Ministry of Higher Education and Scientific Research

Al-Mustaqbal University College

Chemical engineering and petroleum industries

Physical chemistry

Vapor pressure

The vapor pressure (P°) is the pressure of the vapor of a compound in equilibrium with its pure condensed phase (solid or liquid). Vapour pressures depend strongly on the temperature and vary widely with different compounds due to differences in molecule – molecule interactions. The normal boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid is 1 atmosphere (P° = 1 atm).
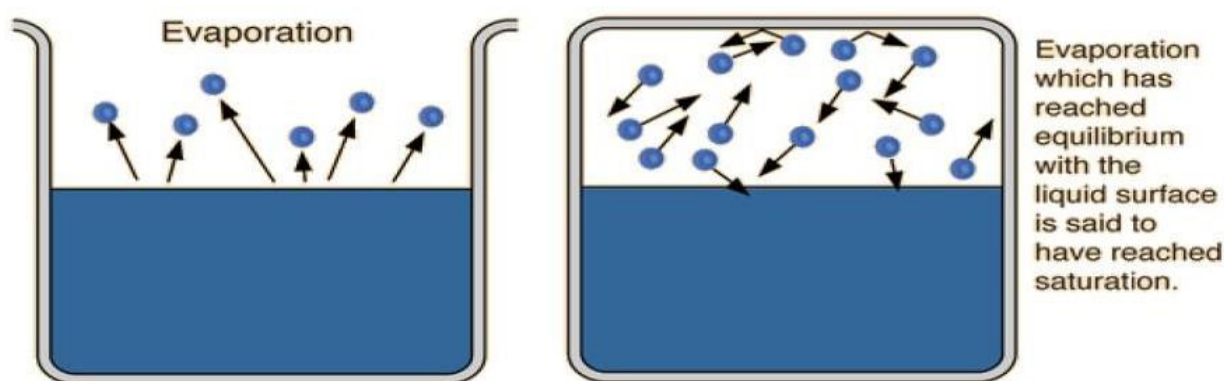
The Clausius Clapeyron Equation

The vaporization curves of most liquids have similar shape. The vapour pressure steadily increase as the temperature increases. A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the pressure P, enthalpy of vaporization, ΔH_{vap}, and temperature T are related.

$$\square = \square\ \square\square\square\ (-\ \Delta\square\square\square\square\ /\ \square\square)$$

where R (= 8.3145 J mol^{-1} K^{-1}) and **A** are the gas constant and unknown constant. This is known as the **Clausius- Clapeyron equation**. If P_1 and P_2 are the pressures at two temperatures T_1 and T_2, the equation has the form:

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

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation above to calculate the vapor pressure P_2 at any other temperature T_2. Also, The Clausius-Clapeyron equation allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Example : The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation,

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

we have:

P_{363} = 1.0 exp (- (40700/8.3145)(1/363 - 1/373) = 0.697 atm

P_{383} = 1.0 exp (- (40700/8.3145)(1/383 - 1/373) = 1.409 atm

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Liquid-Vapor Equilibrium(VLE):

In thermodynamics and chemical engineering, the vapor liquid equilibrium VLE describes the distribution of a chemical species between the vapor phase and a liquid phase. The concentration of a vapor in contact with its liquid, especially at equilibrium, is often expressed in terms of vapor pressure, which will be a partial pressure (a part of the total gas pressure) if any other gas(es) are present with the vapor.

For each component in a binary mixture, one could make a vapor– liquid equilibrium diagram. Such a diagram would graph liquid mole fraction on a horizontal axis and vapor mole fraction on a vertical axis. In such VLE diagrams, liquid mole fractions for components 1 and 2 can be represented as x_1 and x_2 respectively, and vapor mole fractions of the corresponding components are commonly represented as y_1 and y_2, Similarly for binary mixtures in these VLE diagrams:

$x_1 + x_2 = 1$ and $y_1+y_2=1$

Such VLE diagrams are square with a diagonal line running from the ($x_1 = 0$, $y_1 = 0$) corner to the ($x_1 = 1$, $y_1 = 1$)
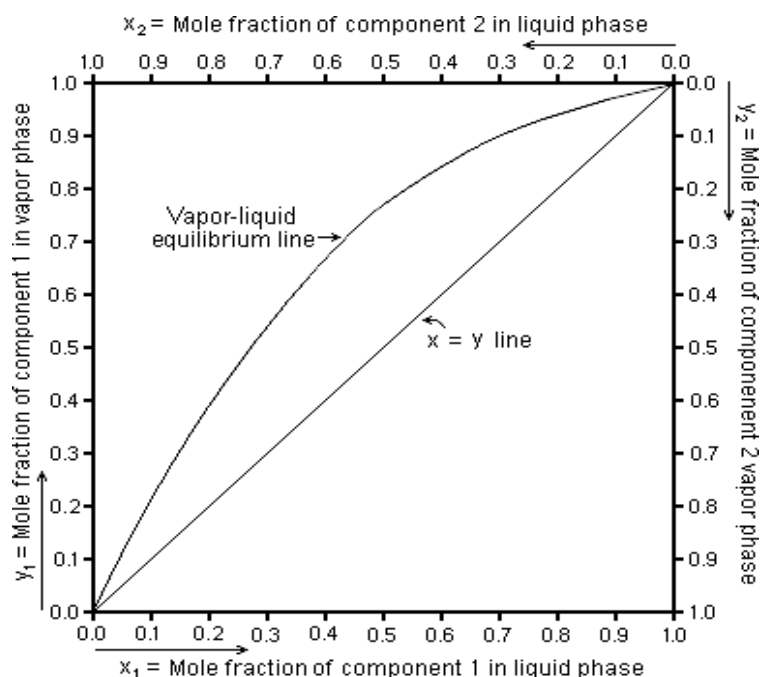
Raoult's law

