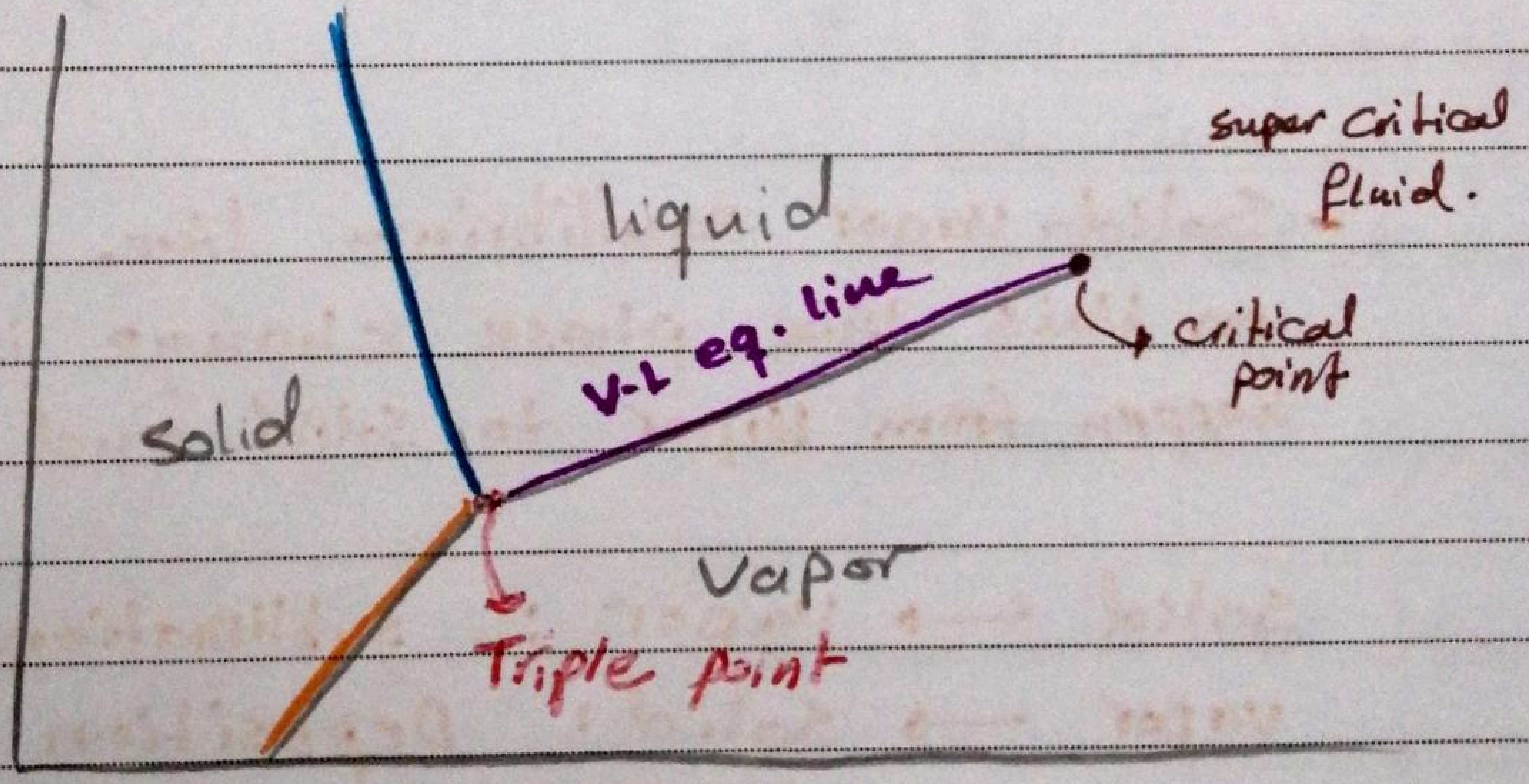
CH6: Multiphase systems:

phase equilibrium:
The Concentrations of all species in each phase no longer Change with time

6.1: Single Component phase diagram.

- phase diagram of H_2O.



- Triple point: point at which Solid, liquid and Vapor Can all Coexist.

- critical point (T_c, P_c): Above and to right of It only one phase is exist. (no phase Separation).

No.

- vapor-liquid equilibrium line:
on this line phase change is happen from Liquid to vapor or opposite.

