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#### **Unit 6 GASEOUS STATE**

#### **CHAPTER MAP**

Gaseous State

#### **IDEAL GASES**

Obey following gas laws under all conditions

- 1. Boyle's law  $P \propto \frac{1}{V}$  (T, n constant)
- 2. Charles' law  $V \propto T$ , (P, n constant)
- 3. Gay Lussac  $P \propto T (V, n constant)$
- 4. Avogadro's Hypothesis  $V \propto n$  (T, P constant)
- 5. Ideal gas equation. PV = nRT

#### REAL GASES

obey Van der Waals equation

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

Critical constant

$$T_C = \frac{8a}{27 Rb}, P_C = \frac{a}{27b^2}$$

and 
$$V_C = 3b$$

Gas

Diffusion

Critical phenomenon

Liquefaction of gases

Graham's Law of diffusion

Critical temperature Critical volume Critical pressure Critical

Joule-Thomson effect

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#### **Important formula**

1. Pressure = 
$$\frac{Force(N)}{Area(m^2)}$$

2. Boyle's law = 
$$PV = K$$
 (or)  $P_1V_1 = P_2V_2 = K$ 

3. Charles' law = 
$$\frac{V}{T}$$
 = Constant (or) V = KT (or)  $\frac{V_1}{T_1} = \frac{V_2}{T_2} = K$ 

4. Gay-Lussac's law = P \propto T (or) 
$$\frac{P}{T}$$
 = K (or)  $\frac{V_1}{T_1} = \frac{V_2}{T_2} = K$ 

5. Avogadro's hypothesis = 
$$V \propto n$$
 (or)  $\frac{V_1}{n_1} = \frac{V_2}{n_2}$  = Constant

7. Dalton's law of Partial pressure : 
$$P_{total} = p_1 + p_2 + p_3 \dots$$

8. 
$$P_{dry gas} = P_{total} - P_{water vapour}$$

9. Graham's law of Diffusion : 
$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

10. Compressibility factor = 
$$Z = \frac{PV}{nRT}(or)\frac{V_{real}}{V_{ideal}}$$

11. Van der Waals equation of state: 
$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

12. Critical volume 
$$V_C = 3b$$

13. Critical pressure 
$$P_C = \frac{a}{27b^2}$$

14. Critical temperature 
$$T_C = \frac{8a}{27 Rb}$$

15. Inversion temperature 
$$T_i = \frac{2a}{Rb}$$

- ❖ Gases at STP  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $O_3$ , He, Ne, Ar, Kr, Xe and Rn (Only 11 elements).
- **❖ The Earth** The Earth is surrounded by a atmosphere of air whose composition is 78% Nitrogen, 21% Oxygen and 1% other gases.
- ❖ Oxygen It is highly essential for our survival.
- **❖ Hydrogen cyanide (HCN)** Deadly poison

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- **❖ Carbon monoxide (CO)** Highly toxic
- $\bullet$  NO<sub>2</sub> and SO<sub>2</sub> less toxic
- **❖ Chemically inert gases** He, Ne, Ar, Kr, Xe and Rn.
- ❖ Gas A substance is normally in a gaseous state at ordinary temperature and pressure.
- ❖ Vapour The gaseous form of any substance that is a liquid or solid at NTP.
- ❖ Pressure It is defined as the force exerted by a gas on unit area of the wall. Pressure =  $\frac{Force}{area} = \frac{F}{a}$
- ❖ Unit of pressure (Pascal) 1 Pascal = 1 Nm<sup>-2</sup>, where 1 N = 1 Kg ms<sup>-2</sup>. Other units of pressure are Bar, atmosphere, Torr, mm of Hg.
- **❖ Atmospheric pressure** The force exerted on a unit area of earth by the column of air above it is called atmospheric pressure.
- **❖ 1 atm** − 760 mm Hg
- ❖ Boyle's law At a given temperature, the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

$$V \propto \frac{1}{P}$$
 at constant T (or)

$$PV = K_1$$
 at constant T (or)

$$P_1V_1 = P_2V_2 = K_1$$

**❖ Charles' law** – For a fixed mass of a gas at constant pressure, the volume is directly proportional to temperature (K).

$$V \propto T$$
 and constant P and n;  $\frac{V}{T}$  = Constant

- **Absolute zero : -273.15°C.**
- ❖ Gay-Lussac's law At constant volume, the pressure of a fixed mass of gas is directly proportional to temperature. P  $\propto$  T at constant V;  $\frac{P}{T}$  = Constant.
- ❖ Avogadro's hypothesis Equal volumes of all gases under the same condition of temperature and pressure contain equal number of molecules.

$$V \propto n \text{ (or) } \frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{Constant}$$

Dedication! Determination!! Distinction!!!

