Paper : Physical Chemistry (I A)
Topic : Physical Properties of liquids

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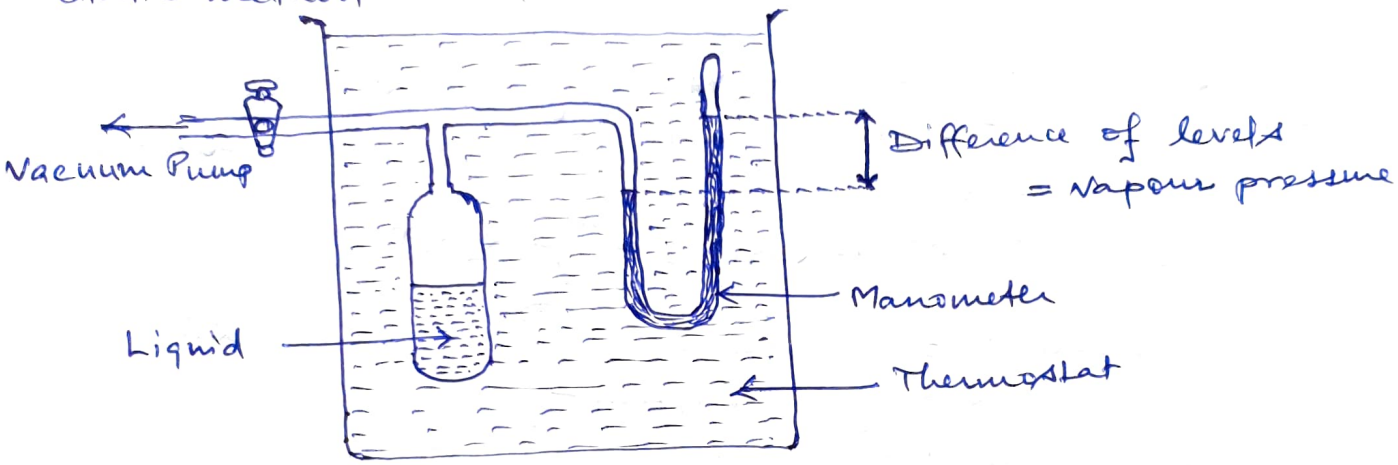
Determination of Vapour Pressure :— The vapour pressure of a given liquid can be measured by Static Method or Dynamic Method.

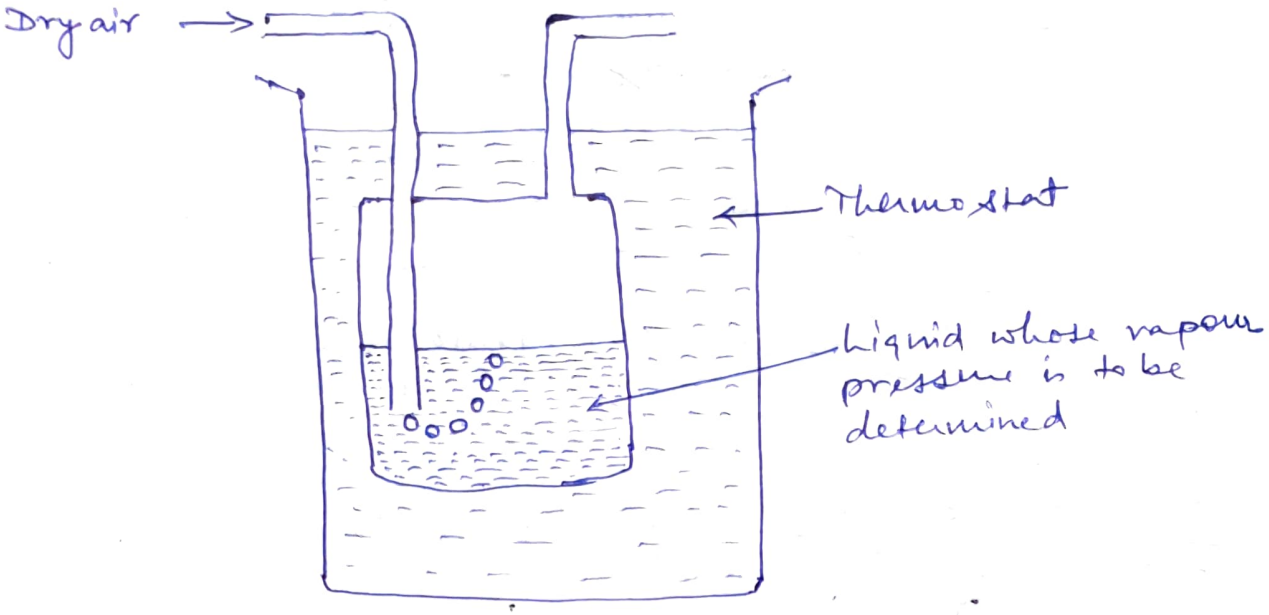
(a) Static Method : A simplified apparatus used for the static method is shown below :



