INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

1 MARK

EASY:

1. Van der Waal's forces are directly proportional to which factor?
   Boiling point of the substances.
2. What type (s) of intermolecular forces exist between Br_2 and CCl_4?
   Dispersion forces
3. The strength of Vander waals forces depends upon which factor?
   It depends upon three factors, size of the molecule, molecular structure, number of electrons present in the molecule.
4. Write down the formula of critical volume for Van der Waal's gas.
   $V_c = 3nb$
5. Write down the relation of critical pressure for Van der Waal's gas
   $P_c = a / 27b^2$
6. Give one example of dipole – dipole interaction.
   Me_2O
7. Which interaction is the strongest interaction?
   Ionic interaction
8. Write down the relation of critical temperature for Van der Waal's gas.
   $T_c = 8a / 27bR$.

5 mark

Easy

1. Define Van der Waal's forces. Discuss their nature. 2 + 3
   The intermolecular attractive forces existing between all molecules when they are close to one another called van der Waal's forces. These forces are very weak in nature and operate only when molecules are very close to one another. The attractive force is opposed by two factors:
   (i) The repulsive force between the electron clouds of the adjacent molecules.
   (ii) The repulsive force between the nuclei of nearby atoms.
   However, the attractive forces overpower the repulsive forces.

Moderate

1. Compare the strength of intermolecular forces in H_2 and Halogens and arrange them in increasing order w.r.t. strength. When a real gas behave as ideal gas?
   H_2 being the smallest molecule, the strength of intermolecular forces among its molecules would be the least. Among the halogens it would go on increasing with increase in their respective size which is directly related with their molecular masses. So trend in the variation of strength would follow the order: $H_2 < F_2 < Cl_2 < Br_2 < I_2$.
   The molecular mass of I_2 being maximum, its molecule will have maximum number of electrons in it and so it will have the maximum strength of intermolecular among its molecules.
   Real gas behaves as ideal gas at its Boyle's temperature.

15 MARKS

Hard

1. (a) What would have happened to the gas if the molecular collisions were not elastic?

2. (b) CO_2 is heavier than O_2 and N_2 gases present in the air but it does not form the lower layer of the atmosphere. Why?
(c) Why in case of hydrogen and helium, the compressibility factor is always greater than 1 and increases with increase in pressure?
(d) Why gases can be liquefied by cooling?
(e) Which type of liquids will have higher boiling points? 'Polar or Non – polar liquids" – Give reason for your answer. 3 + 3 + + 3 + 3 + 3

(a) On every collision, there would have been loss of energy. As a result, the molecules would have slowed down and ultimately settle down in the vessel. Moreover, the pressure would have gradually reduced to zero.
(b) Gasses possess the property of diffusion which is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformly distributed in the atmosphere.
(c) The molecules of hydrogen and helium are of very small mass and consequently the force of attraction between the molecules is always negligible, Thus neglecting the term a/V, the equation $PV - Pb + a/V = RT = P'V'$ is reduced to $PV - Pb = RT = P'V'$
Or, $PV = P'V' + Pb$
i.e., the product PV is greater than $P'V'$ even at low pressure.
(d) All gases are composed of molecules, which are in a state of constant rapid motion. If the temperature is lowered, the kinetic energy of the gas molecules decreases and as a result, molecules move close to each other. Consequently, the volume occupied by the gas also decreases. If this lowering of temperature is continued, at some stage, the molecules will come so close together that they change into the liquid state.
(e) The polar liquids will have comparatively higher boiling points than that of non – polar liquids. It is because the Non – polar liquids will have only weak intermolecular forces existing among their molecules. But greater energy would be required for the vapourisation of polar molecules which possess permanent dipole moment in addition to the intermolecular forces among their molecules.

EASY

1. (a) Discuss types and conditions of hydrogen bonding. 5
(b) Write the equation of state for the real gas with proper notations. Mention the significance of constants a and b. 5
(c) Discuss the critical phenomenon of real gas. 2
(d) Calculate the Boyle temperature for a gas whose van der Waals constant $a = 7.18\ L^2\ atmMol^{-2}$, $b = 0.854\ L\ Mol^{-1}$ and $R = 0.082L\ atm\ K^{-1}\ mol^{-1}$.

(a) Conditions for the formation of Hydrogen – bonding
Hydrogen bond formation depends on few factors------
(i) Hydrogen bonding takes place with an atom having high electronegativity. Higher the electronegativity of the atom, stronger is the hydrogen bonding.
(ii) The atom which is involved in Hydrogen bonding should be small in size because smaller atoms can attract the electron density of the covalent bond more efficiently, thus can produce the polarity in the molecule and consequently the strength of the hydrogen bonding increases.
Types of hydrogen - bonding:
Hydrogen bonding is classified into two groups:
(i) Inter – molecular Hydrogen – bonding: If the hydrogen bonding takes place between two separate molecules of same type or different type then that kind of hydrogen bonding is called intermolecular hydrogen bonding. Example: H_2O, HF, ROH etc.

