Solution: DPP-2 [Vapour Pressure]

Chapter: Solution

"Consistency is the bridge between goals and accomplishment."

TYPE–1 : Basic Concepts of Vapour Pressure

1. **In liquid-gas equilibrium, the pressure of vapours above the liquid is constant at**
   (1) Constant temperature
   (2) Low temperature
   (3) High temperature
   (4) None of these
   Ans: (1) Constant temperature
   Solution: Vapour pressure is an equilibrium property. At a given constant temperature, the rate of evaporation equals the rate of condensation, and the vapour pressure remains constant. It depends only on temperature, not on the amount of liquid or vapour present.
2. **Vapour pressure is the pressure exerted by vapours**
   (1) In equilibrium with liquid
   (2) In any condition
   (3) In an open system
   (4) In atmospheric conditions
   Ans: (1) In equilibrium with liquid
   Solution: Vapour pressure is defined as the pressure exerted by the vapour in thermodynamic equilibrium with its condensed phase (liquid or solid) at a given temperature in a closed system.
3. **The vapour pressure of water depends upon:**
   (A) Surface area of container
   (B) Volume of container
   (C) Temperature
   (D) All
   Ans: (C) Temperature
   Solution: Vapour pressure is an intensive property that depends only on temperature and the nature of the liquid. It does not depend on surface area, volume, or amount of liquid. As temperature increases, more molecules have sufficient energy to escape, so vapour pressure increases.
4. **During evaporation of liquid**
   (1) The temperature of liquid rises
   (2) The temperature of liquid falls
   (3) The temperature of liquid remains unaffected
   (4) The liquid molecules become inert
   Ans: (2) The temperature of liquid falls
   Solution: Evaporation is a cooling process. During evaporation, the molecules with higher kinetic

energy escape from the liquid surface, leaving behind molecules with lower average kinetic energy. Since temperature is proportional to average kinetic energy, the temperature of the remaining liquid decreases.

TYPE–2 : Boiling Point & Vapour Pressure Relationship

1. **The boiling points of C_6H_6, CH_3OH, $C_6H_5NH_2$, and $C_6H_5NO_2$ are 80°C, 65°C, 184°C and 212°C respectively. Which of the following will have highest vapour pressure at room temperature?**
   (1) C_6H_6
   (2) CH_3OH
   (3) $C_6H_5NH_2$
   (4) $C_6H_5NO_2$
   Ans: (2) CH_3OH
   Solution: Lower boiling point ⇒ Weaker intermolecular forces ⇒ Higher vapour pressure at room temperature.
   CH_3OH has the lowest boiling point (65°C), so it has the highest vapour pressure at room temperature.
   Order of VP: $CH_3OH > C_6H_6 > C_6H_5NH_2 > C_6H_5NO_2$
2. **The boiling points of C_4H_6, CH_3OH, $C_4H_5NH_2$, and $C_5H_5NO_2$ are 80°C, 65°C, 184°C and 212°C respectively. Which will show highest vapour pressure at room temperature:**
   (1) C_4H_6
   (2) CH_3OH
   (3) $C_4H_5NH_2$
   (4) $C_5H_5NO_2$
   Ans: (1) C_4H_6
   Solution: Note: In this question, we need to compare vapour pressures at room temperature (25°C). All given boiling points are above room temperature. But C_4H_6 (butyne/butadiene) with BP = 80°C is closest to room temperature among the options if we consider it's actually a low BP compound. Actually, C_4H_6 (1,3-butadiene) has BP ≈ -4°C, which is below room temperature, making it the most volatile. The question seems to have an error in the given BP values, but based on the answer key, C_4H_6 has the highest vapour pressure.
3. **The temperature at which the vapour pressure of a liquid equals external pressure is called**
   (1) Freezing point
   (2) Boiling point
   (3) Melting point
   (4) Critical temperature
   Ans: (2) Boiling point
   Solution: By definition, boiling point is the temperature at which the vapour pressure of a liquid equals the external (atmospheric) pressure. At this point, vapour bubbles can form throughout the liquid, not just at the surface.
   At 1 atm pressure, this is called the normal boiling point.
4. **At higher altitude, the boiling point of water is lowered because**

(1) Atmospheric pressure is low
(2) Temperature is low
(3) Atmospheric pressure increases
(4) Water solidifies to ice

Ans: (1) Atmospheric pressure is low

Solution: At higher altitudes, atmospheric pressure decreases. Since boiling occurs when vapour pressure equals external pressure, water needs to reach a lower vapour pressure to boil. This happens at a lower temperature.

For example: At Mt. Everest (≈ 0.34 atm), water boils at about 70°C.

5. **At higher altitudes, water boils at temperature < 100°C because**

(A) Temperature at higher altitudes is low
(B) Atmospheric pressure is low
(C) The proportion of heavy water increases
(D) Atmospheric pressure becomes more

Ans: (B) Atmospheric pressure is low

Solution: Same concept as above. Lower atmospheric pressure at higher altitudes means the vapour pressure of water equals the external pressure at a temperature below 100°C.

6. **Vapour pressure diagram of some liquids plotted against temperature are shown below**

[Refer to question paper for graph]

Most volatile liquid

(1) A
(2) B
(3) C
(4) D

Ans: (1) A

Solution: In a P vs T graph, the liquid with the highest vapour pressure at any given temperature is the most volatile.

From the graph, at any temperature, curve A is at the top (highest P value), meaning liquid A has the highest vapour pressure $\Rightarrow$ A is the most volatile.

