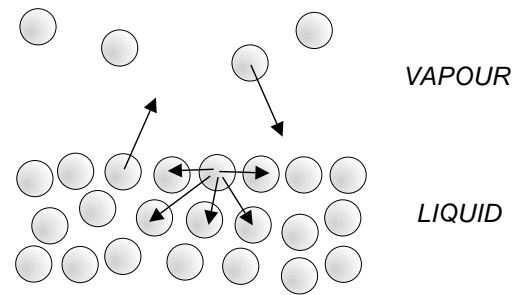# RAOULT'S LAW

Vapour Pressure   If a liquid is placed in a sealed tube and the space above it evacuated, any molecules which escape from the surface of the liquid will be contained and thus exert a pressure. As more molecules enter the space, the possibility of some re-entering also increases.

VAPOUR

LIQUID

Eventually a state of dynamic equilibrium exists where as many particles are leaving as are returning. The pressure at this stage is known as the Saturated Vapour Pressure (SVP). This value is constant for a particular liquid at constant temperature. The value increases exponentially with temperature as can be seen in the diagram below.

THE VARIATION OF VAPOUR PRESSURE WITH TEMPERATURE
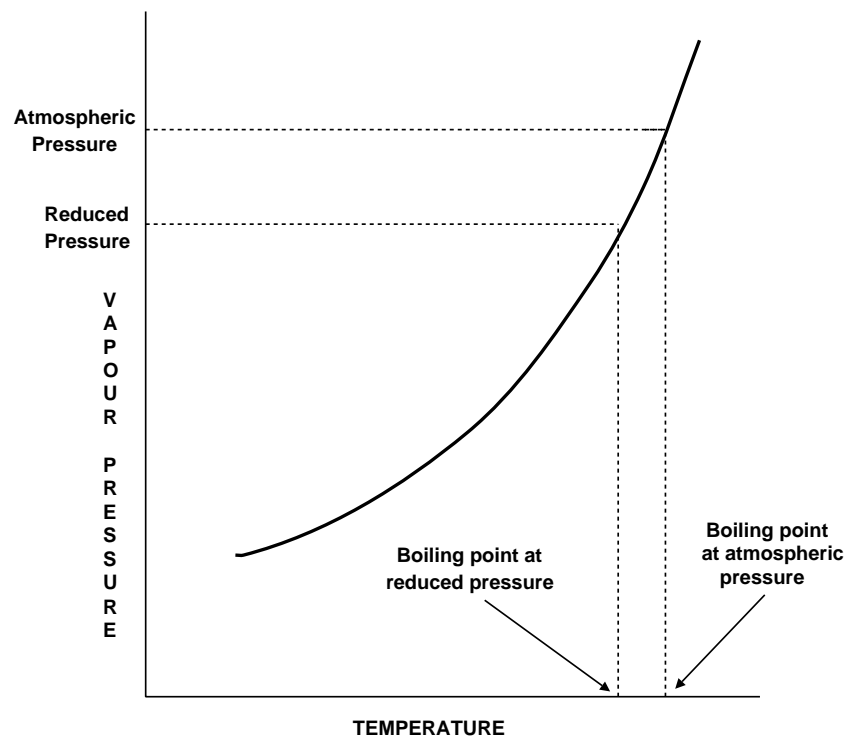
Boiling   A liquid boils when its vapour pressure reaches that of the atmospheric (or applied) pressure.

Decreasing the pressure lowers the boiling point	Liquids can be distilled below their normal boiling point; avoids the risk of decomposition
Increasing the pressure raises the boiling point	Pressure cookers work on this principle; water boils above 100°C so food cooks quicker.

Raoult's Law   'The vapour pressure of a solvent in a solution equals the vapour pressure of the pure solvent multiplied by its mole fraction.'

mole fraction of a component   = $\dfrac{\text{number of moles of that component}}{\text{total number of moles present}}$

Example   *Calculate the mole fractions of each component in a mixture containing heptane C_7H_{16} (150g) and hexane C_6H_{14} (43g).*

Moles of heptane =   150/100 =   1.5 mol
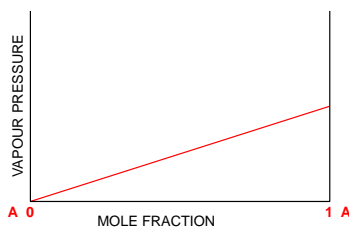*Moles of hexane =   43/86   =   0.5 mol*   *Total = 2 mol*
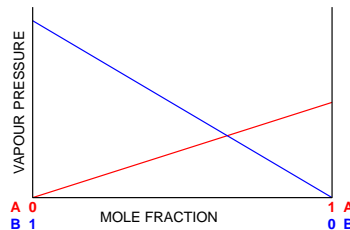*Mole fractions   heptane =   1.5/2   =   0.75*
                       hexane =   0.5/2   =   0.25
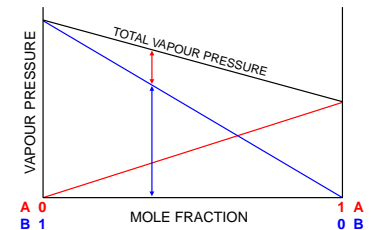
In a mixture of volatile liquids, the total vapour pressure will be the sum of the individual vapour pressures.

