

1. On a PV isotherm for a van der Waals' gas show how the critical point arises. What is the significance of the critical point and how are the parameters defined?

2+2

— Van der Waals gas equation. $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$ — (1)

At a fixed temperature (T), Van der Waals equation describes the dependence $P(V)$.

From P vs. V plot i.e. in PV -plane this dependence is represented as a family of isotherms each of which corresponds to a certain temperature.

In order to explain the isotherm, we need to transform the eqⁿ (1).

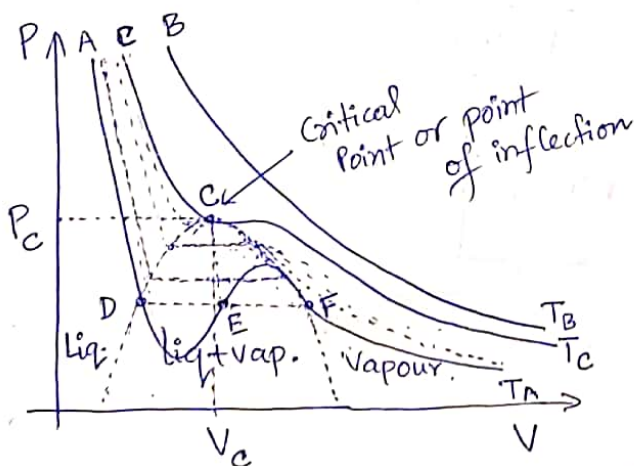
Multiplying V_m^2 on both side of eqⁿ (1)

$$\Rightarrow (PV_m^2 + a)(V_m - b) = RTV_m^2$$

$$\Rightarrow PV_m^3 - PbV_m^2 + aV_m - ab - RTV_m^2 = 0$$

$$\Rightarrow PV_m^3 - (Pb + RT)V_m^2 + aV_m - ab = 0$$

$$\Rightarrow V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{aV_m}{P} - \frac{ab}{P} = 0 \quad \text{--- (2)}$$



i) For temp. below T_c , the gas condenses to a liquid when P is increased.

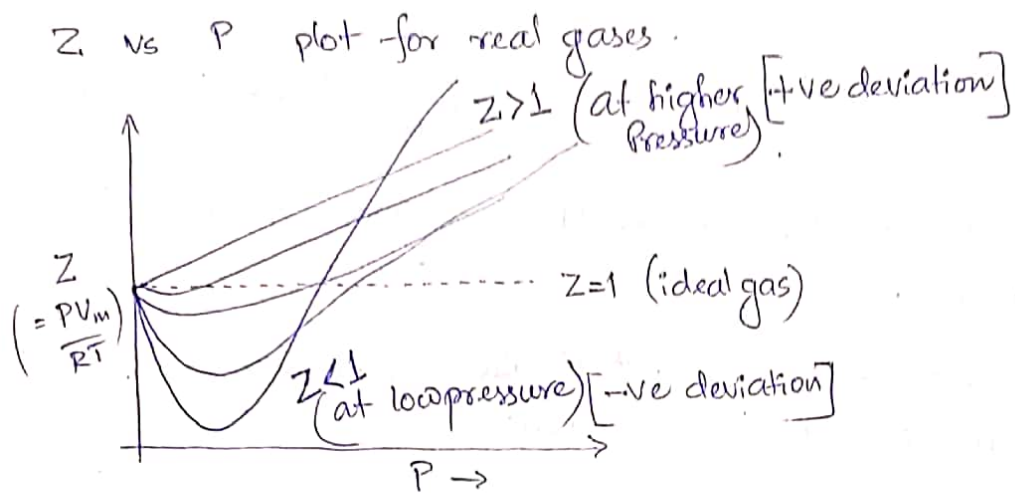
ii) At temp. T_A , decrease in V or increase in P , liquification starts after the point F is reached & it continues until at Point D when we will have all liquid.

$T_B > T_c > T_A$ [Point D, E, F are three ^{real} roots of eqⁿ (2)]

* Above the temp. T_c , no amount of compression will cause the separation out of a liquid phase in equilibrium with vapour phase. P_c is the highest pressure at which liquification can be possible (Pressure at T_c)

* V_c = Volume of gas at critical point i.e. at T_c & P_c .