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- ❖ Ideal gas equation PV = nRT where R is universal gas constant.
- **❖** Values of R −

 $R = 0.082057 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$ 

 $R = 8.314 \text{ x Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ 

 $R = 8.314 \text{ x } 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ 

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ 

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❖ Dalton's law of partial pressures – It states that the total pressure of a mixture of gases is the sum of partial pressures of the gases present.

$$P_{total} = p_1 + p_2 + p_3 \dots$$

❖ Graham's law of Diffusion – The rate of effusion or diffusion is inversely proportional to the square of molecular mass of a gas through an orifice.

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

- ❖ Ideal gases Gases that obey ideal gas equation PV = nRT are ideal gases.
- ❖ Real gases Gases that do not obey the ideal gas equation PV = nRT are real gases. For them either PV > nRT or PV < nRT
- **❖** Van der Waals equation of state –

 $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ . Where a and b are Van der Waals constant.

**❖** Compression factor (Z) –

It is the ratio of PV to nRT.  $Z = \frac{PV}{nRT}$ .

For ideal gases Z = 1 and for real gases Z > 1 or Z < 1.  $Z = \frac{V_{real}}{V_{ideal}}$ 

**❖** Critical constants –

Critical Volume  $V_C = 3b$ 

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

Critical Temperature  $T_C = \frac{8a}{27 Rh}$ 

- **❖** Critical temperature of CO<sub>2</sub> − 303.98 K
- $\diamond$  Critical Temperature  $T_C$  is defined as the temperature below which a gas can be liquefied by the application of pressure.
- **Critical Pressure -** P<sub>C</sub> is the pressure required to liquefy a gas at its critical temperature.

- ❖ Critical Volume V<sub>C</sub> is the volume occupied by one mole of a gas at its critical temperature and critical pressure.
- ❖ **Joule Thomson effect** The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure.
- ❖ Inversion temperature ( $T_i$ ) The temperature below which a gas obey Joule Thomson effect is called inversion temperature.  $T_i = \frac{2a}{Rb}$

#### **Choose the correct Answer:**

- 1. Gases deviate from ideal behavior at high pressure. Which of the following statement(s) is correct for non-ideality?
- a) at high pressure the collision between the gas molecule become enormous
- b) at high pressure the gas molecules move only in one direction
- c) at high pressure, the volume of gas become insignificant
- d) at high pressure the intermolecular interactions become significant
- 2. Rate of diffusion of a gas is
- a) directly proportional to its density
- b) directly proportional to its molecular weight
- c) directly proportional to its square root of its molecular weight
- d) inversely proportional to the square root of its molecular weight
- 3. Which of the following is the correct expression for the equation of state of van der Waals gas?

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

c) 
$$\left[P + \frac{an^2}{v^2}\right](V - nb) = nRT$$
 (d)  $\left[P + \frac{n^2a^2}{v^2}\right](V - nb) = nRT$ 

- 4. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules
- a) are above inversion temperature
  b) exert no attractive forces on each other c) do work
  d) collide without loss of energy
- 5. Equal weights of methane and oxygen are mixed in an empty container at 298 K. The fraction of total pressure exerted by oxygen is
- (a) 1/3

