

1. Answer any 5 of the following:

(a) Why are viscosity of gases increases with increase in temperature whereas viscosity of liquids decreases with increase in temperature ?

- **Viscosity of Gases:**

- Gases have much weaker intermolecular forces compared to liquids.
- The viscosity of a gas arises primarily from the transfer of momentum between layers of gas moving at different velocities.
- As temperature increases, the kinetic energy and thus the random thermal motion (molecular speeds) of gas molecules increase.
- This increased molecular motion leads to a higher frequency of collisions between molecules moving in different layers, resulting in a more effective transfer of momentum from faster layers to slower layers.
- Therefore, the resistance to flow (viscosity) of gases increases with increasing temperature.

- **Viscosity of Liquids:**

- Liquids have significant intermolecular attractive forces (e.g., hydrogen bonding, dipole-dipole interactions, London dispersion forces).
- The viscosity of a liquid arises mainly from the resistance offered by these strong intermolecular forces to the movement of one layer of liquid past another.
- As temperature increases, the average kinetic energy of liquid molecules increases, which helps them to overcome these intermolecular attractive forces more easily.

- This weakening of intermolecular forces with increasing temperature reduces the internal friction between liquid layers.
- Therefore, the resistance to flow (viscosity) of liquids decreases with increasing temperature.

(b) Explain the effect of temperature and pressure on collision frequency of a gas.

- **Collision Frequency (Z):** Collision frequency refers to the number of collisions per unit time experienced by a single molecule in a gas.
- **Effect of Temperature on Collision Frequency:**
 - Collision frequency is directly proportional to the average speed of gas molecules.
 - The average speed of gas molecules is directly proportional to the square root of the absolute temperature ($c_{avg} \propto \sqrt{T}$).
 - As temperature increases, the molecules move faster, leading to a higher number of collisions per unit time with other molecules.
 - Therefore, collision frequency of a gas **increases with an increase in temperature**.
- **Effect of Pressure on Collision Frequency:**
 - Collision frequency is directly proportional to the number density (number of molecules per unit volume, n/V) of the gas.
 - At a constant temperature, increasing the pressure of a gas means increasing its number density (more molecules packed into the same volume or same number of molecules in a smaller volume).
 - A higher number density means that molecules are closer together, leading to a higher probability of collision per unit time.

- Therefore, collision frequency of a gas **increases with an increase in pressure**.

(c) At same temperature the distribution of molecular speeds of hydrogen and helium is same. Explain.

- This statement is incorrect. At the same temperature, the *distribution* of molecular speeds for hydrogen (H_2) and helium (He) is **not the same**.
- **Maxwell-Boltzmann Distribution of Molecular Speeds:** The distribution of molecular speeds for a gas at a given temperature is described by the Maxwell-Boltzmann distribution law. This law states that the fraction of molecules having speeds within a certain range depends on the molar mass (M) of the gas and the absolute temperature (T).
- **Dependence on Molar Mass:**
 - The formulas for different types of speeds (most probable speed, average speed, root mean square speed) all show an inverse relationship with the square root of the molar mass:

$$\blacksquare \quad c_p = \sqrt{\frac{2RT}{M}} * c_{avg} = \sqrt{\frac{8RT}{\pi M}} * c_{rms} = \sqrt{\frac{3RT}{M}}$$

- Hydrogen (H_2) has a molar mass of approximately 2 g/mol.
- Helium (He) has a molar mass of approximately 4 g/mol.
- **Explanation:**
 - Since H_2 has a smaller molar mass than He, its molecules will, on average, move faster than helium molecules at the same temperature.
 - Consequently, the peak of the Maxwell-Boltzmann distribution curve for hydrogen will be shifted to higher speeds compared to that of helium at the same temperature. The curve for hydrogen

will also be broader and flatter, indicating a wider range of speeds.

- Therefore, while both gases will follow the Maxwell-Boltzmann distribution at a given temperature, their specific speed distributions (i.e., the shapes and positions of their curves) will be different, with the lighter hydrogen molecules having a higher range of speeds.

(d) Why the composition of gases in the earth's atmosphere varies with height ?

- The composition of gases in the Earth's atmosphere varies with height primarily due to two main factors: **gravity** and **temperature gradients (and associated atmospheric mixing)**.
- **Gravity:**
 - Earth's gravity acts on all gas molecules, pulling them downwards.
 - Lighter gas molecules (like H_2 and He) are less affected by gravity and can more easily escape to higher altitudes or even outer space.
 - Heavier gas molecules (like N_2 and O_2) are held more strongly by gravity and tend to concentrate closer to the Earth's surface.
 - This gravitational stratification leads to a gradual decrease in the concentration of heavier gases and an increase in the relative abundance of lighter gases as altitude increases. For example, nitrogen and oxygen make up the bulk of the lower atmosphere (troposphere and stratosphere), while hydrogen and helium become more prevalent in the exosphere.
- **Temperature Gradients and Atmospheric Mixing:**

- The atmosphere is divided into layers based on temperature variations (troposphere, stratosphere, mesosphere, thermosphere, exosphere).
- In the lower atmosphere (troposphere), there is significant atmospheric mixing (convection, winds) due to temperature differences and weather phenomena. This mixing tends to keep the composition of the major gases (N_2 , O_2 , Ar, CO_2) relatively uniform up to certain heights. This region is called the homosphere.
- In the upper atmosphere (above the mesopause, into the thermosphere and exosphere), the temperature increases sharply, and the density of the atmosphere becomes very low. At these heights, molecular collisions become less frequent, and gravitational separation becomes much more dominant. This region is called the heterosphere, where gases essentially separate according to their molecular weights.
- **Other factors:**
 - **Photodissociation and Photoionization:** In the upper atmosphere, high-energy solar radiation can break down molecules like O_2 and N_2 into atomic oxygen (O) and atomic nitrogen (N) and also ionize them. This leads to a higher concentration of atomic species and ions at very high altitudes.
 - **Chemical Reactions:** Chemical reactions involving different gases also contribute to the variation in composition, for instance, the formation and destruction of ozone in the stratosphere.

(e) Discuss the effect of detergent concentration on the surface tension of water giving graphical representation. Why surface tension becomes nearly constant at higher concentrations of detergent ?

- **Effect of Detergent Concentration on Surface Tension of Water:**

- Detergents (surfactants) are amphiphilic molecules, meaning they have both a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail.
- When detergents are added to water, the hydrophobic tails are repelled by water molecules, while the hydrophilic heads are attracted.
- To minimize their contact with water, detergent molecules migrate to the air-water interface. They orient themselves such that their hydrophobic tails protrude into the air (or into non-polar phases) and their hydrophilic heads remain in the water.
- By accumulating at the surface, these detergent molecules disrupt the strong cohesive hydrogen bonding network of water molecules at the interface. This reduces the inward pull on the surface molecules, thereby **reducing the surface tension of water**.
- As the concentration of detergent increases, more and more detergent molecules populate the surface, leading to a **progressive decrease in surface tension**.
- **Graphical Representation (Description):**
 - (As per instructions, I cannot draw a diagram, but I can describe it.)
 - A plot of surface tension (y-axis) versus log(detergent concentration) (x-axis) would typically show:
 - **Initial Phase (Low Concentration):** The surface tension decreases sharply as the detergent concentration increases. This is because detergent molecules are efficiently adsorbing onto the surface.
 - **Critical Micelle Concentration (CMC):** At a certain concentration, called the Critical Micelle Concentration (CMC), the surface becomes saturated with detergent

molecules. Beyond this concentration, additional detergent molecules in the bulk solution begin to aggregate and form micelles (spherical clusters with hydrophobic tails inwards and hydrophilic heads outwards).