2. Draw a plot of the compressibility factor Z vs P for any real gas indicating the deviation from ideality. Write an expression for Z obtained from the van der Waal's equation after multiplying by V_m/RT . 2+1



Van der Waals equation -

$$\left(P + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

$$\Rightarrow \frac{PV_m}{RT} = \frac{RT}{V_m - b} \times \frac{V_m}{RT} - \frac{a}{V_m^2} \times \frac{V_m}{RT}$$

$$\Rightarrow \frac{PV_m}{RT} = Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

$$\Rightarrow \boxed{Z = \frac{1}{1 - b/V_m} - \frac{a}{RTV_m}}$$

The phase rule can be expressed as -

$$F = C - P + 2, \text{ where, } F = \text{no. of degrees of freedom / no. of independent intensive variables.}$$

$C = \text{no. of components.}$

$P = \text{no. of phases}$

For two component system i.e. two chemically independent components $C=2$

$$\text{so, } F = 2 - P + 2 = 4 - P$$

4. Justify whether the following statements are true or false.

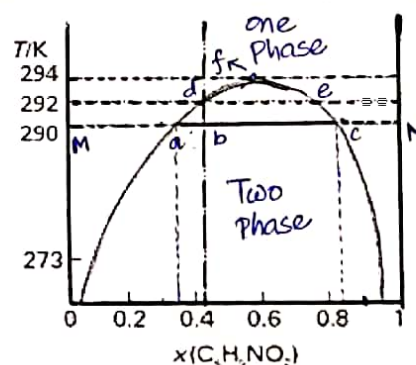
(a) addition of a nonvolatile solute to a pure solvent at constant T always lowers the vapor pressure - True

(b) addition of a solute at constant T and P to a pure solvent A always decreases μ_A - True

5. For the figure alongside a mixture of hexane (C_6H_{14}) and nitrobenzene ($0.41 \text{ mol } C_6H_5NO_2$) was prepared at 290 K.

(a) What are the compositions of the phases, and in what proportions do they occur? To what temperature must the sample be heated in order to obtain a single phase?

(b) Mention point wise specific features of the phase diagram. What kind of a system is this?



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Suppose, $C_6H_{14} = \text{liq. A}$ & $C_6H_5NO_2 = \text{liq. B}$.

a) At point b i.e. 0.41 mol fraction of $C_6H_5NO_2(B)$, composition of the phases

are - $x_A = ab$ & $x_B = bc$

where $ab = x_A = 0.41 - 0.35 = 0.06^*$ & $bc = x_B = 0.85 - 0.41 = 0.44^*$

* all the value are approx val

as, $n_A \propto \frac{1}{x_A}$ & $n_B \propto \frac{1}{x_B} \Rightarrow \frac{n_A}{n_B} = \frac{x_B}{x_A} = \frac{0.44}{0.06} = 7.33 \rightarrow \text{ratio of moles of two liquids in the two phases.}$

The sample must be heated to 294 K to obtain a single phase (A)

b) M = Pure $C_6H_{14}(A)$, a = Maximum solubility of $C_6H_5NO_2$ in C_6H_{14} reached & dilute saturated solⁿ of $C_6H_5NO_2$ in C_6H_{14} , b = overall composition of the two phase system is 0.41 mol frac. of $C_6H_5NO_2$, c = dilute saturated solⁿ of C_6H_{14} in $C_6H_5NO_2$, & N = Saturated solⁿ of C_6H_{14} in $C_6H_5NO_2$ (fully misc single phase). f = only single phase exists above it. ($T_c = \text{Critical solⁿ Temp.} = 294 \text{ K}$).

* This is a Partially Miscible binary liquid-liquid equilibrium.