- (b)  $\frac{1}{2}$
- (c) 2/3
- (d)  $1/3 \times 273 \times 298$
- 6. The temperatures at which real gases obey the ideal gas laws over a wide range of pressure is called
- a) Critical temperature

b) Boyle temperature

Dedication!		Determination!		Distinction!!!			
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c) Inversion ten	•	3 -	d) Reduced temperatu				
		-	ottle is opened up. The	room develops a smell. This			
is due to which	property of g						
a) Viscosity		b) Density	c) Diffusion	d) None			
				igh a long tube are openæd			
simultaneously	at both ends.	The white amm	nonium chloride ring fi				
a) At the center of the tube b) Near the hydrogen chloride bottle							
c) Near the am	c) Near the ammonia bottle d) Throughout the length of the tube						
9. The value of	universal gas	s constant depen	ds upon				
a) Temperature	of the gas		b) Volume of the gas				
c) Number of n	noles of the g	as	d) units of Pressure	and volume.			
10. The value of	of the gas con	stant R is					
a) $0.082  dm^3 atr$	<i>n</i> . b)	0.987 cal mol <sup>-1</sup>	K <sup>-1</sup> c) 8.3 J mol <sup>-1</sup> K	d) 8 erg mol <sup>-1</sup> K <sup>-1</sup>			
11. Use of hot a	air balloon in	sports at meteor	rological observation is	an application of			
a) Boyle's law	b) Newto	on's law c) Ke	lvin's law d) Brown	ı's law			
12. The table in	dicates the v	alue of van der	Waals constant 'a' in (d	$(dm^3)^2 atm. mol^{-2}$			
Gas	$O_2$	$N_2$					
A	1.360	1.390 4.	170 2.253				
The gas which	can be most e	easily liquefied i	S				
_	$N_2$	c) NH <sub>3</sub>	d) CH <sub>4</sub>				
13. Consider th	-		7 - 1				
			a mountain than at sea	level			
_	_	_	solids or liquids				
		-	s the height of the merc	cury column rises			
Select the corre	-	\	, 410 11018110 01 0110 111010	1120			
a) I and II		II and III	c) I and III	d) I, II and III			
· ·			,	7. The molar volume of $CO_2$			
under these con	,	01 CO2 at 100 I	und /1.0 out 15 0.00)	7. The motal volume of Co2			
a) 22.04 dm <sup>3</sup>		$2.24 \text{ dm}^3$	c) 0.41 dm <sup>3</sup>	d) 19.5dm <sup>3</sup>			
			•	its values, the initial pressure			
P becomes	ne and volun	ne or an idear ga	is is increased to twice	its values, the illitial pressure			
	h)	2D	c) P	d) 3D			
a) 4P		2P	,	d) 3P			
	-	-		nydrogen gas is 3 3 times that			
			$C_nH_{2n-2}$ . What is the va				
a) 8	<b>b</b> )		c) 3	d) 1			
17. Equal moles of hydrogen and oxygen gases are placed in a container, with a pin-hole							
_		-	on of oxygen escapes	in the time required for one-			
half of the hydr	_						
a) 3/8	b)	1/2	c) 1/8	d) 1/4			

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		h temperature T, keep		tant is called the
coefficient of th	ermal expansion ie α	$=\frac{1}{v}\left(\frac{\partial V}{\partial T}\right)_{\rm P}$ . For an ideal	gas α is equal to	
a) T	<b>b</b> ) 1/T	c) P		of these
19. Four gases I	P, Q, R and S have ali	most same values of 'b'	but their 'a' values	s (a, b are Vander
Waals Constant	s) are in the order Q	< R < S < P. At a par	ticular temperature	e, among the four
	easily liquefiable one i			/2
a) P	b) Q	c) R	d) S	
20. Maximum d	eviation from ideal ga	as is expected from		
a) CH <sub>4 (g)</sub>	b) NH <sub>3 (g)</sub>	c) H <sub>2 (g)</sub>	d) $N_{2(g)}$	
21. The units of	Vander Waals consta	nts 'b' and 'a' respective		
a) mol L <sup>-1</sup> and I	$\Delta$ atm <sup>2</sup> mol <sup>-1</sup>	b) mol L and L atm m	$100^2$	
c) mol <sup>-1</sup> L and I	$L^2$ atm mol <sup>-2</sup>	d) none of these		
	-	$f CO_2$ is 304K, it can be volume is to directly	-	
temperature			_	
a) both assertion	n and reason are true a	nd reason is the correc	t explanation of as	sertion
		out reason is not the con		
c) assertion is tr	ue but reason is false	d)both assertio	on and reason are	false
23. What is the	density of N <sub>2</sub> gas at 23	27°C and 5.00 atm pres	sure? $(R = 0.082 \text{ I})$	$L atm K^{-1} mol^{-1}$
a) 1.40 g/L	b) 2.81 g/L	c) 3.41 g/L	d) 0.29 g	
_	, , , , , , , , , , , , , , , , , , ,	s correctly describes the		
ideal gas? (T is	measured in K)			
a) ,				
	b) PV			
P				
V	V			
c) V	d) all the ab	ove		
T				
25. 25g of each	of the following gas	es are taken at 27°C a	nd 600 mm Hg pr	essure. Which of
	the least volume?		<b>C</b> 1	
a) HBr	b) HCl	c) HF	d) HI	