- **Plateau Phase (Higher Concentration):** Once the CMC is reached, adding more detergent no longer significantly reduces the surface tension because the surface is already saturated. The excess detergent forms micelles in the bulk, and very few, if any, additional molecules go to the surface.
- **Why surface tension becomes nearly constant at higher concentrations:**
 - At concentrations above the Critical Micelle Concentration (CMC), the surface of the liquid (water) is already completely covered or saturated with detergent molecules.
 - Any additional detergent molecules added to the solution will not go to the surface to further reduce surface tension. Instead, they will aggregate in the bulk of the solution to form micelles.
 - Since no more detergent molecules are adsorbing onto the surface, the cohesive forces at the interface are not further disrupted.
 - Therefore, the surface tension of the water becomes nearly constant (or reaches a minimum plateau value) once the CMC is exceeded, regardless of further increases in bulk detergent concentration.

(f) Explain the dependence of surface tension on temperature and why the surface tension of a liquid becomes zero at its critical temperature.

- **Dependence of Surface Tension on Temperature:**

- Surface tension of a liquid **decreases with increasing temperature**.
- This is because surface tension arises from the cohesive intermolecular forces between liquid molecules. Molecules at the surface experience a net inward pull from the bulk liquid.
- As the temperature of a liquid increases, the average kinetic energy of its molecules also increases.
- This increased molecular motion allows the molecules to overcome the intermolecular attractive forces more easily.
- Consequently, the cohesive forces between molecules weaken, reducing the net inward pull on the surface molecules.
- This leads to a decrease in surface tension.
- Conversely, as temperature decreases, intermolecular forces become stronger, and surface tension increases.
- **Why surface tension becomes zero at its critical temperature:**
 - The **critical temperature (T_c)** of a substance is the temperature above which a gas cannot be liquefied, no matter how high the pressure. At and above the critical temperature, the distinction between liquid and gas phases disappears, and the substance exists as a supercritical fluid.
 - As temperature approaches the critical temperature, the kinetic energy of the liquid molecules becomes very high, and the intermolecular forces become very weak.
 - At the critical temperature, the densities of the liquid phase and the gas (vapor) phase become identical. There is no longer a distinct interface separating the liquid and vapor.
 - Since surface tension is a phenomenon that depends on the difference in intermolecular forces (and thus density) between the two phases at an interface, when this distinction vanishes at

the critical temperature, the net inward cohesive force at the "surface" becomes zero.

- Therefore, the surface tension of a liquid **becomes zero at its critical temperature**. Beyond the critical temperature, the concept of surface tension is no longer applicable.
2. (a) Starting from the postulates of the kinetic theory of gas derive the following equation

- $PV = \frac{1}{3}mN\langle c^2 \rangle$

- **Postulates of Kinetic Theory of Gases (relevant ones):**

- a. Gases consist of a very large number of identical, tiny particles (molecules) that are in continuous, random motion.
- b. The volume occupied by the individual gas molecules is negligible compared to the total volume of the container.
- c. There are no intermolecular forces of attraction or repulsion between the molecules, except during collisions.
- d. Collisions between molecules and between molecules and the walls of the container are perfectly elastic (no loss of kinetic energy).
- e. The average kinetic energy of the gas molecules is directly proportional to the absolute temperature.

- **Derivation:**

- f. **Consider a single molecule in a cubical container:**

- Let's consider a gas molecule of mass 'm' moving with a velocity 'c' in a cubical container of side 'L'.
 - The velocity 'c' can be resolved into three components along the x, y, and z axes: c_x, c_y, c_z .

- By Pythagorean theorem: $c^2 = c_x^2 + c_y^2 + c_z^2$

g. Momentum change during collision with a wall:

- Consider a molecule moving towards the wall perpendicular to the x-axis (say, face A) with velocity component c_x .
- On collision, its velocity component perpendicular to the wall reverses to $-c_x$.
- The change in momentum of the molecule in the x-direction is: $m(-c_x) - m(c_x) = -2mc_x$.
- By Newton's third law, the momentum imparted to the wall is $2mc_x$.

h. Time between successive collisions with the same wall:

- For a molecule to collide with the same wall again, it must travel to the opposite wall (distance L) and back (distance L), covering a total distance of 2L in the x-direction.
- Time taken (Δt) = Distance / Speed = $2L/c_x$.

i. Force exerted by one molecule on the wall:

- Force (F) = Rate of change of momentum = Change in momentum / Time interval
- $F_x = \frac{2mc_x}{2L/c_x} = \frac{mc_x^2}{L}$

j. Pressure exerted by one molecule on the wall:

- Pressure (P) = Force / Area. The area of the wall is L^2 .
- $P_x = \frac{mc_x^2/L}{L^2} = \frac{mc_x^2}{L^3}$ * Since $L^3 = V$ (volume of the container): $P_x = \frac{mc_x^2}{V}$

k. Total pressure exerted by N molecules:

- In a real gas, there are N molecules, each with different velocities. We need to consider the average of the square of the velocity components.
- Since the motion is random, on average, the molecules move equally in all three directions:

$$\bullet \langle c_x^2 \rangle = \langle c_y^2 \rangle = \langle c_z^2 \rangle \text{ * And } \langle c^2 \rangle = \langle c_x^2 \rangle + \langle c_y^2 \rangle + \langle c_z^2 \rangle = 3\langle c_x^2 \rangle \text{ * So, } \langle c_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$$

- The total pressure exerted by N molecules on the walls is the sum of the pressures due to all molecules. Using the average of the square of the velocity ($\langle c^2 \rangle$):

$$\bullet P = \sum_{i=1}^N \frac{mc_{xi}^2}{V} = \frac{m}{V} \sum_{i=1}^N c_{xi}^2 \text{ * Since } \sum c_{xi}^2 = N\langle c_x^2 \rangle \text{ (where } \langle c_x^2 \rangle \text{ is the mean square velocity in x-direction for all molecules)}$$

$$\bullet P = \frac{m}{V} N \langle c_x^2 \rangle \text{ * Substituting } \langle c_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle:$$

$$\bullet P = \frac{m}{V} N \left(\frac{1}{3}\langle c^2 \rangle \right) \text{ * } PV = \frac{1}{3}mN\langle c^2 \rangle$$

- Where:

- P = Pressure of the gas
- V = Volume of the gas
- m = Mass of a single gas molecule
- N = Total number of gas molecules
- $\langle c^2 \rangle$ = Mean square speed of the gas molecules

(b) Calculate the root mean square speed, average speed and most probable speed of H₂ molecules at 298K.

- **Given:**

- Temperature (T) = 298 K
- Molar mass of H₂ (M) = 2.016 g/mol = 0.002016 kg/mol
- Gas constant (R) = 8.314 J mol⁻¹ K⁻¹ (or 8.314 kg m² s⁻² mol⁻¹ K⁻¹)

• **Formulas:**

- Most Probable Speed (c_p) = $\sqrt{\frac{2RT}{M}}$ * Average Speed (c_{avg}) = $\sqrt{\frac{8RT}{\pi M}}$
 * Root Mean Square Speed (c_{rms}) = $\sqrt{\frac{3RT}{M}}$

• **Calculations:**

l. **Root Mean Square Speed (c_{rms}):**

$$\begin{aligned} \blacksquare c_{rms} &= \sqrt{\frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.002016 \text{ kg mol}^{-1}}} * c_{rms} = \sqrt{\frac{7432.224}{0.002016}} \text{ m/s} \\ * c_{rms} &= \sqrt{3686619.04} \text{ m/s} * c_{rms} \approx 1919.98 \text{ m/s} \end{aligned}$$

m. **Average Speed (c_{avg}):**

$$\begin{aligned} \blacksquare c_{avg} &= \sqrt{\frac{8 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\pi \times 0.002016 \text{ kg mol}^{-1}}} * c_{avg} = \sqrt{\frac{19819.264}{0.006339}} * c_{avg} = \\ &\sqrt{3126742.06} \text{ m/s} * c_{avg} \approx 1768.26 \text{ m/s} \end{aligned}$$

n. **Most Probable Speed (c_p):**

$$\begin{aligned} \blacksquare c_p &= \sqrt{\frac{2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.002016 \text{ kg mol}^{-1}}} * c_p = \sqrt{\frac{4954.912}{0.002016}} \text{ m/s} * c_p = \\ &\sqrt{2457893.85} \text{ m/s} * c_p \approx 1567.77 \text{ m/s} \end{aligned}$$