Vapour pressure variation of a single volatile liquid in a mixture.
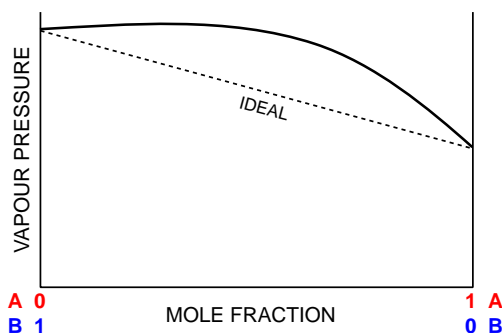
Vapour pressure variation of two liquids in a mixture. **A is more volatile** - **it has the lower boiling point.**

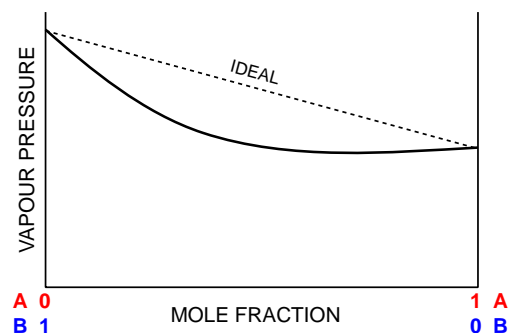Total vapour pressure is the sum of the individual vapour pressures.

Deviations   • very few liquids obey Raoult's Law

• liquids which obey it are called IDEAL LIQUIDS

• for NON-IDEAL liquids, the shape of the vapour pressure curve is affected

POSITIVE DEVIATION

NEGATIVE DEVIATION

Vapour pressure is greater than ideal

Vapour pressure is less than ideal

The different molecules in the liquid mixture must not attract each other as much; it is **easier** to turn them into vapour.
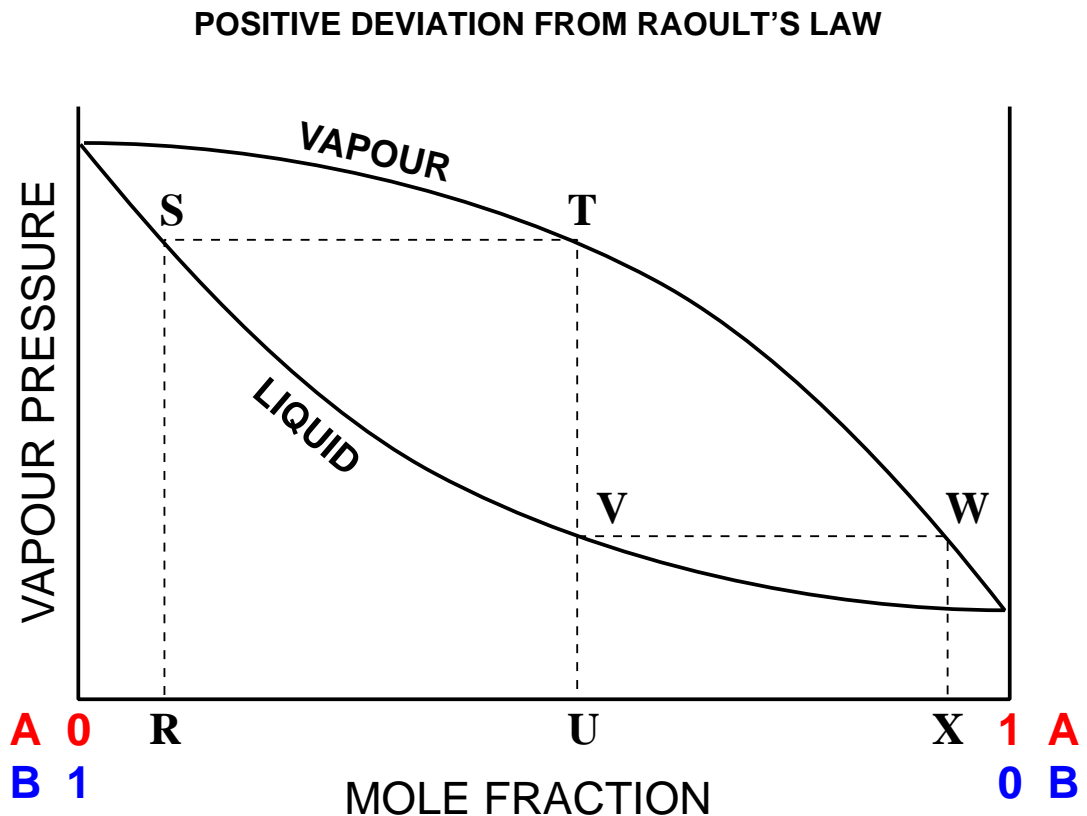
The different molecules attract each other more than if they were on their own; it is **harder** to turn them into vapour.

Fractional
distillation   Vapour pressure curves can explain how fractional distillation works.

POSITIVE DEVIATION FROM RAOULT'S LAW

R   The composition of the mixture to start with. It is then heated up.

S   A liquid boils when its vapour pressure equals the applied pressure

T   The vapour above the liquid has a different composition. It is richer in
the more volatile component.

U   If the vapour was condensed, the liquid collected would have this composition.

V   If the new composition was reheated its would boil again.

W   The vapour above the liquid is now even richer in the more volatile
component. When condensed it would have composition **X.**

In fractional distillation, the boiling and condensing is taking place all the time until
a component boils off and is collected. If the above steps were repeated, the
compostion of the vapour would be pure **A**. This is to be expected as **A** is more
volatile and therefore has a lower boiling point than **B**.

Note   There are several other situations involving deviations from Raoult's Law. Each
can explain what happens when a mixture of liquids is distilled. In some cases the
distillate contains a mixture of components.