# Answer these questions briefly

### 26. State Boyle's law.

At a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure. Mathematically, the Boyle's law can be written as

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$$V \alpha \frac{1}{P}$$
 ----- (1)

(T and n are fixed, T-temperature, n- number of moles)

$$V = k \times \frac{1}{p} \qquad ----- (2)$$

k – proportionality constant When we rearrange equation (2)

PV = k at constant temperature and mass

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27. Name two items that can serve as a model for Gay Lusaac' law and explain.

 $\mathbf{P} \alpha T$  at constant volume.

- (i) Pressure in well inflated tyre is almost constant but when temperature increases in summer days it increases the pressure and sometimes tyres may burst.
- (ii) Guns and other firing equipment's are thrilling examples of Gay Lussac's law.

When gun pin strikes, it ignites the gun powder and this increases the temperature which in turn increases the pressure and bullet is fired from the gun.

- iii) **Heating a closed aerosol cane.** The increased pressure may cause the container to explode. You don't toss an "empty" can of hair spray into a fire.
  - iv) The egg in the bottle experiment.

A glass bottle is taken, inside the bottle put some pieces of cotton with fire. Then place a boiled egg (shell removed) at the top of the bottle. The temperature inside the bottle increases from the fire, rising the pressure. By sealing the bottle with egg, the fire goes on, dropping the temperature and pressure. This causes the egg to be sucked into the bottle.

- 28. Give the mathematical expression that relates gas volume and moles. Describe in words what the mathematical expression means.
- The Mathematical expression between the volume of gas and number of moles is  $\mathbf{V} \alpha \mathbf{n}$  $V_1/n_1 = V_2/n_2 = \text{constant}$
- $\triangleright$  where  $V_1$  &  $n_1$  are the volume and number of moles of a gas,

 $V_2$  &  $n_2$  are a different set of values of volume and number of moles of the same gas at same temperature and pressure.

- > The above relation is expressed as " Equal volumes of all gases under the same condition of temperature and pressure contain equal number of molecules".
- 29. What are ideal gases? In what way real gases differ from ideal gases.

An ideal gas a gas which obeys the gas laws and ideal gas equation

An ideal gas is defined as "one in which all collisions between atoms or molecules are perfectly elastic forces".

The difference between ideal gas and real gas is

Ideal gas	Real gas
1. It obeys gas laws under all conditions of	It obeys gas laws only under low
temperature and pressure	pressure and high temperature
2. No gas is ideal	All gases are real

Dedication!	D	etermination!!	Distinction!!!
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3. Volume	occupied by the	molecules is	Volume occupied by the molecules is not
negligible as compared to the total volume		total volume	negligible as compared to the total volume
occupied by	the gas.		occupied by the gas.
4. The fo	orces of attraction	among the	The forces of attraction among the
molecules o	of the gas are negligib	ole.	molecules cannot be neglected at higher
			pressure and low temperature 74
5. It obeys i	deal gas equation PV	r = nRT	It obeys Van der Waals equation
			$(P + an^2/V^2) \text{ (V-nb)} = nRT$

### 30. Can a Van der Waals gas with a=0 be liquefied? explain.

- > The van der Waals constant 'a' is a measure of the attractive forces among the molecules of the gas
- > Greater the value of 'a' larger the intermolecular force of attraction and the gas can be liquefied.
- ➤ Here a=0 means there is intermolecular attraction and the gas cannot be liquefied.
- 31. Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?
- ➤ Molecule hitting the tiny sticky area on the wall of the container of gas moves faster as they get closer to adhesive surface, but this effect is not permanent.
- ➤ The pressure on the sticky wall is greater than on the ordinary area of walls.

