and solidification and due to compact and rigid structure of solid crystals, further compression becomes difficult.

This indicates that the molecules of a gas must have an appreciable volume, which may be of the same order as the volume occupied by the same number of molecules in the solid phase.

The above postulate is therefore is not valid at high pressures and low temperatures.

2) The forces of attraction between gas molecules are negligible.

If this assumption were strictly true, then the liquefaction of a gas would have not been possible.

The molecules in gases have weak forces of attraction amongst themselves due to which the gases could be liquefied and solidified. This is supported by Joule-Thomson effect.

The change in the temperature is due to the energy consumed in order to overcome the attractive forces amongst the molecules during expansion. When the volume of

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the gas is very large, i.e. at low pressure and high temperature, the molecules are quite far apart and the effect of attractive force is negligible.

At high pressure and low temperature, the volume is very small, the molecules are very close to each other, and the effect of attractive forces becomes appreciable.

Thus, the above postulate also does not hold under the conditions of high pressure and low temperature.

ii] Statements marks

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Boyle's law—

It states that, ' At constant temperature (T) the volume (V) of a given amount of gas varies inversely with its pressure (P).'

i.e. V α 1/P

V = k/P

 \therefore PV = k = constant

Charle's law—

It states that, 'At constant pressure (P) the volume of given amount of gas increases or decreases by 1/273 of its volume at 0° C with every degree rise or fall in temperature (T).'

Hence, V α T (at n and P constant)

 \therefore V = k x T (\therefore K is constant for a given amount of gas)

 $\therefore V/T = k$

Avogadro's Law-

It states that, 'At constant temperature and pressure the volume of a given amount of gas varies directly with its number of moles.'

i.e. V α n (when T and P are constant)

OR

A .i] Joule-Thomson Effect marks When a real gas (except Hydrogen and helium gas), is allowed to expand adiabatically by passing it through a porous plug from a region of high pressure to a region of low pressure, then its temperature decreases. This phenomenon of lowering in temperature produced when a real gas is allowed to expand adiabatically by passing through a porous plug is known as Joule-Thomson effect.

Joule - Thomson Experiment -

The experimental set up consists of thermally insulated tube fitted with a porous plug in the middle and two frictionless pistons A and B on the sides as shown in fig.-



The real gas is kept between pistons A and B at different pressures P_1 and P_2 such across the sides of porous plug, such that $P_1 > P_2$.

The real gas is slowly allowed to expand adiabatically from high pressure region into a lower pressure region through a porous plug, with the help of piston, so that the volume V_1 of the gas at pressure P_1 is forced through the porous plug and allowed to expand to volume V_2 and pressure P_2 by moving piston slowly outward.

The temperatures T_1 and T_2 on the two sides of porous plug are measured. A fall in temperature is observed.

The work done by piston A on gas during compression = P_1V_1 and

The work done by piston B on gas during expansion = $-P_2V_2$.

The net work done by the gas $w = P_1V_1 - P_2V_2$.

As the process is carried out adiabatically, i.e. q = 0, the system performs work at the expense of internal energy, and according to 1^{st} law of thermodynamics

$$\Delta \mathbf{E} = \mathbf{q} + \mathbf{w} = \mathbf{0} + \mathbf{w}$$

 $-\Delta E = -w$

 $-(P_1V_1 - P_2V_2) = -(E_2 - E_1)$

Hence, $E_2 + P_2V_2 = E_1 + P_1V_1$

 $H_2 = H_1 (H = E + PV)$

i.e. $\Delta H = 0$

Thus, during Joule – Thomson effect, enthalpy of the system remains constant. Hence, it is an isoenthalpic process.

ii] Compressibility Factor marks

The deviation of a real gas from ideal behavior is always expressed in terms of a quantity called compressibility factor (z) defined by the equation PV = znRT or

Z = PV/nRT

Where, V is the volume occupied by n moles of a gas at pressure P and temperature T.

When the value of compressibility factor is less than one indicates that the gas is more compressible than an ideal gas and when it is more than, the gas then it is less compressible.

Q.2C marks

Calculate by using Vander Waal's equation the temperature at which 4 moles of SO₂ will have a volume of 10 dm³ at a pressure of $2.027 \times 10^6 \text{ Nm}^{-2}$. (Given a= $0.68 \text{ Nm}^4 \text{mol}^{-2}$; b= $5.64 \times 10^{-5} \text{ m}^3 \text{mol}^{-1}$; R= $8.314 \text{ NmK}^{-1} \text{mol}^{-1}$)

Given - $a = 0.68 \text{ Nm}^4 \text{mol}^{-2}$; $b = 5.64 \text{ x } 10^{-5} \text{ m}^3 \text{mol}^{-1}$; $R = 8.314 \text{ Nm}\text{K}^{-1}\text{mol}^{-1}$; $P = 2.027 \text{ x } 10^6 \text{ Nm}^{-2}$; $V = 10 \text{ dm}^3 = 10 \text{ x } 10^{-3} \text{ m}^3$ and n = 4 moles.

We know that,

$$\left[P + \frac{an^2}{V^2}\right][V - nb] = nRT$$

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$$\left[(2 \cdot 027 \times 10^6) + \frac{0.68(4)^2}{(1x10^{-2})^2} \right] \left[1x10^{-2} - 4x 5.64 \times 10^{-5} \right] = 6x8.314 \times T$$

∴T = 627.7412 K

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Q.5 A] marks

Consider a gas molecule enclosed in a container of volume V. This molecule being surrounded by other molecules will get attracted equally in all directions. This uniformly distributed forces neutralize one another and there is no resultant attractive force of the molecule.

As this molecule approaches wall of the container, it experiences attractive force from the bulk of molecules behind it, as a result, the molecule will strike the wall of container with lesser velocity and will exert lower pressure than it would have in the absence of intermolecular attraction.

Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas, i.e. $P_{(ideal)} = P_{(observer)} + P_x$

where P_x – pressure correction due to the forces of attraction.

The attractive force exerted on a single striking molecule would depend upon the number of molecules present in the bulk, i.e. density (d) of the gas.

And the number of molecules striking the side of the container in unit time would also depend upon the density.

Hence the total attractive force P_x which pulls the striking molecule backwards is proportional to the square of the density, i.e. $P_x \alpha d^2$

$$P_{x}\alpha \frac{n^{2}}{V^{2}}$$
 $\therefore \left(density = \frac{number \ of \ moles \ (n)}{volume \ (V)} \right)$

or $P_x = \frac{an^2}{V^2}$

 $\mathbf{P}_{(\text{ideal})} = \mathbf{P}_{(\text{observer})} + \frac{an^2}{V^2}$

And $V_{(corrected)} = V_{actual} - nb$

where, a is a constant depending upon the nature of the gas. It is often called as Van der Waals constant of pressure correction.

Thus, an ideal gas equation (PV = nRT), in terms of correction due to volume of gas molecule (Van der Walls equation) can be written as

$$\left[P + \frac{an^2}{V^2}\right][V - nb] = nRT$$