Order of volatility: A $>$ B $>$ C $>$ D

7. **On the basis of intermolecular forces predict the correct order of decreasing boiling points of the compounds:**

(1) $CH_3OH > H_2 > CH_4$
(2) $CH_3OH > CH_4 > H_2$
(3) $CH_4 > CH_3OH > H_2$
(4) $H_2 > CH_4 > CH_3OH$

Ans: (2) $CH_3OH > CH_4 > H_2$

Solution:

- CH_3OH: Has hydrogen bonding (strongest IMF) $\Rightarrow$ Highest BP (64.7°C)
- CH_4: Only London dispersion forces, MW = 16 $\Rightarrow$ BP = -161°C
- H_2: Only London dispersion forces, MW = 2 (smallest) $\Rightarrow$ Lowest BP (-253°C)

Stronger IMF $\Rightarrow$ Higher boiling point

TYPE–3 : Volatility & Intermolecular Forces

1. **Among the following substances, the lowest vapour pressure is exerted by:**
   (A) Water
   (B) Mercury
   (C) Acetone
   (D) Ethanol
   Ans: (B) Mercury
   Solution: Mercury is a metal with very strong metallic bonding. It has extremely low vapour pressure at room temperature (≈ 0.002 mmHg at 25°C).
   Order of VP: Acetone > Ethanol > Water > Mercury
   Mercury's VP is so low that it's often considered negligible in many calculations.
2. **Which of the following is correct?** **[NSEC-2017]**
   A liquid with
   (A) low vapour pressure will have a low surface tension and high boiling point
   (B) high vapour pressure will have high intermolecular forces and high boiling point
   (C) low vapour pressure will have high surface tension and high boiling point
   (D) low vapour pressure will have low surface tension and low boiling point
   Ans: (C) low vapour pressure will have high surface tension and high boiling point
   Solution: The relationship between these properties:

IMF	Vapour Pressure	Surface Tension	Boiling Point
Strong	Low	High	High
Weak	High	Low	Low

   Low VP $\Rightarrow$ Strong IMF $\Rightarrow$ High surface tension + High BP

TYPE–4 : Effect of Solute on Vapour Pressure

1. **An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase?**
   (1) Addition of water
   (2) Addition of NaCl
   (3) Addition of Na_2SO_4
   (4) Addition of 1.00 molal KI
   Ans: (1) Addition of water
   Solution: According to Raoult's Law: $P_{solution} = x_{solvent} \times P^0_{solvent}$
   Adding water (solvent) increases the mole fraction of solvent ($x_{solvent}$), which increases the vapour pressure of the solution.
   Adding any solute (NaCl, Na_2SO_4, or more KI) would decrease $x_{solvent}$ and thus decrease the vapour pressure.

TYPE–5 : Conceptual & Application Based

1. **A liquid is kept in a closed vessel. If a glass plate (negligible mass) with a small hole is kept on top of the liquid surface, then the vapour pressure of the liquid in the vessel is:**

(A) More than what would be if the glass plate were removed
(B) Same as what would be if the glass plate were removed
(C) Less than what would be if the glass plate were removed
(D) Cannot be predicted

Ans: (B) Same as what would be if the glass plate were removed

Solution: Vapour pressure is an equilibrium property that depends only on:

- Temperature
- Nature of the liquid

It does NOT depend on:

- Surface area of the liquid
- Volume of the container
- Presence of obstacles like glass plates

The glass plate with a hole will only slow down the rate of reaching equilibrium, but the final equilibrium vapour pressure remains the same.

2. **The vapour pressure of water at 20°C is 17.54 mmHg. What will be the vapour pressure of the water in the apparatus shown after the piston is lowered, decreasing the volume of the gas above the liquid to one half of its initial volume (assume temperature constant)?**

[Refer to question paper for diagram]

(A) 8.77 mmHg
(B) 17.54 mmHg
(C) 35.08 mmHg
(D) Between 8.77 and 17.54 mmHg

Ans: (B) 17.54 mmHg

Solution: Key concept: Vapour pressure depends only on temperature, not on volume.

When the piston is lowered:

- Volume decreases to half
- Momentarily, the vapour would be compressed
- But since liquid water is present, some vapour will condense
- Equilibrium is re-established at the same temperature
- Final VP = 17.54 mmHg (unchanged)

Note: Boyle's law ($P_1V_1 = P_2V_2$) does NOT apply here because the system is in equilibrium with liquid water, which acts as a reservoir.

TYPE–6 : Numerical Problem

1. **The vapor pressure of water at 80°C is 355 torr. A 100 mL vessel contained water-saturated oxygen at 80°C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 mL vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, and what was the total pressure in the final equilibrated state? Neglect the volume of any water which might condense.**

Ans: $P_{O_2} = 810$ mm Hg, $P_{H_2O} = 355$ mm Hg, $P_{total} = 1165$ mm Hg

Solution:

Step 1: Find initial P_{O_2} in 100 mL vessel

$$P_{O_2} = P_{total} - P_{H_2O} = 760 - 355 = 405 \text{ torr}$$

Step 2: Apply Boyle's law for O_2 (non-condensable gas)

$$P_1V_1 = P_2V_2$$

$$405 \times 100 = P_2 \times 50$$

$$P_{O_2} = \frac{405 \times 100}{50} = 810 \text{ torr}$$

Step 3: Find P_{H_2O} in new vessel
Water vapour pressure depends only on temperature, not volume. Since T = 80°C (constant):

$$P_{H_2O} = 355 \text{ torr (unchanged)}$$

Some water vapour will condense to maintain this equilibrium pressure.
Step 4: Calculate total pressure

$$P_{total} = P_{O_2} + P_{H_2O} = 810 + 355 = \boxed{1165 \text{ torr}}$$