### 32. Explain the following observations

### a) Aerated water bottles are kept under water during summer

- $\triangleright$  In aerated water bottles the CO<sub>2</sub> is passed through the aqueous solution under pressure.
- ➤ The solubility of gas is decreases with increase of temperature. In summer season the temperature is raise the solubility is decreases.
- > Due to this will increase very high pressure above the surface of the liquid inside the bottle and bottle will not able to withstand the pressure and bottle may explode.
- > To avoid this Aerated water bottles are kept under water during summer.
- $\triangleright$  As a result, the temperature decrease and solubility of CO<sub>2</sub> is increases in aqueous solution resulting the pressure inside the bottle decreases.

# b) Liquid ammonia bottle is cooled before opening the seal

- ➤ Liquid ammonia bottle contains the gas under very high pressure. If the bottle is opened, the sudden decrease in pressure will increase the volume of gas.
- As result, the gas is come out the bottle with greater force will cause breakage of bottle and accident.
- $\triangleright$  The pressure of the gas over liquid ammonia is decreased by dipping  $H_2O$ .
- ➤ Once it attains the temperature of water, it can be opened so that no gas will come out of the mouth of the tube with force.

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- c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter.
  - ➤ In summer due to high temperature the air expands and hence to avoid tyre burst, the pressure is kept less.
  - As a result, when the vehicle runs and the tyre air gets heated and expands, resulting e increased pressure is still kept below the bursting limit.

# d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude.

- According Boyle's law the volume of gas is inversely proportional to the pressure at a given temperature.
- As the weather balloon ascends, the atmospheric pressure is less, pressure of the gas tends to decrease and so volume as well as the size of the balloon increases.

#### 33. Give suitable explanation for the following facts about gases.

#### a) Gases don't settle at the bottom of a container

- ➤ Gases are less denser than solids and liquids. They have negligible intermolecular force of attraction between free particles, so are free to move.
- ➤ Hence gases don't settle at bottom of the container.

#### b) Gases diffuse through all the space available to them

- ➤ Gases have the tendency to mix with one another spontaneously and form a homogeneous mixture.
- This is due to the fact that gas particles are mainly in random at very high velocities and there in so much of inter molecular empty space in the volume of any gas.
- > This permit them to mix spontaneous and this phenomenon is known as diffusion.

# 34. Suggest why there is no hydrogen $(H_2)$ in our atmosphere. Why does the moon have no atmosphere?

- $\triangleright$  Under ordinary conditions on earth, hydrogen exist as diatomic (H<sub>2</sub>). Because of its light weight, which enable into escape from earth gravity more easily than heavier gases. So, no hydrogen is there in atmosphere.
- Moon has no atmosphere because the value of acceleration due to gravity (g) on the surface of moon is small. The molecules of atmospheric gases on the surface of the moon have thermal velocities greater than escape velocity.

# 35. Explain whether a gas approaches ideal behavior or deviates from ideal behaviour if a) it is compressed to a smaller volume at constant temperature.

When the gas is compressed, there is a decrease in volume and molecules are close to each other and hence inter molecular attraction becomes more and hence it deviates from ideal behavior.

# b) the temperature is raised at while keeping the volume constant

➤ When volume constant, the pressure is directly proportional to the temperature.

 $P_{age}$  75

- ➤ The temperature is raised the pressure is always increases which leads the intermolecular force of attraction between the gas molecules.
- So it deviates from the ideal behavior

#### c) more gas is introduced into the same volume and at the same temperature.

- Fig. If more gas is introduced in the same volume and temperature is constant, more will be the pressure.
- The increase in pressure is always increases which leads the intermolecular force of attraction between the gas molecules.
- > So it deviates from the ideal behavior

# 36. Which of the following gases would you expect to deviate from ideal behaviour under conditions of low temperature $F_2$ , $Cl_2$ , or $Br_2$ ? Explain.

- ➤ These molecules are held together by a weak van der Waals forces.
- > The forces of attraction between the molecules with increase in the size of the molecule.
- $\triangleright$  Br<sub>2</sub> deviate from ideal behavior, since the Br<sub>2</sub> has the biggest size provides maximum attraction between bromine molecules.