• **Results:**

- Root Mean Square Speed (c_{rms}) \approx 1920 m/s
- Average Speed (c_{avg}) \approx 1768 m/s

- Most Probable Speed (c_p) \approx 1568 m/s
 - **Note:** As expected, $c_p < c_{avg} < c_{rms}$.
- (c) Draw labelled diagram of P-V isotherms of CO₂. Explain these isotherms and continuity of states.
- **P-V Isotherms of CO₂ (Description):**
 - (As per instructions, I cannot draw diagrams. I will describe the features of the isotherms.)
 - The diagram would typically show several curves on a P-V (Pressure-Volume) graph, each representing a constant temperature (isotherm).
 - **High Temperature Isotherms (e.g., above 31.1°C for CO₂):**
 - These curves resemble ideal gas isotherms (hyperbolas, $PV = \text{constant}$).
 - As pressure increases, volume decreases smoothly, without any abrupt changes, indicating that the substance remains entirely in the gaseous phase.
 - **Isotherm at Critical Temperature ($T_c = 31.1^\circ\text{C}$ for CO₂):**
 - This is the **critical isotherm**. It exhibits a horizontal inflection point, known as the **critical point (C)**.
 - At the critical point, the slope (dP/dV) is zero, and the second derivative (d^2P/dV^2) is also zero.
 - Below the critical point, the substance is entirely gaseous. Above the critical point (on this isotherm), it is also gaseous. At the critical point, the liquid and gas phases become indistinguishable.
 - **Isotherms Below Critical Temperature (e.g., 21.5°C or 13.1°C for CO₂):**

- These isotherms show three distinct regions:

1. **Gaseous Region (High Volume, Low Pressure):**

The curve initially slopes downwards (similar to an ideal gas). As pressure increases, the gas compresses.

2. **Liquid-Vapor Equilibrium Region (Horizontal Plateau):**

At a certain pressure, the curve becomes horizontal. This indicates that as volume decreases (pressure is constant), the gas starts to condense into liquid. Both liquid and vapor phases coexist in equilibrium. The length of the horizontal segment represents the range of volumes over which liquefaction occurs. This constant pressure is the vapor pressure of the liquid at that temperature.

3. **Liquid Region (Low Volume, High Pressure):**

Once all the gas has condensed into liquid, the curve becomes very steep. This signifies that liquid is nearly incompressible; a large increase in pressure is required for a small decrease in volume.

- **Explanation of Isotherms and Continuity of States:**

- **Liquefaction:** The isotherms clearly illustrate the conditions under which a gas can be liquefied. Below the critical temperature, a gas can be liquefied by increasing the pressure. The horizontal portion of the isotherm represents the phase transition from gas to liquid.
- **Critical Point:** The critical point (C) is a unique state defined by the critical temperature (T_c), critical pressure (P_c), and critical volume (V_c). Above T_c , a gas cannot be liquefied, no matter how high the pressure. It exists as a supercritical fluid. At T_c , the meniscus separating the liquid and gas phases disappears.

- **Continuity of States:** The concept of continuity of states implies that there is no fundamental difference between the liquid and gaseous states. One can transition smoothly from a liquid to a gas (or vice versa) without undergoing a phase transition, provided the path taken in the P-V-T diagram goes around the critical point.
 - For example, starting from a point in the liquid region, one can first increase the temperature above T_c (to become a supercritical fluid), then decrease the pressure, and finally decrease the temperature back below T_c (to become a gas), without ever crossing a two-phase region (horizontal plateau). This demonstrates that liquid and gas are continuous phases of matter, differing mainly in density and the degree of order. The critical point serves as a boundary beyond which the distinction between liquid and gas ceases to exist.

3. (a) Using the van der Waals equation of state, derive the following relation :

- $$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$
- State law of corresponding states based on this relation and significance of this relation.
- **Derivation of Reduced Equation of State:**
 - The van der Waals equation of state for one mole of gas is:
 - $$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$
 - Critical constants are related to van der Waals constants as:
 - $V_c = 3b$ (or $b = V_c/3$)
 - $P_c = \frac{a}{27b^2}$ (or $a = 27b^2P_c$)

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

- We define reduced variables:

$$\blacksquare \text{Reduced Pressure: } P_r = \frac{P}{P_c} \Rightarrow P = P_r P_c \text{ * Reduced}$$

$$\text{Volume: } V_r = \frac{V_m}{V_c} \Rightarrow V_m = V_r V_c \text{ * Reduced Temperature: } T_r = \frac{T}{T_c} \Rightarrow T = T_r T_c$$

- Substitute these into the van der Waals equation:

$$\blacksquare (P_r P_c + \frac{a}{(V_r V_c)^2})(V_r V_c - b) = R(T_r T_c) \text{ * Now, substitute the expressions for a, b, } P_c, V_c, \text{ and } T_c \text{ in terms of a, b, R:}$$

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

- Substitute into the reduced equation:

$$\blacksquare (P_r \frac{a}{27b^2} + \frac{a}{(V_r 3b)^2})(V_r 3b - b) = R(T_r \frac{8a}{27Rb}) * (P_r \frac{a}{27b^2} + \frac{a}{9V_r^2 b^2})(3bV_r - b) = \frac{8aT_r}{27b}$$

- Factor out common terms:

$$\blacksquare \frac{a}{b^2} (\frac{P_r}{27} + \frac{1}{9V_r^2}) b(3V_r - 1) = \frac{8aT_r}{27b} \text{ * Divide both sides by } \frac{a}{b}:$$

$$\blacksquare \frac{1}{b} (\frac{P_r}{27} + \frac{1}{9V_r^2}) b(3V_r - 1) = \frac{8T_r}{27b} * \frac{1}{27} (P_r + \frac{3}{V_r^2})(3V_r - 1) = \frac{8T_r}{27}$$

- Multiply both sides by 27:

$$\blacksquare (P_r + \frac{3}{V_r^2})(3V_r - 1) = 8T_r \text{ * Rearrange to solve for } P_r:$$

$$\blacksquare P_r + \frac{3}{V_r^2} = \frac{8T_r}{3V_r - 1} * P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

- **Law of Corresponding States:**

- **Statement:** The law of corresponding states states that all fluids, when compared at the same reduced temperature (T_r) and reduced pressure (P_r), have approximately the same reduced volume (V_r) and deviate from ideal gas behavior to roughly the same extent. In other words, if two different substances have the same reduced temperature and reduced pressure, they will also have approximately the same reduced volume.
- **Significance of this relation:**
 - **Universality:** The reduced van der Waals equation ($P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$) is a universal equation because it does not contain any specific constants for a particular gas (a, b, R). It applies to all gases that obey the van der Waals equation. This means that if we express the properties of different gases in terms of their critical constants, their behavior becomes qualitatively similar.
 - p. **Prediction of Properties:** It allows for the prediction of the properties of gases and liquids at various conditions if their critical constants are known. For instance, if the P_c and T_c of a new substance are known, its density at a given P_r and T_r can be estimated by determining V_r .
 - q. **Deviation from Ideal Behavior:** The deviation of real gases from ideal gas behavior can be compared and understood more uniformly using reduced variables.
 - r. **Engineering Applications:** It is highly useful in chemical engineering and process design for scaling up or down processes, predicting phase behavior, and designing equipment for various fluids based on data from known substances.

