

IMP TOPIC FOR 2009

1. Inter molecular Interactions
 1. Ion- dipole interactions forces
 1. Diffusion of gases – derivation
 2. Pressure dependence
 2. Thermal conductivity & viscosity
 3. Law of corresponding states

CIVIL SERVICES EXAM

Gaseous state:-

1. Derive the Maxwell-Boltzmann distribution Law [20 Marks] [1977]
2. What is meant by the equation of state of a gas, state and explain Van der Waals equation and use it to
 - Discuss the isotherms of a real gas near the critical point and
 - Obtain a reduced equation of state [20 Marks] [1970]
3. State and explain Van der Waals' equation and show how it can be used to determine molecular weight through limiting density. [20 Marks] [1972]
4. Discuss the physico-chemical principles underlying the liquefaction of gases. [20 Marks] [1973]
5. Derive the equation denoting the law of corresponding states from Van der Waals' equation of state.
6. Explain clearly the terms: Critical pressure (P_c); critical temperature (T_c), and critical volume (V_c). Derive an expression correlating these values with constants 'a' and 'b' of the Van der Waals' equation $(p + \frac{a}{v^2})(v-b) = RT$. [60 Marks] [1974]
7. Explain the term root mean square velocity. How is it related to the molecular weight of a gas. [20 Marks] [1976]
8. Explain the law of corresponding states. [8 Marks] [1977]
9. Starting with Van der Waals' equation obtain expressions for critical constants (P_c , V_c , T_c) of a gas. Show that for all gases obeying Van der Waals' equation $\frac{RT_c}{P_c V_c} = 2.66$.
10. Calculate the pressure exerted by 2 moles of nitrogen confined to a 5-litre flask at 27°C using ;

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➤ **Ideal gas equation**

➤ **Van der waal's equation.**

11. State and explain the law of corresponding states. For large no. of substances, the quantity RT_c/P_cV_c lies between 3.4 and 3.7. comment on the fact.

[20 Marks] [2000]

12. What do you understand by liquification of gases? Explain critical temperature and critical pressure. Draw schematic diagram for liquification of air.

[15 Marks] [2007]

13. Derive the van der waal's equation of state for real gases. What are the units of van der waal's constants.

[20 Marks] [2007]

14. Define the terms: critical temperature, critical pressure and critical volume. How are these constants determined experimentally?

[20 Marks] [2007]

15. State and explain Maxwell's law of distribution of velocity of molecules of a gas at a definite temperature. What is meant by most probable velocity.

[20 Marks] [2008]

IFS

2000

16. Calculate the rms velocity and the most probable velocity for hydrogen gas at 0°C

2001

17. Calculate the avg and rms speeds of N_2 at 500°C .

18. Define Boyle temperature. What is its significance? Estimate the Boyle temperature of N_2 from Vander Waal's constants. Given : $a = 1.39 \text{ dm}^3 \cdot \text{atm}$; $b = 0.039 \text{ dm}^3$. $R = 0.082 \text{ dm}^3 \cdot \text{atm} \cdot \text{K}^{-1}$

2002

19. Calculate the rms velocity of the molecule of a gas whose density is 1.4 gm/litre at a pressure of 76 mm Hg .

20. Write a note on Maxwell's law of distribution of velocities. Drive relation for most probable, avg and mean square velocities.

2003

21. Write a note on Liquification of gases.

[10 Marks] [C]

2006

22. Write a short note on liquification of gases. Discuss

➤ Ion dipole and

➤ London Dispersion forces.