In separation science, one often exploits the preference of a substance for one phase over another to separate a mixture. This is the principle behind distillation. We have seen that under ideal condition, the vapor pressure of a volatile liquid obeys Raoult's law. Say we have a liquid mixture containing two components 1 and 2. Let the mole fraction of 1 in the liquid be x_1 and the mole fraction of 2 be x_2. $x_1 + x_2 = 1$ necessarily. If at some temperature T, the vapor pressure of the pure component 1 is P_1 and that of the pure component 2 is P_2, then the partial pressures of the two substances in the vapor phase are described by Raoult's law if the solution is ideal:

$$P_1 = x_1 P_1^* \qquad P_2 = x_2 P_2^*$$

Vapour Pressure Diagram for Ideal Solution
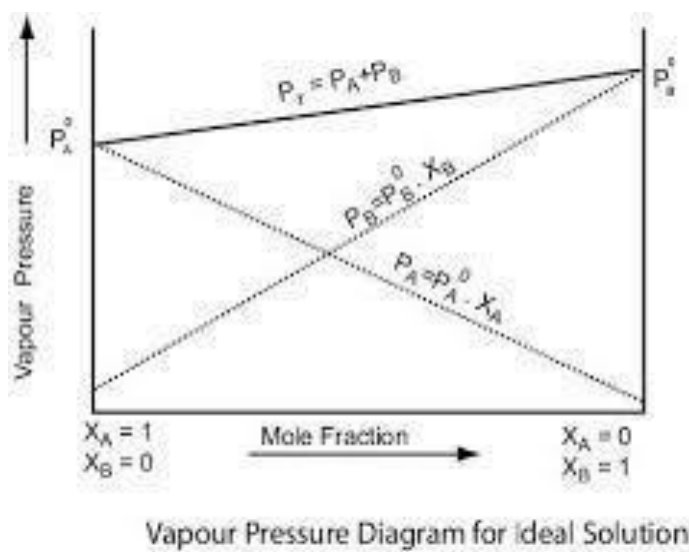
The total pressure of the two vapors is

$$P = P_1 + P_2 = x_1 P^*_1 + x_2 P^*_2 = P_2 - x_1 (P^*_2 - P^*_1) \ldots\ldots\ldots\ldots (1\text{-}2)$$

This is plotted curve in Fig. and clearly it is just a linear function of x_1. To produce this total pressure, the mole fraction of component 1 *in the liquid must be x_1*. But what is the mole fraction of component 1 in the vapor? To find out what it is, we simply divide the vapor pressure of 1 by the total pressure and get:

$$\frac{x_1 P_1^*}{P_2^* - x_1(P_2^* - P_1^*)} = y_1. \qquad \ldots\ldots\ldots(1\text{-}3)$$

To distinguish this from the mole fraction of component 1 in the liquid phase, we denote the mole fraction of component 1 in the vapor phase y_1. This is certainly not equal to x_1 (except if coincidentally $P_1 = P_2$). Therefore, when a liquid evaporates, the composition of its vapor is necessarily deferent from the composition of the liquid. This is easy to rationalize in terms of Raoult's law: the more volatile component should become enriched in the vapor phase. Using Eq (1-3) we can solve for x_1 in terms of y_1 and re-express the total pressure in Eq.(1-2) as a function of y_1:

$$P = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*)y_1}$$

Example : Calculate the vapor pressure of a mixture containing 252 g of n-pentane (Mw = 72) and 1400 g of n-heptane (Mw = 100) at 20^oC. The vapor pressure of npentane and n-heptane are 420 mm Hg and 36 mm Hg respectively.

Solution

According to Raoult's law, the vapor pressure exercised by a component of a mixture can be calculated as follows $P = P^o\ x$

where

P is the vapor pressure of the component in the mixture.

P^o is the vapor pressure of the pure component.

x is the molar fraction of the component in the mixture.

Calculation of molar fractions (x)

moles n-pentane = 252/72 = 3.5

moles n-heptane = 1400/100 = 14

Totals = 3.5 + 14 = 17.5 moles

$x_{n\text{-pentane}}$ = 3.5/17.5 = 0.2

$x_{n\text{-eptane}}$ = 14/17.5 = 0.8

Thus:

$P_{n\text{-pentane}}$ = 0.2 x 420 = 84 mm Hg

$P_{n\text{-eptane}}$ = 0.8 x 36 = 28.8 mm Hg

and the vapor pressure of mixture is

$P_{mixture}$ = 84 + 28.8 = 112.8 mm

Example: Calculate the boiling point (at 1 atm) of a solution containing 116 g of acetone (Mw = 58) and 72 g of water (Mw = 18) by using the following table:

Temperature °C	Vapor pressure (atm) Acetone	Vapor pressure (atm) Water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

Solution

A liquid starts to boil when its vapor pressure matches the atmospheric pressure (1 atm inthis case).   Thus, according to Raoult's law

$P = x_{acetone} P^o_{acetone} + x_{water} P^o_{water} = 1$ atm

From the given data we can calculate the molar fractions

Moles acetone $= 116/58 = 2$

moles water $= 72/18 = 4$

total moles $= 6$

$x_{acetone} = 2/4 = 1/3$

$x_{water} = 4/6 = 2/3$

Thus

$P = 2/3\ P^o_{acetone} + 1/3\ P^o_{water} = 1$ atm

By trials, using the table, we can find the values of vapor pressure which satisfies the above equation. The best result is obtained by using the values at 80^oC :

$P = 2/3\ 0.456 + 1/3\ 2.12 = 1.01$ atm

then the boiling point is about 80^oC.