(b) Calculate the fraction of oxygen gas molecules at 27°C and 1 atm possessing velocities between 400 ± 10 m/s.

- **Given:**

- Temperature (T) = 27°C = 27 + 273.15 = 300.15 K
- Molar mass of Oxygen (O₂) = 32.0 g/mol = 0.032 kg/mol
- Gas constant (R) = 8.314 J mol⁻¹ K⁻¹
- Velocity range: $c = 400 \pm 10$ m/s, so $c_1 = 390$ m/s and $c_2 = 410$ m/s
- Since the range is small ($\Delta c = 20$ m/s), we can use the probability distribution function for a single speed 'c' multiplied by the small range.
- Maxwell-Boltzmann Distribution function for the fraction of molecules (dN/N) with speeds between c and c + dc:

$$\frac{dN}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} c^2 e^{-Mc^2/2RT} dc$$

- **Calculations:**

- s. **Calculate the constant term:**

$$\begin{aligned} A &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} * A = 4\pi \left(\frac{0.032 \text{ kg/mol}}{2\pi \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}} \right)^{3/2} \\ *A &= 4\pi \left(\frac{0.032}{15705.5} \right)^{3/2} *A = 4\pi (2.0375 \times 10^{-6})^{3/2} *A = \\ &= 4\pi (2.0375^{3/2} \times 10^{-9}) *A = 4\pi (0.00291 \times 10^{-9}) = \\ &= 4\pi (2.91 \times 10^{-12}) *A \approx 3.656 \times 10^{-11} \end{aligned}$$

- t. **Calculate the exponential term:**

$$\begin{aligned} e^{-Mc^2/2RT} &* \text{Let's use the average velocity in the range, } c = 400 \text{ m/s.} \\ \frac{Mc^2}{2RT} &= \frac{0.032 \text{ kg/mol} \times (400 \text{ m/s})^2}{2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}} * \frac{Mc^2}{2RT} = \frac{0.032 \times 160000}{5000.86} * \frac{Mc^2}{2RT} = \\ &= \frac{5120}{5000.86} \approx 1.0238 * e^{-1.0238} \approx 0.3592 \end{aligned}$$

- u. **Calculate the fraction (dN/N):**

$$\begin{aligned} \frac{dN}{N} &= A \times c^2 \times e^{-Mc^2/2RT} \times \Delta c \times \frac{dN}{N} = (3.656 \times 10^{-11}) \times \\ &(400)^2 \times 0.3592 \times 20 \times \frac{dN}{N} = (3.656 \times 10^{-11}) \times 160000 \times \\ &0.3592 \times 20 \times \frac{dN}{N} = (3.656 \times 10^{-11}) \times 16 \times 10^4 \times 0.3592 \times \\ &20 \times \frac{dN}{N} = (3.656 \times 16 \times 0.3592 \times 20) \times 10^{-7} \times \frac{dN}{N} = \\ &420.27 \times 10^{-7} = 4.2027 \times 10^{-5} \end{aligned}$$

• **Result:**

- The fraction of oxygen gas molecules possessing velocities between 400 ± 10 m/s is approximately 4.20×10^{-5} .

(c) Derive an expression for the coefficient of viscosity of a gas, η in terms of the mean free path, λ and show that η of a gas is dependent on temperature, but is independent of pressure.

• **Derivation of Coefficient of Viscosity (η):**

- Consider a gas flowing in layers in the x-direction with a velocity gradient in the z-direction (velocity increases with z). Let the velocity of the layer at height z be u_z .
- The velocity gradient is du/dz .
- A molecule moving from a layer at $z - \lambda$ to a layer at z (where λ is the mean free path) will carry momentum from the lower layer to the higher layer. Similarly, a molecule moving from $z + \lambda$ to z will carry momentum from the higher layer to the lower layer. This transfer of momentum constitutes the viscous drag.
- **Momentum of a molecule:** $P = mu$
- **Change in momentum transferred per collision:**
 - From a layer at $z - \lambda$ to z : $m[u_z - (u_z - \lambda \frac{du}{dz})] = m\lambda \frac{du}{dz}$
 - From a layer at $z + \lambda$ to z : $m[(u_z + \lambda \frac{du}{dz}) - u_z] = m\lambda \frac{du}{dz}$
- Number of molecules crossing unit area per unit time:**

In any given direction (say, upwards or downwards along the z-axis), the number of molecules crossing a unit area per unit time is approximately $\frac{1}{6} N_v \langle c \rangle$, where N_v is the number density (molecules/volume) and $\langle c \rangle$ is the average molecular speed. For flow across a plane, the factor is often approximated as $\frac{1}{3}$.

- **Net momentum transferred per unit area per unit time (Force per unit area):** This is the shear stress, which is equal to $\eta \frac{du}{dz}$.
- Consider molecules from two layers: one at $z - \lambda$ and one at $z + \lambda$.
 - Flux of molecules from $z - \lambda$ to z is $\frac{1}{3} N_v \langle c \rangle$.
 - Momentum transferred upwards = $\frac{1}{3} N_v \langle c \rangle m (u_z - \lambda \frac{du}{dz})$ *
 Flux of molecules from $z + \lambda$ to z is $\frac{1}{3} N_v \langle c \rangle$.
 - Momentum transferred downwards = $\frac{1}{3} N_v \langle c \rangle m (u_z + \lambda \frac{du}{dz})$
 - The net rate of downward momentum transfer per unit area (force) is:
 - $F/A = \frac{1}{3} N_v \langle c \rangle m (u_z + \lambda \frac{du}{dz}) - \frac{1}{3} N_v \langle c \rangle m (u_z - \lambda \frac{du}{dz})$
 * $F/A = \frac{1}{3} N_v \langle c \rangle m [2\lambda \frac{du}{dz}]$ * $F/A = \frac{2}{3} N_v m \langle c \rangle \lambda \frac{du}{dz}$ * By definition, $F/A = \eta \frac{du}{dz}$ * Therefore, the coefficient of viscosity $\eta = \frac{2}{3} N_v m \langle c \rangle \lambda$
- Using the more precise value from kinetic theory (after rigorous integration over velocities), the constant becomes 1/2:
 - $\eta = \frac{1}{2} N_v m \langle c \rangle \lambda$

○ We know:

- $N_v = \frac{N}{V} = \frac{P}{kT}$ (where k is Boltzmann constant)
- Mean free path $\lambda = \frac{1}{\sqrt{2}\pi d^2 N_v} = \frac{kT}{\sqrt{2}\pi d^2 P}$ (where d is molecular diameter)

- Average speed $\langle c \rangle = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$ * Substitute these into the expression for η :

$$\eta = \frac{1}{2} \left(\frac{N}{V} \right) m \langle c \rangle \left(\frac{1}{\sqrt{2}\pi d^2 (N/V)} \right) * \eta = \frac{1}{2} m \langle c \rangle \frac{1}{\sqrt{2}\pi d^2} * \eta = \frac{m \langle c \rangle}{2\sqrt{2}\pi d^2} *$$

$$\text{Substitute } \langle c \rangle = \sqrt{\frac{8kT}{\pi m}} * \eta = \frac{m}{2\sqrt{2}\pi d^2} \sqrt{\frac{8kT}{\pi m}} = \frac{1}{2\sqrt{2}\pi d^2} \sqrt{\frac{8mkT}{\pi}} * \eta =$$

$$\frac{1}{\pi d^2} \sqrt{\frac{mkT}{\pi}} \text{ (This is a simplified form, sometimes constants are absorbed)}$$