[10 Marks] [C]

2007

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23. Explain and illustrate the terms, dipole-dipole attraction and ion-dipole attraction, which of these a comparatively stranger. [10

Marks] [C]

24. Suggest explanations for the fact that gases diffuse through all the space available to them. [10 Marks] [

C]

2008

25. Explain the Grohom'slaw of diffusion. [10 Marks] [C]

26. Explain the Maxwell's distribution of molecular velocities and show that

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

Where, 'n' is the number of molecules (of mass 'm')per cc, dnc/dc is the number of molecules per unit range of velocity, 'c' is the velocity and the rest of the symbols have their usual significance. [20 Marks]

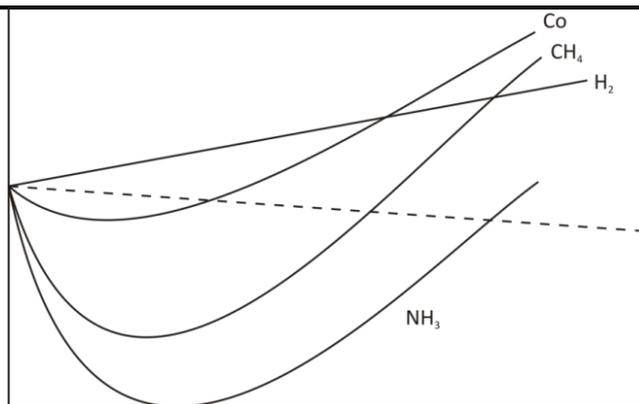
The Gaseous & State

- Equation of state for real gases
- Intermolecular interactions
- Liquefactions of gases and critical phenomenon.
- Maxwell's distribution of speeds
- Intermolecular collisions
- Collisions on the wall and effusion
- Real gases obey the equation $PV = nRT$ only approximately and that too under conditions of low pressure and high temperature. The higher the preuusse and the lower the temperature, the greater are the deviations from the ideal behaviour. In general, the most easily liquefiable and highly soluble gases show larger deviations. Gases like carbon dioxide, sulphur dioxide and ammoina. Show much larger deviations than hydrogen, oxygen, nitrogen etc.
- The deviations from ideal behaviour are best represented in terms of the compressibility factor (also called the compression factor) ,z, which is defined as

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} = \frac{pVm}{RT}$$

- For an gas, $Z = 1$ under all conditions of temp and pressure. The deviation of Z from unity is, thus, a measure of the imperfection of the gas under consideration.
- [A+ moderately low pressure, CO, NH₃& CO₂are more compressible than an ideal gas i.e. PV is less than (Pv ideal) so that $Z < 1$ this is due to fact that at low pressure, on the long range attractive force & are dominant and favour compression]

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Deviation of real gases for ideal behaviour

- Behaviour at high temperatures (Amit's notes) → molecular repulsion dominates
- Boyle temperature is the temperature at which or within this range, product PV remains constant.
- The Boyle temperature is different for different gases Boyle temperature for Hydrogen is -165°C and for helium it is -240°C . Thus at 165°C obeys Hydrogen gas Boyle's law for an appreciable range of pressure

Assumptions: - Gas molecules have finite size and

- i) The no. of collisions with the walls of the container are exactly the same for point and finite size molecules.
- ii) The molecular density is small

Equation of state for real gases :-

- J.D, vanderwaals proposed his famous equation of state for a non-ideal (i.e. Imperfect gas). He modified the ideal gas equation by suggesting that the gas molecules were not mass point but these exist inter-molecular forces of attraction between them. The two correction terms introduced by vanderwaals are described below

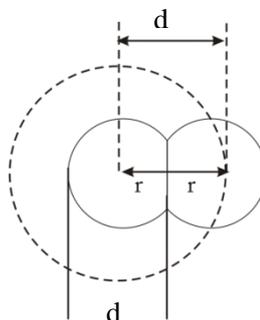
Assumptions:-

1. Correction due to volume of gas molecules

- The ideal gas equation $Pv = nRT$ is derived on the assumption that the gas molecules are mass points, i.e. they do not have finite volume. Vander waals abandoned this assumption and suggested that a correction term nb should be subtracted from the total volume V in order to get the ideal volume which is compressible. In order to understand the meaning of the correction term nb , let us consider two gas molecules as impenetrable and uncompressible sphere, each of which has a diameter d , as shown in fig 3. It is evident that the centres of the two spheres cannot approach each other more closely than the distance d for this pair of molecules, therefore, a sphere of radius d , and hence

