Vapour: A substance diffused or suspended in the air, especially one normality normally liquid or solid.

Vapor pressure:
The pressure excerted by the gas in equilibrium with a solid or liquid in a closed container at a given temp. is called vapor pressure

Vaporization:
The change of phase from liquid/solid phase to vapor/gaseous phase.

Condensation: The change of phase from vapor to liquid.

Sublimation: The change of phase from solid to vapor.

Bubble point: The temperature at which a vapour just starts to ~~condense~~ vaporize

Dew point: The temp. at which a vapor just starts to condense

Freezing (solidifying): The change of phase from liquid to solid.

Melting (fusion): The change of phase from solid to liquid

Saturated liquid (or) vapour: Liquid or vapor in equilibrium with the other

Subcooled liquid: Liquid at a temp. lower ~~in~~ at eq the saturated liquid.

Superheated vapor: vapor at a temp. higher than the saturated vapor.

Supercritical: Above the critical point or higher than critical temp & pressure. (In a supercritical region, a substance is neither gas nor liq but supercritical fluid, which exhibits properties that lie between the gas and the liquid)

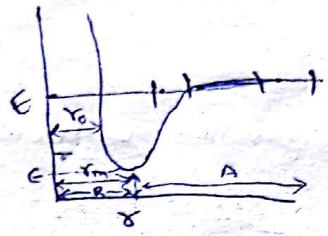
Critical point: The point at which a substance in one phase, as the liqui has the same density, pressure and temp as in another phase, as the gaseous.

Normal Boiling point:
Temp. at which vapor pressure equals to 1 atm. pressure is called NBP.

Boiling point:
Condition at which rapid vaporisation of liquid.
This can be achieved when vapor pressure of liquid = atmospheric pressure.

13/7/17

Liquefaction and the Liquid State:



E - Inter molecular energy
R - repulsion
A - Attraction
r - Distance bet. molecules

Attraction force between molecules.

$$E = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

ϵ = Intermolecular energy between two colliding molecules

r = distance between centers of colliding molecules

r_0 = distance of separation when energies of attraction and repulsion are balanced.

ϵ = Minimum Intermolecular energy.

(i) By knowing the value of ϵ, we can say it is liquid (or) not.

(ii) Slightly energised molecules easily break away from the surface and changes into vapor state & this phenomena is called vaporization.

(iii) Dew point is temperature at which vapor pressure of liquid is equal to partial pressure of the vapor.

At this point, the gas containing vapor is said to be Saturated.

Relative Saturation = Partial Pressure / vapor Pressure

The temp. at which the gas is ready to condense. At any temp at which rate of condensation is equal to rate of vaporization. Then pressure at that condition is called vapor pressure.

Difference between Saturated vapor & Superheated vapor

Temp. difference.

Vapor will be same & temp.

temp. difference between Super Saturated & Saturated vapor = degree of Superheated vapor.

$$\text{Quality of wet vapor (Steam quality)} = \frac{\text{wt. of vapor}}{\text{wt. of vapor + wt. of entrained liquid}} \times 100$$

15/7/17

Effect of Temp. on vapor Pressure:

Vapour Pressure increases with increase in temp. as K.E increases.

Illustrated by the effect of temp. on vapor pressure is Clapeyron equation.

$$\frac{dP}{dT} = \frac{\lambda}{[T(V_m - V_L)]} \cdots \rightarrow (1)$$

where, P - Vapor pressure, T - absolute temp.,

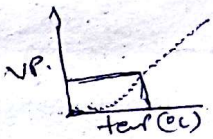
λ - heat of vapourization, at T, V_m - volume of gas, and V_L → volume of liquid.

(i) Latent heat of vaporization (λ) is constant up to wide range of temp.

(ii) volume of gas molecule is more than the volume of liquid molecules (V_L is neglible)

(iii) Vapor behaves like an ideal gas

$$V_m = \frac{RT}{P}$$



$$\frac{dP}{dT} = \frac{\lambda}{TV_m}$$

$$\Rightarrow \frac{dP}{dT} = \frac{\lambda(P)}{T(RT)}$$

$$\Rightarrow \frac{dP}{P} = \frac{\lambda}{R}\frac{1}{T^2}dT$$

$$\Rightarrow \int_{P_0}^{P_2} \frac{dP}{P} = \frac{\lambda}{R}\int_{T_0}^{T_2} \frac{dT}{T^2}$$

$$\Rightarrow \ln\left(\frac{P_2}{P_0}\right) = \frac{-\lambda}{R}\left[\frac{1}{T_2} - \frac{1}{T_0}\right]$$

$$\log\frac{P}{P_0} = \frac{\lambda}{2.303R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

This equation is applicable to any vaporisation process.