- A more common result after proper averaging is:
 - $\eta = \frac{1}{\pi d^2} \sqrt{\frac{mkT}{\pi}}$ or $\eta = \frac{2}{3\pi d^2} \sqrt{mkT}$ (constants vary slightly by derivation method).
 - A widely accepted result for a hard sphere model is:

$$\circ \eta = \frac{1}{3\sqrt{\pi}} \frac{\sqrt{mkT}}{d^2} \text{ or } \eta = \frac{1}{2d^2} \sqrt{\frac{mkT}{\pi}} * \text{Let's stick with the form involving } \lambda \text{ and then analyze.}$$

$$\circ \eta = \frac{1}{2} \rho \langle c \rangle \lambda, \text{ where } \rho = N_v m \text{ (density).}$$

- **Dependence on Temperature and Independence of Pressure:**

- From the formula $\eta = \frac{1}{2} N_v m \langle c \rangle \lambda$:

- **Temperature Dependence:**

- Average speed $\langle c \rangle \propto \sqrt{T}$.
 - Mean free path $\lambda \propto T$ (since $\lambda \propto 1/P$ and $P \propto T$ at constant volume, or more directly, $\lambda = kT/(\sqrt{2}\pi d^2 P)$; if P is constant, $\lambda \propto T$).
 - Number density N_v depends on T at constant P ($N_v = P/kT \propto 1/T$).
 - So, $\eta \propto \frac{1}{T} \cdot \sqrt{T} \cdot T = \sqrt{T}$.
 - More accurately: $\eta \propto \sqrt{T}$. As temperature increases, the average speed of molecules increases, leading to a more efficient transfer of momentum, thus increasing viscosity.
- **Pressure Independence:**
- When we substitute the expressions for N_v and λ that explicitly contain pressure:
 - $N_v = P/kT$ * $\lambda = kT/(\sqrt{2}\pi d^2 P)$ * $\eta = \frac{1}{2} \left(\frac{P}{kT} \right) m \langle c \rangle \left(\frac{kT}{\sqrt{2}\pi d^2 P} \right)$
 - Notice that P cancels out:
 - $\eta = \frac{1}{2\sqrt{2}\pi d^2} m \langle c \rangle$ * Since 'm', 'd', and 'k' are constants, and $\langle c \rangle$ only depends on temperature, the coefficient of viscosity of a gas is effectively **independent of pressure** (at moderate pressures).
 - **Explanation:** While an increase in pressure increases the number of molecules per unit volume (N_v), which would tend to increase collisions and viscosity, it also simultaneously decreases the mean free path (λ) in the same proportion. A shorter mean free path means molecules travel shorter distances between collisions,

reducing the effective momentum transfer per molecule. These two effects (increase in N_v and decrease in λ) cancel each other out, leading to the independence of viscosity from pressure.

- (This independence holds true for ideal gases and at moderate pressures. At very high pressures, where intermolecular forces become significant, or at very low pressures, where the mean free path becomes comparable to the container size, deviations occur.)

4. (a) Derive the expression of Barometric law :

- $p = p_0 \exp(-Mgh/RT)$
- Explain the effects of temperature and molar mass of the gas on the variation of pressure with height.

• **Derivation of Barometric Law:**

v. **Consider a thin layer of gas:**

- Imagine a column of gas of unit cross-sectional area and infinitesimal height 'dh' at a height 'h' from a reference level.
- Let the pressure at height 'h' be 'p' and at height 'h + dh' be 'p + dp'.
- The pressure difference 'dp' is due to the weight of the gas in the layer 'dh'.
- The weight of the gas in this layer is the mass of the gas (dm) in the layer multiplied by acceleration due to gravity (g).
- $dp = - \frac{\text{Weight of gas in layer}}{\text{Area}} * dp = - \frac{dm \cdot g}{1}$ (assuming unit area)
- The negative sign indicates that pressure decreases with increasing height.

w. Relate mass to density and volume:

- Mass of gas in the layer, $dm = \rho \cdot V_{\text{layer}}$ * Since the cross-sectional area is 1, $V_{\text{layer}} = 1 \cdot dh = dh$.
- So, $dm = \rho \cdot dh$ * Substituting this into the pressure equation: $dp = -\rho g dh$

x. Relate density to pressure using Ideal Gas Law:

- For an ideal gas, $PV = nRT$.
- $n = \frac{m_{\text{total}}}{M}$ (where m_{total} is total mass of gas, M is molar mass)
- So, $PV = \frac{m_{\text{total}}}{M} RT \Rightarrow P = \frac{m_{\text{total}}}{V} \frac{RT}{M}$ * Since density $\rho = \frac{m_{\text{total}}}{V}$, we have $P = \rho \frac{RT}{M}$ * Rearranging for density: $\rho = \frac{PM}{RT}$

y. Substitute density into the pressure differential equation:

- $dp = -\left(\frac{PM}{RT}\right) g dh$
- Separate variables (p on one side, h on the other):
 - $\frac{dp}{P} = -\frac{Mg}{RT} dh$

z. Integrate both sides:

- Integrate from initial pressure p_0 at height $h_0 = 0$ to pressure 'p' at height 'h':
 - $\int_{p_0}^p \frac{dp}{P} = \int_0^h -\frac{Mg}{RT} dh$ * $[\ln P]_{p_0}^p = -\frac{Mg}{RT} [h]_0^h$ (Assuming T is constant, an isothermal atmosphere)
 - $\ln P - \ln p_0 = -\frac{Mgh}{RT}$ * $\ln\left(\frac{P}{p_0}\right) = -\frac{Mgh}{RT}$
- Exponentiate both sides:

$$\bullet \quad \frac{P}{p_0} = e^{-Mgh/RT} \quad *p = p_0 \exp(-Mgh/RT)$$

- **Effects of Temperature and Molar Mass:**

- **Effect of Temperature (T):**

- The term $-Mgh/RT$ is in the exponent. As temperature (T) increases, the denominator RT increases, making the entire exponential term (Mgh/RT) smaller (less negative).
- This means that $\exp(-Mgh/RT)$ becomes closer to 1.
- **Interpretation:** At higher temperatures, molecules have higher kinetic energy and are more spread out. The pressure decrease with height is less pronounced. The atmosphere is less dense and extends to higher altitudes. This implies that the pressure falls off less rapidly with increasing height at higher temperatures.

- **Effect of Molar Mass (M):**

- As the molar mass (M) of the gas increases, the term Mgh/RT (in the exponent) increases, making the exponent more negative.
- This means that $\exp(-Mgh/RT)$ becomes smaller.
- **Interpretation:** Heavier gases are more strongly affected by gravity. Their density decreases more rapidly with height. Therefore, the pressure of a gas with a higher molar mass falls off more steeply with increasing height compared to a lighter gas. This explains why lighter gases like H_2 and He are more abundant in the upper atmosphere, while N_2 and O_2 are concentrated closer to the surface.

(b) Determine the molar mass of a gas if its pressure falls to one - fourth of its value in a vertical distance of 8 km at 27°C.

• **Given:**

- Initial pressure = p_0 * Final pressure (p) = $p_0/4$
- Vertical distance (h) = 8 km = 8000 m
- Temperature (T) = 27°C = 27 + 273.15 = 300.15 K
- Gas constant (R) = 8.314 J mol⁻¹ K⁻¹
- Acceleration due to gravity (g) = 9.81 m s⁻² (standard value)

• **Barometric Law:** $p = p_0 \exp(-Mgh/RT)$

• **Solving for Molar Mass (M):**

aa. Substitute the given values:

- $\frac{p_0}{4} = p_0 \exp\left(-\frac{M \times 9.81 \text{ m s}^{-2} \times 8000 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}}\right)$ 2. Divide both sides by p_0 :
- $\frac{1}{4} = \exp\left(-\frac{78480M}{2496.06}\right) * \frac{1}{4} = \exp(-31.449M)$

bb. Take the natural logarithm (ln) of both sides:

- $\ln\left(\frac{1}{4}\right) = -31.449M * \ln(1) - \ln(4) = -31.449M * 0 - 1.38629 = -31.449M * -1.38629 = -31.449M$

cc. Solve for M:

- $M = \frac{-1.38629}{-31.449} * M \approx 0.04408 \text{ kg/mol} * M \approx 44.08 \text{ g/mol}$

• **Result:**

- The molar mass of the gas is approximately **44.08 g/mol**. (This value is close to that of CO₂, which is 44.01 g/mol).