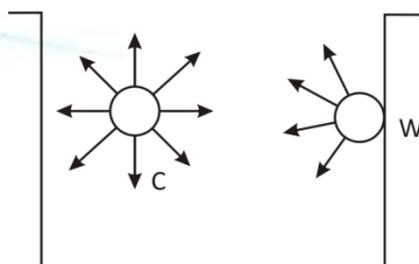
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of volume $\frac{4}{3}\pi d^3$, constitutes what is known as the excluded volume. The excluded volume per molecule is thus half the above volume. i.e. equal to $\frac{2}{3}\pi d^3$. the actual volume of one gas molecule of radius r is



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- $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi(d/2)^3 = \frac{1}{6}\pi d^3 V_{\text{actual}} = V_{\text{ideal}} + nb$
- Excluded volume per molecule = $\frac{2}{3}\pi d^3 = 4 \times \frac{1}{6}\pi d^3 = 4$ times the actual volume of the gas molecule. The excluded volume per mole of the gas would be $N_A \times 4 \times \frac{1}{6}\pi d^3 = b$, where N_A is the Avogadro number. The compressible volume per mole of the gas would thus be $v-b$. if volume V of the gas contains n moles, then the excluded volume would be nb . Hence the ideal volume which is compressible would be $(v-nb)$
- The volume b per mole is also known as co-volume.
- In the derivation of the ideal gas equation, it was assumed that there are no intermolecular forces of attraction. Actually it is not so. In order to take into account the effect of intermolecular forces of attraction let us consider a molecule lying somewhere in the midst of the vessel, as shown at the point C



- As can be seen, it is being attracted uniformly on all sides by the neighbouring molecules. These forces neutralize one another and there is no resultant attractive force on the molecule, however, as the molecule approaches the wall of the vessel as shown at W, it experiences attractive forces from the bulk of the molecules behind it. Hence it will strike the wall with a lower velocity and will exert a lower pressure than it would have done if there was no force of attraction. It is, therefore necessary to add a certain quantity to the pressure of

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the gas in order to get the ideal pressure. This correct pressure, therefore, should be $P + P$

Calculation of the correction Factor P :

- The force of attractive exerted on a single molecule which is about to strike the wall evidently depends upon the number of molecules per unit volume in the bulk of the gas, i.e. it depends directly upon the density of the gas. Further the number of molecules striking the wall at any given instant also depends directly upon the density of the gas. Thus, the total inward attractive pull on the molecules which gives a measure of the correction factor. P , is proportional to the square of the density (δ) of the gas i.e

- $P_{\text{ideal}} = P_{\text{actual}} + P_{\text{correction}}$; Pressure

$$P \propto \delta^2$$

- But, density is inversely proportional to the volume and if V is the volume occupied by one mole of a gas, the value of P for one mole of a gas will be inversely proportional to the square of volume.

- Hence, $P \propto \frac{a}{V^2}$

- where a is a constant depending upon the nature of the gas

$$P_{\text{ideal}} - P_{\text{actual}} = nRT$$

The kinetic gas equation for mole of a real gas therefore takes the form.

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

- Where V^m stands for the molar volume of the gas.

Hence, the vanderwaals equation for n mole & of a gas becomes

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

- Unit for the vanderwaals constants: - the units for the vanderwaals constant a and b depends upon the unit in which P and V are expressed. It is evident from above equation that constant a is expressed by the factor pV^2/n^2 i.e.

- Pressure $\times (\text{vol})^{2/\text{mol}^2}$. If pressure is expressed in atm and volume in dm^3 , the value of a will be in $\text{dm}^6 \text{atm mol}^{-2}$. As regards b , it is incompressible volume per mole of a gas. Hence it must have the same unit as volume per mole, e.g, $\text{dm}^3 \text{mol}^{-1}$

- The constant value a is a measure of the vanderwaals forces of cohesion existing between the molecules of a given gas. The greater the value of a , the strength of vanderwaals forces. The greater the value of a , the greater is the ease with which a gas can be liquified gas.