5. What is the vapour pressure at 25.0 °C of a solution composed of 42.71 g of naphthalene (a non-volatile compound, MW = 128 g/mol) and 40.65 g of ethanol (MW = 46 g/mol). (The vapour pressure of pure ethanol at 25.0 °C is 96 torr)

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— From Raoult's law, $P_{\text{solution}} = x_{\text{solvent}} \cdot P_{\text{solvent}}^{\circ}$

here, $P_{\text{ethanol}}^{\circ} = 96 \text{ torr}$ (vap. pressure of pure solvent)

$$\text{no. of moles of naphthalene} = \frac{42.71 \text{ g}}{128 \text{ g/mol}} = 0.334 \text{ mol}$$

$$\text{no. of moles of ethanol} = \frac{40.65 \text{ g}}{46 \text{ g/mol}} = 0.883 \text{ mol}$$

$$\begin{aligned} \text{so, mole fraction of ethanol } (x_{\text{solvent}}) &= \frac{n_{\text{ethanol}}}{n_{\text{naphthalene}} + n_{\text{ethanol}}} \\ &= \frac{0.883}{0.883 + 0.334} \end{aligned}$$

$$\Rightarrow x_{\text{solvent/ethanol}} = 0.726$$

$$\text{Now, } P_{\text{solution}} = 0.726 \times 96 \text{ torr} = 69.7 \text{ torr. (A)}$$

6. 20 grams of a solute are added to 100 g of water at 25°C. The vapour pressure of pure water is 23.76 mm Hg; the vapour pressure of the solution is 22.41 mmHg.

(a) Calculate the molar mass of the solute.

(b) What mass of this solute is required in 100 g of water to reduce the vapour pressure to one half the value for pure water?

2+1

from Raoult's law,

$$a) \quad P_{\text{solution}} = x_{\text{solvent}} \cdot P_{\text{solvent}}^{\circ} \quad \text{--- (1)}$$

$$\Rightarrow 22.41 = x_{\text{solvent}} \cdot 23.76 \text{ mmHg}$$

$$\Rightarrow x_{\text{solvent}} = 0.94318$$

$$x_{\text{solute}} = 1 - 0.94318 = 0.05682$$

$$\Rightarrow x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solvent}} + n_{\text{solute}}} = 0.05682$$

$$\Rightarrow \frac{(20/M_{\text{solute}})}{(100/18) + (20/M_{\text{solute}})} = 0.05682$$

$$\Rightarrow \frac{100 M_{\text{solute}}}{360.2} = 16.6$$

$$\Rightarrow \boxed{M_{\text{solute}} = 59.79 \text{ g/mol}} \rightarrow \text{molar mass of solute (A)}$$

$$b) \quad P'_{\text{solution}} = \frac{23.76}{2} = 11.88 \text{ mmHg}$$

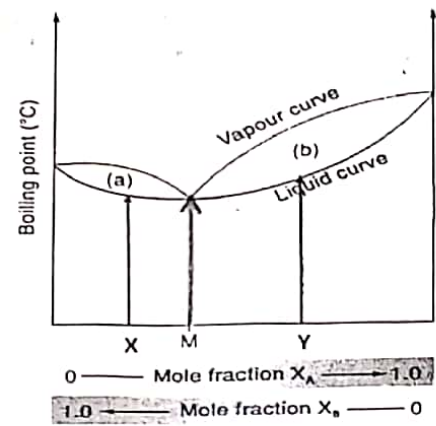
$$\text{eqn (1)} \Rightarrow x_{\text{solvent}} = 0.5 = x_{\text{solute}}$$

Now, Suppose m is the mass of solute required to obtain P'_{solution}

$$\frac{(m/59.79)}{(\frac{100}{18}) + (\frac{m}{59.79})} \Rightarrow \frac{100 \times 59.8}{18m} = 1$$

$$\Rightarrow \boxed{m = 332.2 \text{ g}} \quad \text{(A)}$$

7. For the boiling point composition curve shown on the right, what kind of deviation from Raoult's law is observed? For the points marked, X and Y on the diagram, what is the distillate and residue expected in each case? What is depicted by the point marked M?



+ve (Positive) deviation from Raoult's law shows a minimum in the boiling point-composition curve.

For the start point X \rightarrow Distillate = Azeotropic mixture M
 \rightarrow Residue = pure B.

For the start point Y \rightarrow Distillate = Azeotropic mixture M
 \rightarrow Residue = pure A

* The point marked M denotes the Azeotropic mixture M.
 It is a constant boiling point mixture. At this point Vapour has the same composition as the unboiled liq. mixture.