(c) The Critical constants for water are $T_c = 647\text{K}$, $P_c = 218 \text{ atm}$ and $V_c = 0.05 \text{ dm}^3 \text{ mol}^{-1}$. Calculate the van der Waals constants and critical compressibility factor.

- **Given Critical Constants for Water:**

- Critical Temperature (T_c) = 647 K
- Critical Pressure (P_c) = 218 atm
- Critical Volume (V_c) = $0.05 \text{ dm}^3 \text{ mol}^{-1} = 0.05 \text{ L mol}^{-1}$ (since $1 \text{ dm}^3 = 1 \text{ L}$)

- **Gas Constant (R):** Use R in units consistent with atm and L:

- $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$

- **Formulas relating critical constants to van der Waals constants (a and b):**

- $V_c = 3b \Rightarrow b = V_c/3$ * $P_c = \frac{a}{27b^2} \Rightarrow a = 27P_c b^2$ * (We can use $T_c = \frac{8a}{27Rb}$ as a check or to calculate a/b ratio)

- **Calculations for van der Waals constants:**

dd. **Calculate 'b':**

$$b = \frac{V_c}{3} = \frac{0.05 \text{ L mol}^{-1}}{3} \Rightarrow b \approx 0.01667 \text{ L mol}^{-1}$$

ee. **Calculate 'a':**

$$a = 27P_c b^2 \Rightarrow a = 27 \times 218 \text{ atm} \times (0.01667 \text{ L mol}^{-1})^2 \Rightarrow a = 27 \times 218 \times (0.0002778) \text{ L}^2 \text{ atm mol}^{-2} \Rightarrow a = 5886 \times 0.0002778 \text{ L}^2 \text{ atm mol}^{-2} \Rightarrow a \approx 1.635 \text{ L}^2 \text{ atm mol}^{-2}$$

- **Calculations for Critical Compressibility Factor (Z_c):**

- **Formula:** $Z_c = \frac{P_c V_c}{RT_c}$

- **Substitute values:**

$$Z_c = \frac{(218 \text{ atm}) \times (0.05 \text{ L mol}^{-1})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (647 \text{ K})} \Rightarrow Z_c = \frac{10.9}{53.09} \Rightarrow Z_c \approx 0.2053$$

- **Results:**

- **Van der Waals constant 'a'** $\approx 1.635 \text{ L}^2 \text{ atm mol}^{-2}$
- **Van der Waals constant 'b'** $\approx 0.01667 \text{ L mol}^{-1}$
- **Critical Compressibility Factor (Z_c)** ≈ 0.2053

- **Note:** For a van der Waals gas, the theoretical critical compressibility factor is always $3/8 = 0.375$. The calculated value for water (0.2053) deviates significantly from this, indicating that water does not strictly follow the van der Waals equation and has more complex intermolecular interactions (like hydrogen bonding).

5. (a) Starting with the Clapeyron equation, derive the expression for Clausius-Clapeyron equation that explains the effect of temperature on pressure of a liquid.

- **Clapeyron Equation:**

- The Clapeyron equation describes the slope of a phase boundary curve in a P-T diagram:

- $$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

- Where:

- dP/dT is the slope of the phase coexistence curve (e.g., vapor pressure curve).
 - ΔH is the molar enthalpy change during the phase transition (e.g., $\Delta_{vap}H$ for vaporization, $\Delta_{fus}H$ for fusion).
 - T is the absolute temperature at which the phase transition occurs.
 - ΔV is the molar volume change during the phase transition (e.g., $V_{gas} - V_{liquid}$ for vaporization).

- **Derivation of Clausius-Clapeyron Equation (for liquid-vapor equilibrium):**

ff. **Apply Clapeyron Equation to Vaporization:**

- For the liquid-vapor equilibrium, $\Delta H = \Delta_{vap}H$ (molar enthalpy of vaporization) and $\Delta V = V_{gas} - V_{liquid}$.
- So, $\frac{dP}{dT} = \frac{\Delta_{vap}H}{T(V_{gas} - V_{liquid})}$

gg. **Approximation 1: Neglecting Volume of Liquid:**

- For most liquid-vapor equilibria, especially at temperatures well below the critical temperature, the molar volume of the gas (V_{gas}) is significantly larger than the molar volume of the liquid (V_{liquid}).
- So, we can approximate: $V_{gas} - V_{liquid} \approx V_{gas}$ * The equation becomes: $\frac{dP}{dT} = \frac{\Delta_{vap}H}{TV_{gas}}$

hh. **Approximation 2: Ideal Gas Behavior for Vapor:**

- Assume that the vapor behaves as an ideal gas. For one mole of an ideal gas, $PV_{gas} = RT$, so $V_{gas} = \frac{RT}{P}$.

ii. **Substitute Ideal Gas Volume into the Equation:**

- $\frac{dP}{dT} = \frac{\Delta_{vap}H}{T(\frac{RT}{P})} * \frac{dP}{dT} = \frac{P\Delta_{vap}H}{RT^2}$

jj. **Rearrange and Integrate:**

- Divide by P: $\frac{1}{P} \frac{dP}{dT} = \frac{\Delta_{vap}H}{RT^2}$ * The left side is equivalent to $\frac{d(\ln P)}{dT}$:
 - $\frac{d(\ln P)}{dT} = \frac{\Delta_{vap}H}{RT^2}$

- This is the differential form of the Clausius-Clapeyron equation.
- To get the integrated form, assume $\Delta_{vap}H$ is constant over the temperature range of integration:

$$\bullet \int \frac{d(\ln P)}{dT} dT = \int \frac{\Delta_{vap}H}{RT^2} dT \quad * \ln P = -\frac{\Delta_{vap}H}{R} \int T^{-2} dT$$

$$* \ln P = -\frac{\Delta_{vap}H}{R} \left(-\frac{1}{T}\right) + C \text{ (where C is the integration constant)}$$

$$\bullet \ln P = \frac{\Delta_{vap}H}{RT} + C \text{ (This is one form)}$$

- **Definite Integral Form (between two temperatures and pressures):**

$$\bullet \int_{P_1}^{P_2} \frac{d(\ln P)}{dT} dT = \int_{T_1}^{T_2} \frac{\Delta_{vap}H}{RT^2} dT \quad * \ln \left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- This is the integrated form of the Clausius-Clapeyron equation.

• **Explanation of Effect of Temperature on Pressure of a Liquid:**

- The Clausius-Clapeyron equation directly shows how the vapor pressure (P) of a liquid changes with temperature (T).
- Since $\Delta_{vap}H$ (enthalpy of vaporization) and R are positive constants, the term $\frac{\Delta_{vap}H}{RT^2}$ is always positive. This means $d(\ln P)/dT$ is always positive.
- This indicates that as temperature (T) increases, the natural logarithm of vapor pressure (ln P) increases, which means the **vapor pressure (P) of a liquid increases exponentially with increasing temperature.**
- Physically, as temperature rises, more molecules in the liquid gain sufficient kinetic energy to overcome the intermolecular

forces and escape into the vapor phase, leading to a higher equilibrium vapor pressure.

(b) The vapour pressure of water at 90°C is 70.13 kPa and the molar enthalpy of vaporization between 90°C and 100°C is 2.268 kJ/g. Calculate the vapour pressure of water at 100°C.