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$$\text{So}^2 - 6.71$$

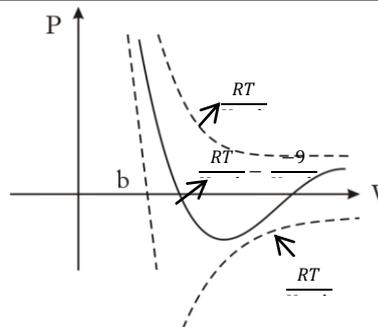
$$\text{Cl}^2 - 6.49$$

NH₃ – 4.71

C₂H₆ – 5.49

C₂H₄ – 4.74

HBr – 4.45



Discussion of the Vender Waals Equation:-

Case -1- When the pressure is not too high :- when the pressure is not very high, the volume V_m will be sufficiently large and b may be ignored in comparison. The vanderwaalsequon for one mole of a gas, viz.

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

May be written as

$$\left(p + \frac{a}{v_m^2}\right) V_m = RT$$

$$\text{Or } P v_m + a/v_m = RT$$

$$P v_m - RT - a/v_m$$

- Thus the product $P v_m$ is less than RT by an amount of equal to a/v_m . As pressure increase, V_m decreases, a/v_m increases and therefore, $P v_m$ becomes smaller and smaller. This explains the dip in the isotherms of most of the gases.

Case -2- When the pressure is too high :- when the pressure is considerably high, but volume V_m will be quite small. Now it may not be possible to ignore b but, as P is quite high, the quantity, the quantity a/v_m^2 may be come negligible in comparison with P in which , therefore reduces to

$$2. P(V_m - b) = RT$$

$$P V_m - RT +$$

$$P b$$

- Thus, $P v_m$ is now greater than RT by an amount equal to $P b$. As the pressure increases the product $P b$ increases and therefore, $P v_m$ increases. This explaining why value of $P v_m$, after reaching a minimum, increases with further increases of pressure

Case -3- when the temperature is high:- it is at a given pressure the temperature is considerably high the value will be sufficiently large to make the value of a/v_m^2 negligibly small. At high temperature b may also be negligible in comparison to V_m which is now sufficiently large. Under these conditions this

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vanderwaalsequation approaches the ideal gas equation, $P_{vm} = RT$. This explains why the deviations become less at high temperature.

Exceptional behaviour of hydrogen and helium:-

- Since both hydrogen and helium have comparatively small masses, the attractive forces between their molecules are too small. In other words, the correlation term a/Vm^2 due to the attraction remains negligible at ordinary temperature. Thus $P_{vm} = RT + Pb$

Boyle temperature :- temp. at which a real gas obeys Boyle's law, as known as Boyle temperature T_B . It is given by the expression

$$\text{➤ } T_B = a/bR$$

Where a and b are the van der Waals constants. T_B for CO_2 gas

$$a = 3.59 \text{ dm}^6 \text{ atm mol}^{-2} \text{ and } b = 0.0427 \text{ dm}^3 \text{ mol}$$

$$T_B = \frac{a}{Rb} = \frac{3.59}{(0.0427)(0.08206)}$$

$$T_B = 1026 \text{ K}$$

Ans.

$$P = \frac{nRT}{v-nb} - \frac{n^2 a}{v^2}$$

$$\left[\frac{\partial P}{\partial v} \right]_T = 0 \rightarrow \left[\frac{nRT}{v-nb} - \frac{nRTv}{(v-nb)^2} + \frac{2an^2}{v^3} \right] \left(\frac{\partial v}{\partial P} \right)_T = 0$$

$$\therefore T_B = \frac{a}{bR} \left[1 - \frac{nb}{v} \right]^2$$

$$\text{As } P \rightarrow 0, V \rightarrow \infty, \frac{nb}{v} \rightarrow 0$$

$$\therefore T_B = \frac{a}{bR}$$