This eqn is called Clasius - clapeyron eqn.

Vapor pressure plots:

(i) From the experimental data, various types of plots have been derived for relating vapor pressure to temp.

(ii) A better method which has been extensively used is to plot the logarithm of the vapor pressure, log (P) against the reciprocal of the absolute temperature, $(1/T)$

(iii) The resulting curves show much less curvature than a rectangular plot and may be read accurately over a wide range of temp.

Another method is to plot the logarithm of the pressure against temp. on a uniform scale.

This method does not reduce the curvature of the vapor pressure lines as much as the usage of reciprocal temp. scale but is more easy to construct and read.

For deriving consistent vapor-pressure data for homologous series of closely related compounds, Coats and Brown developed a special method of plotting, which is suitable for the hydrocarbons.

Antonie Equation:

Antonie proposed an equation to calculate the vapor pressure of the substance by the following equation.

$$\log P = A - \frac{B}{T+C}$$

P = vapour pressure (mm Hg)

A = Empirical Constant

B = Empirical Constant

T = Temperature (K)

C = Empirical Constant

A graph relating to Antonies equation is called Cox chart.

14/7/17

Critical Properties:

The maximum properties attained by a given substance is known as critical properties.

Raoult's law:

According to Raoult's law the pressure exerted by a component in solution is directly proportional to molefraction of component.

$$P_A = N_A P_A \qquad (P_A \rightarrow \text{vapour pressure})$$

If any solution obeys Raoult's law, it is termed as ideal solution.

Conditions:

(i) no chemical combination or molecular association between unlike molecules takes place in the formation of the solution.

(ii) The size of the component molecules are approximately equal.

(iii) The attractive forces between like & unlike are approximately equal

(iv) The component molecules are nonpolar & no component is concentrated at surface of the solution.

Liquefaction:

The phase transitions from solid and gas to liquid (melting and condensation, respectively) may be reffered to as liquefaction. The melting point (sometimes called liquefaction point) is the temp. and pressure at which a solid becomes a liquid.

Effect of temp on vapor Pressure:

Illustrated by the effect of temp. on vapour pressure is Clapeyron equation.

$$\frac{dP}{dT} = \frac{\lambda}{T(V_G - V_L)} \rightarrow (1)$$

where, $P \rightarrow$ vapor pressure

T - absolute temperature

λ - heat of vaporization at temp. T

V_G - volume of gas

V_L - volume of liquid.

If the volume of liquid is neglected and applicability of the ideal gas law assumed, the above reaction reduces to

(a) Clausius – Clapeyron equation.

$$\frac{dP}{dT} = \frac{\lambda\, dT}{RT^2} \rightarrow (2)$$

$PV = nRT$

$V = \frac{P}{RT}$

(or) $d(\ln P) = -\frac{\lambda d}{R}\left(\frac{1}{T}\right) \rightarrow (3)$

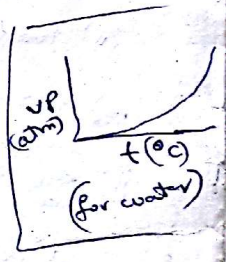
where, $R \rightarrow$ gas-law constant

$\lambda \rightarrow$ molal (latent) heat of vaporization

when the temp. does not vary over wide range, it may be assumed that the molal (latent) heat of vaporization is constant and the above equation may be integrated between limits P_0 and P and T_0 & and T_0

$$\ln\left(\frac{P}{P_0}\right) = \frac{\lambda}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \rightarrow (4)(4)$$

$$\log\left(\frac{P}{P_0}\right) = \left(\frac{\lambda}{2.303\,R}\right)\cdot\left(\frac{1}{T_0} - \frac{1}{T}\right).$$



(1) **Prob**:- The vapor pressure of ethyl ether at 0°C is 185mm Hg. The latent heat of vaporization is 92.5 cal/g. Calculate the vapor pressure at 20°C and 35°C. ~~(with gas law~~

Sol:- Molecular weight of ethyl ether = 74

$(C_2H_5)_2O$: $24+5$, 29×2, 38, 16, 74

$\lambda = (92.5 \times 74) = 6845$ cal/g-mole.

$R = 1.99$ cal/g-mole K.