- **Given:**

- $T_1 = 90^\circ\text{C} = 90 + 273.15 = 363.15 \text{ K}$
- $P_1 = 70.13 \text{ kPa}$
- $T_2 = 100^\circ\text{C} = 100 + 273.15 = 373.15 \text{ K}$
- Enthalpy of vaporization ($\Delta_{vap}H$) = 2.268 kJ/g

- **Convert $\Delta_{vap}H$ to J/mol:**

- Molar mass of water (H_2O) = 18.015 g/mol
- $\Delta_{vap}H_{molar} = 2.268 \text{ kJ/g} \times 18.015 \text{ g/mol} = 40.864 \text{ kJ/mol} = 40864 \text{ J/mol}$

- **Gas constant (R) = 8.314 J mol⁻¹ K⁻¹**

- **Clausius-Clapeyron Equation:**

- $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

- **Calculations:**

kk. Calculate the term $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$:

- $\left(\frac{1}{363.15} - \frac{1}{373.15}\right) = (0.0027536 - 0.0026799) \text{ K}^{-1} = 0.0000737 \text{ K}^{-1}$

ll. Calculate the right-hand side (RHS) of the equation:

$$\begin{aligned} \blacksquare \quad RHS &= \frac{40864 \text{ J/mol}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times 0.0000737 \text{ K}^{-1} \quad *RHS = 4915.22 \times \\ &0.0000737 \quad *RHS \approx 0.3623 \quad 3. \text{ Now, solve for } P_2: \\ \blacksquare \quad \ln\left(\frac{P_2}{70.13 \text{ kPa}}\right) &= 0.3623 \quad * \frac{P_2}{70.13 \text{ kPa}} = e^{0.3623} \quad *e^{0.3623} \approx 1.4365 \\ *P_2 &= 70.13 \text{ kPa} \times 1.4365 \quad *P_2 \approx 100.74 \text{ kPa} \end{aligned}$$

• **Result:**

- The vapor pressure of water at 100°C is approximately **100.74 kPa**.
- (Note: Standard atmospheric pressure at 100°C is 101.325 kPa, so this value is very close, as expected).

(c) Calculate the surface tension of liquid toluene and the radius of the capillary tube, if the level of water and toluene rose in the capillary is 9.8 cm and 5.2 cm, respectively. Given surface tension of water at 20°C = 72.75 dyne cm⁻¹, density of water = 998.2 kg m⁻³ and density of toluene = 890.5 kg m⁻³.

• **Given:**

○ **For Water (W):**

- Height (h_W) = 9.8 cm = 0.098 m
- Surface tension (γ_W) = 72.75 dyne cm⁻¹ = 72.75 × 10⁻³ N m⁻¹ (since 1 dyne = 10⁻⁵ N, 1 cm = 10⁻² m, so 1 dyne/cm = 10⁻⁵ N / 10⁻² m = 10⁻³ N/m)
- Density (ρ_W) = 998.2 kg m⁻³

○ **For Toluene (T):**

- Height (h_T) = 5.2 cm = 0.052 m
- Density (ρ_T) = 890.5 kg m⁻³

- Acceleration due to gravity (g) = 9.81 m s⁻² (standard value)

- **Capillary Rise Formula:**

- $\gamma = \frac{1}{2} r h \rho g \cos \theta$ * For most liquids in a clean glass capillary that wet the surface, $\cos \theta \approx 1$ (i.e., contact angle $\theta \approx 0^\circ$). So, $\gamma = \frac{1}{2} r h \rho g$

- **Strategy:**

mm. Use water data to find the radius (r) of the capillary tube.

nm. Use the calculated 'r' and toluene data to find the surface tension of toluene.

- **Step 1: Calculate the radius (r) of the capillary tube using water data.**

- $\gamma_W = \frac{1}{2} r h_W \rho_W g$ * Rearrange for r: $r = \frac{2\gamma_W}{h_W \rho_W g}$ * $r = \frac{2 \times (72.75 \times 10^{-3} \text{ N m}^{-1})}{(0.098 \text{ m}) \times (998.2 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})}$ * $r = \frac{0.1455}{959.034}$ * $r \approx 0.0001517 \text{ m}$ *
Convert to cm or mm for easier interpretation: $r \approx 0.01517 \text{ cm} \approx 0.1517 \text{ mm}$

- **Step 2: Calculate the surface tension of liquid toluene (γ_T) using 'r' and toluene data.**

- $\gamma_T = \frac{1}{2} r h_T \rho_T g$ * $r = 0.0001517 \text{ m}$ * $h_T = 0.052 \text{ m}$ * $\rho_T = 890.5 \text{ kg m}^{-3}$ * $g = 9.81 \text{ m s}^{-2}$ * $\gamma_T = \frac{1}{2} \times (0.0001517 \text{ m}) \times (0.052 \text{ m}) \times (890.5 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})$ * $\gamma_T = 0.5 \times 0.0001517 \times 0.052 \times 890.5 \times 9.81$ * $\gamma_T = 0.5 \times 0.0001517 \times 456.92$ * $\gamma_T \approx 0.03468 \text{ N m}^{-1}$ * Convert to dyne cm^{-1} : $0.03468 \text{ N m}^{-1} = 0.03468 \times 10^3 \text{ dyne cm}^{-1}$ (since $1 \text{ N/m} = 1000 \text{ dyne/cm}$)

- $\gamma_T \approx 34.68 \text{ dyne cm}^{-1}$

- **Results:**

- The radius of the capillary tube is approximately **0.0152 cm** (or 0.152 mm).
- The surface tension of liquid toluene is approximately **34.68 dyne cm⁻¹**.

6. (a) Define coefficient of viscosity. Write SI unit of viscosity. Derive the expression for determination of viscosity of a liquid by using Ostwald's viscometer method.

- **Coefficient of Viscosity (η):**

- The coefficient of viscosity (dynamic viscosity) is a measure of a fluid's resistance to flow (or shear deformation) under stress.
- It is defined as the tangential force per unit area required to maintain a unit velocity gradient between two parallel layers of fluid.
- Mathematically, for laminar flow, it is given by Newton's law of viscosity: $F/A = \eta \frac{du}{dy}$, where F is the tangential force, A is the area of the layer, du/dy is the velocity gradient perpendicular to the flow, and η is the coefficient of viscosity.

- **SI Unit of Viscosity:**

- The SI unit of viscosity is the **Pascal-second (Pa·s)**, which is equivalent to **Newton-second per square meter (N·s·m⁻²)** or **kilogram per meter per second (kg·m⁻¹·s⁻¹)**.
- In the CGS system, the unit is the Poise (P), and 1 Pa·s = 10 P. A common sub-unit is centipoise (cP), where 1 cP = 1 mPa·s.

- **Derivation of Expression for Ostwald's Viscometer Method:**

- **Ostwald's Viscometer Principle:** This method compares the viscosity of a liquid (test liquid) with that of a reference liquid (usually water) by measuring the time taken for a fixed volume of each liquid to flow through a capillary tube under gravity.

- **Poiseuille's Equation:** The flow of a liquid through a capillary tube is described by Poiseuille's equation:

- $$V = \frac{\pi r^4 \Delta P t}{8 \eta L}$$

- Where:

- V = Volume of liquid flowing
- r = Radius of the capillary tube
- ΔP = Pressure difference across the capillary
- t = Time of flow
- η = Coefficient of viscosity
- L = Length of the capillary tube

- **Applying to Ostwald's Viscometer:**

- i. In Ostwald's viscometer, the volume (V), capillary radius (r), and capillary length (L) are constant for both the test liquid and the reference liquid.
- ii. The pressure difference (ΔP) across the capillary is due to the hydrostatic head of the liquid column.