A sufficient amount of liquid whose vapour pressure is to be determined is placed in the bulb connected to a mercury manometer and a vacuum pump. All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of liquid evaporates. The system is then maintained at a fixed temperature for enough time so that the equilibrium is established. The difference in the levels of mercury in the manometer is equal to the vapour pressure of the liquid. By adjusting the thermostat at a different temperature, the vapour pressure of the liquid at another temperature can be determined. This method is used for the liquids having vapour pressures up to one atmosphere.

(b) Dynamic Method : The apparatus used for the dynamic method is given by in the next page.

An inert gas is passed through the given liquid at a constant temperature (T). The gas saturated with the vapour of the liquid leaves the flask at the exit tube.



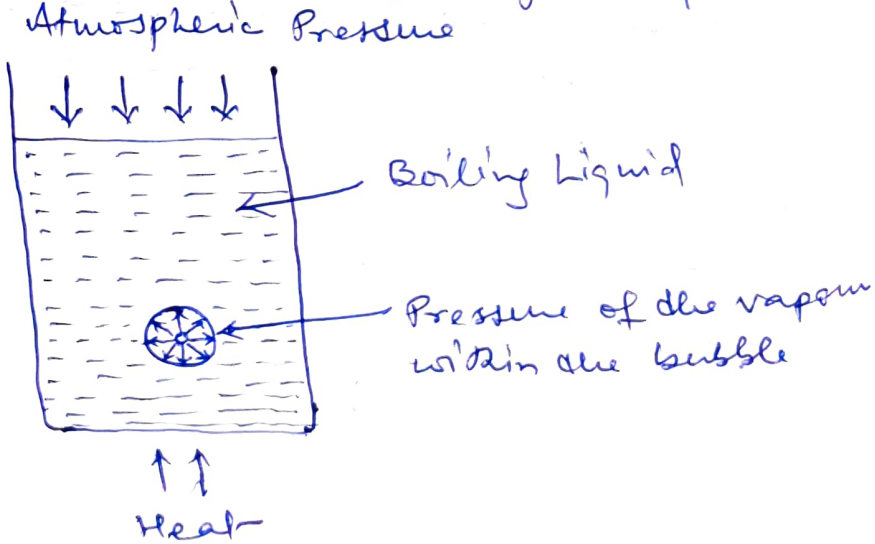
If V be the volume of the gas passed and w the loss in weight of the liquid, the vapour pressure is given by the expression

$$\text{Vapour Pressure} = \frac{w}{MV} \times RT$$

where M = molecular weight of the liquid and
R = gas constant

This method is particularly suited for liquids of very low vapour pressure.

Effect of Vapour Pressure on Boiling Points :— When a liquid is heated, tiny bubbles are formed in it. These bubbles rise to the liquid surface and burst. The temperature at which it happens is the boiling point of the liquid. Let us consider an individual bubble as depicted in the figure given by.



The liquid vaporises into the bubble and the vapour pressure in the bubble keeps it in form. However, the pressure of the atmosphere exerted on the liquid top tends to collapse the bubble. As the bubble goes to the surface, the vapour pressure in the bubble equals the atmospheric pressure. Thus the bubble collapses and the liquid boils. A liquid boils when the pressure of the vapour within the bubble equals the atmospheric pressure exerted on the bubble at the liquid surface. The boiling point of the liquid, may, therefore, be defined as the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure.

Because the atmospheric pressure varies with altitude and other conditions, the boiling points are reported at 760 torr (1 atm). Therefore, the normal boiling point of a liquid is the temperature at which the vapour pressure of the liquid is 760 torr or 1 atm. The boiling point of ethanol is found to be equal to 78°c and that of water, 100°c.

The boiling point of a liquid can be lowered by reducing the external pressure by vacuum pump. Then the vapour pressure of the liquid is equal to the external pressure at a lower temperature. The boiling point of a liquid can be increased by raising the external pressure. Thus the vapour pressure of the liquid is equal to the external pressure at a higher temperature. A domestic pressure cooker works on this principle. The pressure inside the cooker is maintained above the atmospheric pressure and the liquid contained in it would boil at a higher temperature than 100°c. Thus the food is cooked in a shorter time.

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