$R = 1.99$

$T_0 = 273$ K, $T_1 = 293$ K, $T_2 = 308$ K.

at 20°C

$$\log\left(\frac{P}{185}\right) = \left[\frac{6845}{2.303 \times 1.99}\right] \times \left[\left(\frac{1}{273}\right) - \left(\frac{1}{293}\right)\right]$$

$\log\frac{P}{185} = 0.373$

$\log\left(\frac{P}{185}\right) = -1.267$

$\log P = -1.894$

$\therefore P = 437$ mm Hg.

at 35°C

$$\log\left(\frac{P}{185}\right) = \left[\frac{6845}{2.303 \times 1.99}\right] \times \left[\left(\frac{1}{273}\right) - \left(\frac{1}{308}\right)\right]$$

$P =$ ___ mm Hg.

20/7/2017

Antoine Equation:

The Antoine equation is a mathematical expression of the relation between the vapor pressure and the temp. of pure liquid or solid substances. The basic form of the eqn is

$$\log P = A - \frac{B}{C+T}$$

where P = Vapor pressure (mm Hg)

A, B, & C = Empirical Constants.

T = Temperature (K)

A graph relating Antoine equation is called Cox chart.

Critical Temp:

The critical temp. of a substance is the temp. at the above which vapor of the substance cannot be liquefied (no matter how much pressure is applied). Every substance has a critical temp.

Critical Pressure:

The (minimum) pressure required to liquefy a gas at its critical temp. is termed the critical pressure.

Critical State:

The state of a substance in which two of its phases have the same temp., Pressre and volume. (Also called as critical point).

Critical volume:

The volume at the critical state is termed as Critical volume.

Critical Density:

The density at a critical state ~~state~~ is termed as critical density.

Reduced Conditions:

T_c, P_c, V_c [c - critical]

T, P, V } - existing

Reduced temp. $T_r = T/T_c$

Reduced Pressure, $P_r = P/P_c$

Reduced volume, $V_r = V/V_c$

Estimation of Critical Properties of organic Substances:

A knowledge of the critical properties of pure substances is of great importance in correlating or estimating related properties. Because of the difficulty of direct experimental measurements it is desirable to have reliable methods of estimating the values of the critical properties from molecular structures and easily determined properties.

Critical temp. may be estimated from the following equations expressed in terms of the normal boiling point and group contributions:

$$\frac{T_b}{T_c} = 0.567 + \Sigma \Delta_T - (\Sigma \Delta_T)^2$$

$\Sigma \Delta_T$ = Summation of increments for the atoms and atomic groups as given in Table:

Critical pressure may be estimated from the following eqn.

$$\sqrt{\frac{M}{P_c}} = 0.34 + \Sigma \Delta_P$$

where, M = molecular wt.

$\Sigma \Delta_P$ = Summation of increments for atoms and atomic groups as given in Table.

P_c = critical Pressure in atmosphere.

Critical volume of organic Compounds can be estimated from the following eqn.

$$V_c = 40 + \Sigma \Delta_V$$

V_c = critical volume in cubic centimeters per gram-mole.

$\Sigma \Delta_V$ = Summation of contributions for each atom or atomic group present as given in Table

Critical compressibility factors are calculated directly from experimental or estimated values of the three critical constants by the relations

$$z_c = \frac{P_c V_c}{R T_c}$$

z_c – obtained from estimated values of P_c, V_c & T_c deviates from the experimental value.

Lydersen has developed an independent correlation of critical compressibility factor by relating it to the molal heat of vaporization. thus

$$z_c = \frac{1}{3.43 + 0.0067 \lambda_b^2}$$

λ_b = heat of vaporization at the normal boiling point in Kilo-calories per gram-mole.

This equation holds for both organic & inorganic compounds with an average deviation from experimental values (of 3.8% based upon 156 compounds).

Critical Properties of Inorganic Substance:

For inorganic compounds good correlations for critical constants are not available.

For simple molecules containing one or two atoms

$$\frac{T_b}{T_c} = 0.567$$

and for other inorganic molecules

$$\frac{T_b}{T_c} = 0.635$$

A tabulation of experimental values of critical constants for a selected list of inorganic and organic compounds are given in tables:

Vapor Pressure plots:

(i) Equal Pressure Reference Substance plots:

During plot, the temp. of Substance at given term vapor pressure versus temp. of Reference Substance at Same vapor Pressure.

(ii) Equal temp. - Reference Substance plots:

The logarithm vapor prerepsure of given Substance at given temp. versus logarithm of vapor pressure of reference Substance at Same temp. (Cox plots).

Vapor Pressure of Immiscible liquid:

Agitated mixtures of immiscible liquids will boil at a temp. lower than the boiling point of either of pure liquids. Their Combined vapor pressure are bound to reach the external pressure before the vapor pressure of either of the individual components get there. (2 liquids are said to be immiscible if they are completely insoluble in each other.

Vaporisation with Superheated Steam:

Superheated steam is a Steam at a temperature higher than its vaporization (boiling) point at the absolute pressure where the temp. is measured.