#### 37. Distinguish between diffusion and effusion.

Diffusion	Effusion		
1. The spreading of the molecules of a gas	Effusion is the escape of gas molecules		
throughout the available space or second	through a very small hole.		
substance is called diffusion.			
2. Diffusion refers to the ability of the gases to	Effusion is a ability of a gas to travel		
mix with each other	through a small pin-hole.		
3. <b>Example:</b> spreading of something such as	Example: pouring out something like the		
brown tea liquid spreading through the water	soap studs bubbling out from a bucket of		
in a tea cup.	water.		

### 38. Aerosol cans carry clear warning of heating of the can. Why?

- Aerosols are colloids in which air (gas) is dispensed in liquid. On heating the can, the pressure of the gas increases and it can burst out.
  - ➤ Hence they carry clear warning that they should not be heated or kept in near fire.

# 39. Would it be easier to drink water with a straw on the top of Mount Everest?

- > Drinking through a straw is slightly more difficult on the top a mountain.
- ➤ This is because the atmospheric pressure and the temperature is low at top mountain.
- ➤ When you drink through a straw you are decreasing the pressure in your mouth, so the atmospheric pressure pushes the liquid up the straw.
- ➤ On mountain there is less pressure so there is less pressure to push the water into the straw.

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(ACTC) ADVANCED CHEMISTRY TUITION CENTRE, 41/1 PWD ROAD, NAGERCOIL, 9952340892. 40. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume.

The Vander Waals equation for a real gas is

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

#### **Pressure Correction:**

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The pressure of a gas is directly proportional to the force created by the bombardment of molecules on the walls of the container. The speed of a molecule moving towards the wall of the container is reduced by the attractive forces exerted by its neighbours. Hence, the measured gas pressure is lower than the ideal pressure of the gas. Hence, Vander Waals introduced a correction term to this effect.

#### Inter-molecular forces of attraction

Van der Waals found out the forces of attraction experienced by a molecule near the wall are directly proportional to the square of the density of the gas.

$$p' \alpha \rho^2$$
  $\rho = \frac{n}{V}$ 

Where n is the number of moles of gas and V is the volume of the container

P' 
$$\alpha \frac{n^2}{V^2}$$

P'  $= \frac{an^2}{V^2}$ 

Where a is proportionality constant and depends on the nature of gas

Therefore, 
$$P_{ideal} = P + \frac{an^2}{V^2}$$

#### **Volume Correction:**

As every individual molecule of a gas occupies a certain volume, the actual volume is less than the volume of the container, V. Van der Waals introduced a correction factor V' to this effect. Let us calculate the correction term by considering gas molecules as spheres.

V =excluded volume

Excluded volume for two molecules =  $\frac{4}{3}\pi(2r)^3$ 

$$= 8 \left(\frac{4}{3} \pi r^3\right) = 8 V_m$$

Where V is a volume of a single molecule  $=\frac{8V_m}{2} = 4V_m$ 

Excluded volume for n molecule =  $n(4V_m) = nb$ 

Where b is van der waals constant

Which is equal to 
$$4V_m$$
  $\longrightarrow$   $V = nb$ 

$$V_{ideal} = V - nb$$

Replacing the corrected pressure and volume in the ideal gas equation PV = nRT we get the van der Waals equation of state for real gases as below,

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

The constants a and b are van der Waals constants and their values vary with the nature of the gas. It is an approximate formula for the non-ideal gas.

#### 41. Derive the values of van der Waals equation constants in terms of critical constants.

The van der waals equation for n moles is

$$\left(\boldsymbol{p} + \frac{an^2}{V^2}\right)(\boldsymbol{V} - \boldsymbol{n}\boldsymbol{b}) = \mathbf{n}\mathbf{R}\mathbf{T} \qquad ----- (1)$$

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For 1 mole

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad ----- (2)$$

From the equation we can derive the values of critical constants Pc, Vc and Tc in terms of a and b, the van der waals constant, on expanding the above equation

$$PV + \frac{a}{v} - Pb - \frac{ab}{v^2} - RT = 0$$
 ----- (3)