(ii) Intra – molecular Hydrogen – bonding: If the hydrogen bonding takes place within the molecule itself, then that is called intra – molecular Hydrogen bonding. Example: Ortho – nitro phenol, Salicyldehyde.

(b) Equation of state for real gas (van der Waals equation) is given by

$(P + n^2a/V^2)(V – nb) = nRT$

P = pressure of gas, V = volume of gas, n = number of moles of gas, R = molar gas constant, T = absolute temperature, a and b = van der Waals constant.

For one mole of gas equation of state is $(P + a/V^2)(V – b) = RT$

'a' and 'b' are van der Waals constants in the equation of state for real gas.

'a' is a measure of intermolecular force of attraction among the molecules. Higher is the value of 'a' higher is the intermolecular forces of attraction and easier is to liquefy the gas. The effect of intermolecular attraction is to reduce the pressure of gas from the ideal value that appears in absence of 'a'.

'b' is related to size (radius) of a molecule, higher is the value of 'b' higher is the size of the molecule. The molecules in a real gas has non – zero volume and molecules behave as small but impenetrate sphere, as a result n moles of gas molecules vove not in a volume V but less than V equal to V – nb where 'b' is roughly the volume taken up by Avogadro number (N_A) molecules themselves. Effect of 'b' (size) is to increase the pressure from that expected for ideal gas behaviour where 'b' is zero. It can be shown that $b = 4N_A(4/3\pi r^3)$, Where N_A is Avogadro number and r is the radius of the molecule.

(c) Critical phenomenon is observed by real gas which has both 'a' and 'b' values. To understand it we consider a gas taken in a bulb which is connected to a mercury manometer. The bulb is gradually cooled, at temperatures liquid and vapour phases of the gas becomes clearly visible. The bulb is surrounded by a jacket which is used to function as a thermostat. The temperature of the thermostat is slowly increased until the meniscus just vanishes. The temperature and the pressure at which the meniscus disappears are noted. The bulb is then very slowly cooled and the temperature and pressure are again noted at which the surface of separation just reappears. This average of the two temperature (T_C) and critical pressure (P_C). The mercury manometer is used to measure P_C. The molar volume of the gas at T_C and P_C is called critical volume V_C. A beautiful colour appears when the system is at T_C, P_C. This phenomenon of real gas is called critical phenomenon.

Boyle temperature is given by $T_B = a / Rb$ where a and b are van der Waals constant.

$a = 7.18\ L^2\ atm\ mol^{-2}$ $b = 0.854\ L\ mol^{-1}$ $R = 0.082\ L\ atm\ K^{-1}\ mol^{-1}$

So $T_B = 7.18\ L^2\ atm\ mol^{-2} / (0.854\ L\ mol^{-1})(0.082\ L\ atm\ K^{-1}\ mol^{-1}) = 102.53\ K$.

Moderate

1. (a) Out of N_2 and NH_3, which one will have greater value for van der Waal's constant 'a' and which one will have greater value for van der Waal's constant 'b'? 5

(b) What is the application of Potential Energy Surface (PES)? 5

(c) Using van der Waals equation, calculate the pressure exerted by one mole of carbon dioxide. When it occupies a volume of 0.05 litre at 100°C, given that a = 3.592, b = 0.0426 and R = 0.0821 litre atmosphere/degree mole. Write down the different types of interaction forces. 5

(a) (i) As NH_3 is more liquefiable (due to hydrogen bonding), intermolecular forces of attraction are stronger than in N_2. Hence, NH_3 will have greater value for 'a'.

(ii) As NH_3 molecule is larger in size than N_2, hence , NH_3 will have greater value for 'b'(For NH_3 $a = 4.17\ L^2\ atm\ mol^{-2}$ $b = 0.0371\ L\ mol^{-1}$.For N_2 $a = 1.39\ L^2\ atm\ mol^{-2}$ $b = 0.0319\ L\ mol^{-1}$.)

(b) A potential energy surface is a tool for finding the analysis of molecular shapes and chemical kinetics of a reaction. Once the necessary points are evaluated on a PES, the point can be classified according to the first and second derivatives of the energy with respect to position. These correspond to the gradient and the curvature of the curve respectively. Stationary points have physical meaning i.e. energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate.

(c) It is given that , n = 1 mole V = 0.05 litre; a = 3.592 atms. Litre^2 mole^{-2} b= 0.0426 litre /mole; R = 0.0821 litre atmosphere/degree/mol; T = 100ºC + 273 = 373K
Van der Waal's equation, for one mole
$(P + a/V^2) (V – b) = RT$
$P + a /V^2 = RT / (V – b)$
$P = RT/ (V – b) – a/V^2$
Substituting the value of a, b, V and T in the equation
$P = (0.0821 \times 373)/ (0.05 – 0.0426) - 3.592/0.0025 = 2701.5$ atm.

The following types of intermolecular force exists between the molecules of different substances:
1. Dipole – dipole interaction
2. Induced dipole – induced dipole
3. Ion – dipole
4. Ion – induced dipole
5. Instantaneous dipole - Instantaneous induced dipole forces.