☐ VAPOUR PRESSURE OF DROPLETS - KELVIN EQUATION

The Clausius-Clapeyron equation is derived ignoring the effects of the interface. The Laplace-Young equation shows that the surface effects become significant as the curvature of the surface becomes more pronounced. Therefore, the vapour pressure of the liquid droplets should not be expected to be the same as that of the bulk liquid.

Consider a case when a vapour-liquid system with a planar interface is broken into a large number of small droplets as illustrated in fig (8) The vapour pressure changes from P_o to P_v and the pressure of the liquid changes from P_o to P_l. The condition for reversible change is given by

$$d\mu_l = d\mu_v \qquad \dots(1)$$

where the subscripts l and v denote the vapour and he liquid phase, respectively. Since all other hermodynamic variables except pressure remain onstant during the change, we get from equation (1),

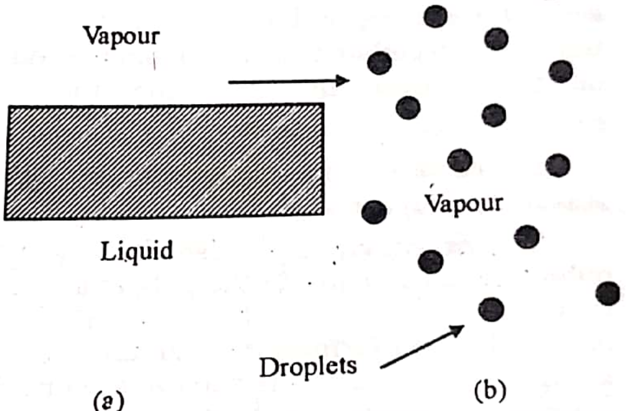

Fig. 8 **(a) Vapour in equilibrium with bulk liquid, (b) Vapour in equilibrium with droplets of liquid.**

$$\int_{P_0}^{P_l} V_l dP = \int_{P_0}^{P_v} V_v\, dP \qquad \dots (2)$$

The left-hand side of this equation is written as

$$\int_{P_0}^{P_l} V_l dP = V_l(P_l - P_0) = V_l(P_l - P_v) + V_l(P_v - P_0) \qquad \dots (3)$$

This shows that equation (2) may be written as

$$V_l(P_l - P_v) = \int_{P_0}^{P_v} V_v\, dP + V_l(P_v - P_0) \qquad \dots (4)$$

It should be seen that the two terms on the right-hand side involve the same pressure difference but volumes in different phases. Since the volume of the liquid is much smaller than that of the gas, we may ignore the second term on the right-hand side. Now we integrate the first term on the right-hand side and substitute the results of the Laplace-Young equation on the left-hand side to get the following equation,

$$V_l \frac{2\gamma}{r} = \int \frac{RT}{P} dP = RT \ln \frac{P_v}{P_0} \qquad \dots (5)$$

This equation is known as ***Kelvin equation***. This equation shows that as r decreases, the vapour pressure increases. The following values for water droplets at 298K are calculated from the Kelvin equation.

r/(nm)	0.5	1.0	10	50	100
P_v/P_0	8.29	2.88	1.11	1.02	1.01
Molecules per drop	18	140	1.4×10^5	1.75×10^7	1.4×10^8

The Kelvin equation points out the difficulties associated with the formation of a new phase. Suppose we start with a vapour phase and compress it to the saturation vapour pressure P_0. Formation of the liquid phase requires molecules coming together and coalescing. It is quite unlikely that a very large number of molecules will come together at once to form a drop (Even the formation of a small drop with $r = 100$ nm involves the simultaneous aggregation of 1.4×10^8 molecules). It is more likely that a few molecules coalesce, starting with a pair, to form very tiny droplets. The Kelvin equation shows that the equilibrium vapour pressure for such droplets is several times larger than that for the bulk liquid. So, the droplets are likely to evaporate rather than come together to form the bulk liquid. From this analysis, we can conclude that the pressure has to be considerably larger than the equilibrium vapour pressure of the bulk phase P_0 before condensation can occur.

In practice, condensation usually starts on dust particles or on surface sites on the walls of a vessel. The presence of these sites for nucleation prevents supersaturation of the vapour phase.

The Kelvin equation also shows why liquids become superheated before boiling. Consider a bubble of radius r inside the bulk of a liquid. The pressure inside the bubble must be greater than that of the bulk liquid. The smaller the bubble, the greater the pressure. Therefore there is a barrier for the formation of small bubbles which leads to the superheating of liquids. Violent bumping often ensues as spontaneous nucleation leads to bubbles big enough to survive to ensure smooth boiling at the true boiling temperature, nucleation centres such as small pieces of sharp-edged glass or pumice stone or bubbles (cavities) of air should be introduced. This is actually done in practice.

Similar behaviour is observed with the freezing of liquids and the crystallization of solutes from saturated solutions. For example, extremely pure water may be cooled to – 40°C before it begins to solidify.

Even though the Kelvin equation is useful in solving the difficulties involved in phase transformation but it cannot be used quantitatively. First, the surface tension depends on the radius of curvature, and for small radii this dependence becomes very important. Therefore, one cannot use the Kelvin equation for droplets of every conceivable size. Second, macroscopic thermodynamics cannot be applied to systems, such as tiny droplets, consisting of a small number of molecules. Fluctuations from equilibrium become very important and should be incorporated into theory.