- $$\Delta P = h \rho g$$

- Where:

- h = Average height of the liquid column (hydrostatic head)
- ρ = Density of the liquid
- g = Acceleration due to gravity

- c. **Substituting ΔP into Poiseuille's Equation:**

$$\blacksquare V = \frac{\pi r^4 (h \rho g) t}{8 \eta L}$$

d. **For Liquid 1 (reference liquid, e.g., water):**

$$\blacksquare V = \frac{\pi r^4 h \rho_1 g t_1}{8 \eta_1 L} \quad (1)$$

e. **For Liquid 2 (test liquid):**

$$\blacksquare V = \frac{\pi r^4 h \rho_2 g t_2}{8 \eta_2 L} \quad (2)$$

f. **Equating (1) and (2) since V, r, h, g, L are constant:**

$$\blacksquare \frac{\pi r^4 h \rho_1 g t_1}{8 \eta_1 L} = \frac{\pi r^4 h \rho_2 g t_2}{8 \eta_2 L}$$

g. **Cancel common terms:**

$$\blacksquare \frac{\rho_1 t_1}{\eta_1} = \frac{\rho_2 t_2}{\eta_2} \quad \text{8. Rearrange to find } \eta_2 \text{ (viscosity of the test liquid):}$$

$$\blacksquare \eta_2 = \eta_1 \frac{\rho_2 t_2}{\rho_1 t_1}$$

- **Conclusion:** This expression allows for the determination of the viscosity of an unknown liquid (η_2) by measuring its flow time (t_2) and density (ρ_2), and knowing the viscosity (η_1), flow time (t_1), and density (ρ_1) of a reference liquid (e.g., water) at the same temperature.

(b) The viscosity of a liquid is $5 \times 10^{-4} \text{ Nsm}^{-2}$ at 27°C and $2.5 \times 10^{-4} \text{ Nsm}^{-2}$ at 327°C . Calculate the energy of activation of viscous flow assuming it to be constant in this temperature range.

- **Given:**

$$\circ \eta_1 = 5 \times 10^{-4} \text{ Nsm}^{-2} \text{ at } T_1 = 27^\circ\text{C} = 300.15 \text{ K} \quad \eta_2 = 2.5 \times 10^{-4} \text{ Nsm}^{-2} \text{ at } T_2 = 327^\circ\text{C} = 600.15 \text{ K}$$

- **Arrhenius-type equation for viscosity:**

- The dependence of viscosity on temperature for liquids often follows an Arrhenius-type equation:

- $\eta = Ae^{E_a/RT}$

- Where:

- η = viscosity
- A = pre-exponential factor (constant)
- E_a = energy of activation for viscous flow
- R = gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- T = absolute temperature

- Taking the natural logarithm:

- $\ln \eta = \ln A + \frac{E_a}{RT}$

- For two different temperatures:

- $\ln \eta_1 = \ln A + \frac{E_a}{RT_1}$ * $\ln \eta_2 = \ln A + \frac{E_a}{RT_2}$

- Subtracting the first from the second:

- $\ln \eta_2 - \ln \eta_1 = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$ * $\ln \left(\frac{\eta_2}{\eta_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

• Calculations:

- oo. Substitute the given values:

- $\ln \left(\frac{2.5 \times 10^{-4}}{5 \times 10^{-4}} \right) = \frac{E_a}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{600.15 \text{ K}} - \frac{1}{300.15 \text{ K}} \right)$ * $\ln(0.5) =$
 $\frac{E_a}{8.314} (0.001666 - 0.003331)$ * $-0.6931 = \frac{E_a}{8.314} (-0.001665)$

2. Solve for E_a :

- $E_a = \frac{-0.6931 \times 8.314}{-0.001665}$ * $E_a = \frac{5.762}{0.001665}$ * $E_a \approx 34600 \text{ J mol}^{-1}$ * $E_a \approx$
 34.6 kJ mol^{-1}

- **Result:**

- The energy of activation of viscous flow is approximately **34.6 kJ mol⁻¹**.

(c) (i) The heat of Vaporization of water is 1.5 times that of CCl₄. Which liquid will have the higher surface tension and why ?

- **Relationship between Heat of Vaporization and Surface Tension:**

- Both heat of vaporization ($\Delta_{vap}H$) and surface tension (γ) are measures of the strength of intermolecular forces in a liquid.
- **Heat of vaporization** is the energy required to overcome all intermolecular forces to convert a liquid into a gas.
- **Surface tension** arises from the net attractive forces experienced by molecules at the surface, pulling them inwards.
- Liquids with stronger intermolecular forces will require more energy to vaporize (higher $\Delta_{vap}H$) and will also exhibit greater cohesive forces at their surface (higher surface tension).

- **Comparison:**

- Given that the heat of vaporization of water is 1.5 times that of CCl₄. This implies that the intermolecular forces in water are significantly stronger than those in CCl₄.
- Water exhibits strong **hydrogen bonding**, which is a powerful intermolecular force.
- CCl₄ is a nonpolar molecule with only weak London dispersion forces.

- **Conclusion:**

- Since water has a much higher heat of vaporization, it means its molecules are held together by stronger intermolecular

forces. Consequently, water will have a **higher surface tension** than CCl_4 .

- This is why water has a surface tension of ~ 72 dyne/cm at 20°C , whereas CCl_4 has a much lower surface tension of ~ 26 dyne/cm at 20°C .

(c) (ii) Comment on the effect of addition of sucrose on the viscosity of water ?

- **Effect of Addition of Sucrose on Viscosity of Water:**

- When sucrose (a sugar) is added to water, the viscosity of the solution **increases significantly**.

- **Reasons:**

pp. **Increased Intermolecular Interactions (Hydrogen Bonding):** Sucrose molecules are highly polar and contain many hydroxyl ($-\text{OH}$) groups. These hydroxyl groups can form extensive hydrogen bonds with water molecules. This leads to increased intermolecular attractions within the solution, making it more resistant to flow.

qq. **Increased Molecular Size and Entanglement:** Sucrose molecules are relatively large compared to water molecules. When these large molecules are dissolved in water, they create more "obstacles" for the free movement of water molecules. The movement of solvent molecules is hindered by the larger solute molecules, leading to increased internal friction. This is often referred to as an increase in molecular "entanglement" or hydrodynamic resistance.

rr. **Hydrodynamic Volume:** Each sucrose molecule, along with the water molecules hydrogen-bonded to it, effectively creates a larger "hydrodynamic volume" that needs to move together. This effectively increases the "size" of the flowing units within the liquid, contributing to higher viscosity.

- **Practical Observation:** This effect is commonly observed when making sugar solutions or syrups; they are noticeably thicker (more viscous) than pure water.

(c) (iii) Is it possible to liquify an ideal gas ? Explain.

- **Is it possible to liquefy an ideal gas? No.**
- **Explanation:**
 - **Definition of an Ideal Gas:** An ideal gas is a theoretical construct based on specific assumptions from the kinetic theory of gases:
 - i. The volume occupied by the individual gas molecules is negligible compared to the total volume of the container.
 - ii. There are **no intermolecular forces of attraction or repulsion** between the molecules.
 - iii. Collisions between molecules are perfectly elastic.
 - **Mechanism of Liquefaction:** Liquefaction of a real gas occurs when the kinetic energy of the gas molecules is reduced (by lowering temperature) to a point where the **intermolecular attractive forces** become dominant. These attractive forces then pull the molecules together to form the liquid phase. Simultaneously, increasing pressure helps to bring molecules closer, facilitating the attractive forces.
 - **Why Ideal Gases Cannot Be Liquefied:** Since a fundamental postulate of the ideal gas model is the **absence of intermolecular forces of attraction**, there are no forces available to pull the molecules together to form a liquid phase, regardless of how much the temperature is lowered or how high the pressure is applied. Without these attractive forces, the molecules will simply continue to move freely and randomly, maintaining the gaseous state.

- Therefore, an ideal gas cannot be liquefied. Liquefaction is a phenomenon unique to real gases, where intermolecular forces play a crucial role.

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