Multiply equation (3) by  $\frac{V^2}{P}$ 

$$\frac{V^{2}}{P} \left( PV + \frac{a}{V} - Pb - \frac{ab}{V^{2}} - RT \right) = 0$$

$$V^{3} + \frac{aV}{P} + bV^{2} - \frac{ab}{V^{2}} - \frac{RTV^{2}}{P} \qquad ------ (4)$$

When the above equation is rearranged in powers of V.

$$V^{3} + \left[\frac{RT}{P} + b\right]V^{2} + \left[\frac{a}{P}\right]V - \left[\frac{ab}{P}\right] = 0 \qquad ----- (5)$$

When equation (5) is a cubic equation in V. On solving this equation,

We will get three solutions. At the critical point all these three solutions of V are equal to the critical volume Vc. The pressure and temperatures becomes Pc and Tc respectively i.e., V = Vc;

$$V - Vc = 0$$

$$(V - Vc)^{3} = 0 \qquad [(a-b)^{3} = a3 - 3a^{2}b + 3ab^{2} - b^{3}]$$

$$V^{3} - 3VcV^{2} + 3Vc^{2}V - Vc^{3} = 0 \qquad ------ (6)$$

As equation (5) is identical with equation (6), we can equate the coefficients of V2, V and constant terms in (5) and (6)

$$-3\operatorname{VcV}^{2} = -\left[\frac{RT_{c}}{P_{c}} + b\right]\operatorname{V}^{2}$$

$$3\operatorname{Vc} = \frac{RT_{c}}{P_{c}} + b$$

$$3\operatorname{Vc}^{2} = \frac{a}{P_{c}}$$

$$3\operatorname{Vc}^{2} = \frac{ab}{P_{c}}$$
-----(9)

Divide equation (9) by equation (8)

$$\frac{V_c^3}{3V_c^2} = \frac{ab/P_c}{a/P_c}$$
$$\frac{V_c}{a} = b$$

---- (11)

i.e., 
$$Vc = 3b$$
 ----- (10)

when equation (10) is substituted in (8)

$$3Vc^{2} = \frac{a}{P_{c}}$$

$$Pc = \frac{a}{3Vc^{2}} = \frac{a}{3(3b^{2})} = \frac{a}{3 \times 9b^{2}} = \frac{a}{27b^{2}}$$

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

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Substituting the values of Vc and Pc in equation (7),

$$3Vc = b + \frac{RT_c}{P}$$

$$3(3b) = b + \frac{RT_c}{\left(\frac{a}{27b^2}\right)}$$

$$9b - b = \left(\frac{RT_c}{a}\right) 27b^2$$

$$8b = \frac{T_cR27b^2}{a}$$

$$Tc = \frac{8ab}{27Rb^2} = \frac{8a}{27Rb}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3Vc^2Pc$$
 and  $b = \frac{V_c}{3}$ 

# 42. Why do astronauts have to wear protective suits when they are on the surface of moon?

- Astronauts must wear space suits since the surface of moon, there is no air to breath and no air pressure.
- > Space is extremely cold and filled with dangerous radiation.
- > Space suits are specially designed to protect astronauts from the cold, radiation and low pressure in space. It also provide air to breathe.

# 43. When ammonia combines with HCl, NH<sub>4</sub>Cl is formed as white dense fumes. Why do more fumes appear near HCl?

$$NH_3 + HC1 \rightarrow NH_4C1$$

- > The rate of diffusion is inversely proportional to the molecular weight of the gas.
- ➤ Lower the molecular weight faster is the diffusion.
- > The molar mass of HCl is 36.5 g.mol<sup>-1</sup> while the molar mass of NH<sub>3</sub> is 17 g.mol<sup>-1</sup>.
- ➤ Hence NH<sub>3</sub> diffuses faster than HCl. Hence white fumes appear near HCl. (**Or**)
- i) When ammonia combines with HCl, NH<sub>4</sub>Cl is formed as white dense fumes. The reaction takes place in neutralization between a weak base and a strong acid.
- ii) The property of the gas is diffusion.
- iii) Diffusion of gases- Ammonia and hydrogen chloride. Concentrated ammonia solution is placed on a pad in one end of a tube and concentrated HCl on the pad at the other. After