Equilibrium vapor pressure & Composition:

If the validity of Raoult's law is assumed, it is necessary to have only the vapor-pressure data for the pure components in order to predict the pressure and composition of the vapor in equilibrium with the solution. The total vapor pressure of the Solution will be the Same sum of the partial pressure of the Components, each of which may be calculated from eqn. $P_A = P_A \left(\frac{n_A}{n_A + n_B + n_C + \dots}\right) = N_A P_A$

Nonvolatile Solutes:

A non-volatile solute has a low tendency to escape as vapor from a solution. Its vapor pressure is less than the vapor pressure of the Solvent.

Problems:

(2) The vapor pressure of chloroform is 61.0 mm Hg at 0°C and 526 mm Hg at 50°C. Estimate, From Cox chart, the vapor Pressure at 100°C.

Sol:- Two experimental values of the vapor pressure at 0 and 50°C are represented by points on Cox chart. A straight line is Projected through these two points to the abscissa representing 100°C. The ordinate at this point is approximately 2430 mm Hg, the estimated vapor pressure at 100°C. The experimental observed value is 2430 mm Hg.

(3) The vapor Pressure of normal butyl ($C_4H_{10}O$) alcohol at 40°C is 18.6 mm Hg. Estimate the temp. at which the vapor pressure is 760 mm Hg. the normal boiling Point.

Sol: The experimental values of the vapor pressure at 40°C is represented by a point on Cox chart. A Straight line is drawn from this point to the point of Convergence of the alcohol group. This point of Convergence is located by extending the curves for methyl and propyl alcohols. The abscissa of the point at which this lines crosses the 760-mm ordinate is about 117°C. The experimentally observed boiling Point of normal butyl alcohol is 117.7°C.

(4) It is desired to purify myristic acid ($C_{13}H_{27}COOH$) by distillation with steam under atmospheric pressure of 760 mm. Calculate the temp. at which the distillation will proceed and the number of Pounds of steam accompanying each pound of acid distilled.

Sol:- ~~100-mole of mixed vapors~~

Vapor Pressure of myristic at 99°C = 0.032 mm Hg

The vapor pressure of myristic acid is negligible in its effect on the boiling point of the mixture, which may be assumed to be that of water at 760 mm Hg, or 99°C

$C_{13}H_{27}COOH = 228$

Sol:- Basis 1 lb-mole of mixed vapor.

Mole of Myristic acid = $\frac{0.032}{740} = 4.3 \times 10^{-5}$ lb-mole

$= 4.3 \times 10^{-5} \times 228$ lb

$= 0.0098$ lb.

Mole of water = $\frac{740}{740} = 1$ lb-mole $= 1 \times 18 = 18$ lb

Steam per lb of acid (Myristic acid) = $\frac{18}{0.0098} = 1840$ lb.
(wt. of steam)

(4) Calculate the total pressure and the composition of the vapours in ~~Constant~~ Contact with a Solution at 100°C Containing 35% benzene (C_6H_6), 40% toluene ($C_6H_5CH_3$ or C_7H_8) and 25% orthoxylene (C_8H_{10}) by weight.

Vapor pressure at 100°C:

Benzene = 1340 mm Hg

Toluene = 560 mm Hg

o-xylene = 210 mm Hg

Sol:-

Basis: 100 lb of solution

Mol. wt. of Benzene = 78

Toluene = 56092

xylene = ~~210~~ 106

wt. / mole wise of Benzene = 35 lb

Toluene = 40 lb

o-xylene = 25 lb

Mole of Benzene = $\frac{35}{78} = 0.449$ lb mole

Toluene = $40/92 = 0.435$ lb-mole

o-xylene = $25/106 = 0.236$ lb-mole

1.120 lb-mole

Mole fraction in liq-phase:-

Vapor pressure, Benzene = $1340 \times \frac{0.449}{1.120}$ (mole fraction)
(Partial pressure)

$= 1340 \times 0.401 = 536$ mm Hg

Toluene = $560 \times \frac{0.435}{1.120} =$ "

$= 560 \times 0.388 = 217$

o-xylene = $210 \times \frac{0.236}{1.120} = 210 \times 0.211 = 44$

536
217
44
797 mm Hg
↓
Total pressure

Mole percentage composition (for liquid)

Benzene =

Vapor percent.

Benzene = $\frac{536}{797} \times 100$

$= 0.673 \times 100$

Toluene = $(217/797) \times 100$

$= 0.272 \times 100$

o-xylene = $(44/797) \times 100$

$= 0.055 \times 100$

67.3
27.2
5.5
100