Liquid → vapor : evaporation
Vapor → liquid : Condensation

- for given $\underline{\underline{P}}$ on this line → T(boiling point) Can obtain

Remark: boiling is happen when Vapor pressure equal total pressure (pressure on system).

- T at $P = 1atm$ ⇒ Normal boiling point

- Solid-vapor equilibrium line.
on this line phase change is happen from Vapor to Solid and opposite..

Solid → vapor : Sublimation.
vapor → Solid : Deposition

- For given point on the line
P: vapor pressure
T: Sublimation point.

- Solid-liquid equilibrium line:
  phase change from:
  Solid → liquid : melting
  liquid → solid : freezing

Note: phase change can only happen on the equilibrium lines.

Example: At given (T, P) → if it fall on liquid region → Subcooled liquid.
↳ if it fall on vapor-liquid equili. line, There are 3 probabilites
↳ Saturated vapor
↳ vapor and liquid mixture
↳ Saturated liquid.

* هل يمكن حدوث تغير في phase على غير الـ equilibrium line ؟
↳ لا مستحيل

* عند وجود المادة في أحد المناطق الثلاث تكون one phase بشكل مؤكد

* عند وجود المادة على equilibrium line لا يمكننا الجزم بحالتها ولها ثلاث خيارات
↳ sat.
↳ sat.
↳ mix of two phases

Saturated
↳ All the matter on one phase but on the equilibrium line.

Note: Read P. 242. last paragraph.

- Estimation of vapor pressure:
  - vapor pressure of a species is a measure of its volatility
  - vapor pressure ($p^*(T)$) → it is function in T.

to estimate it:

- Clapeyron equation

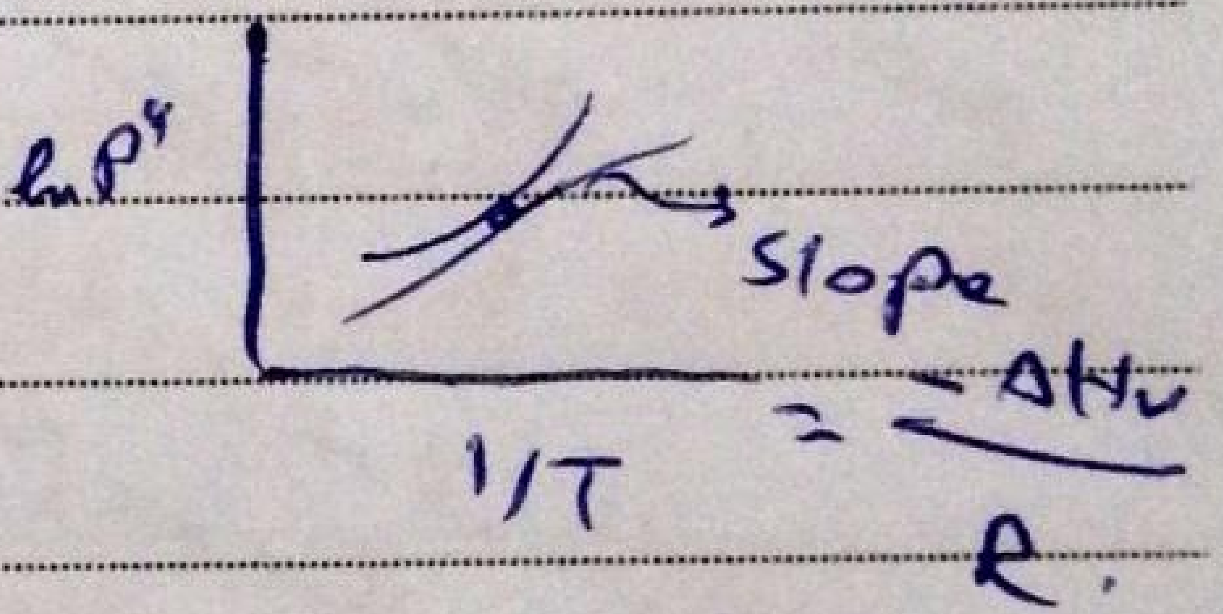
$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\hat{V}_g - \hat{V}_L)}$$

$\Delta\hat{H}_v$: latent heat of vaporization

$\hat{V}$: molar volume of (g) gas (L) liquid

replace $\hat{V}_g$ with $\frac{RT}{p^*}$

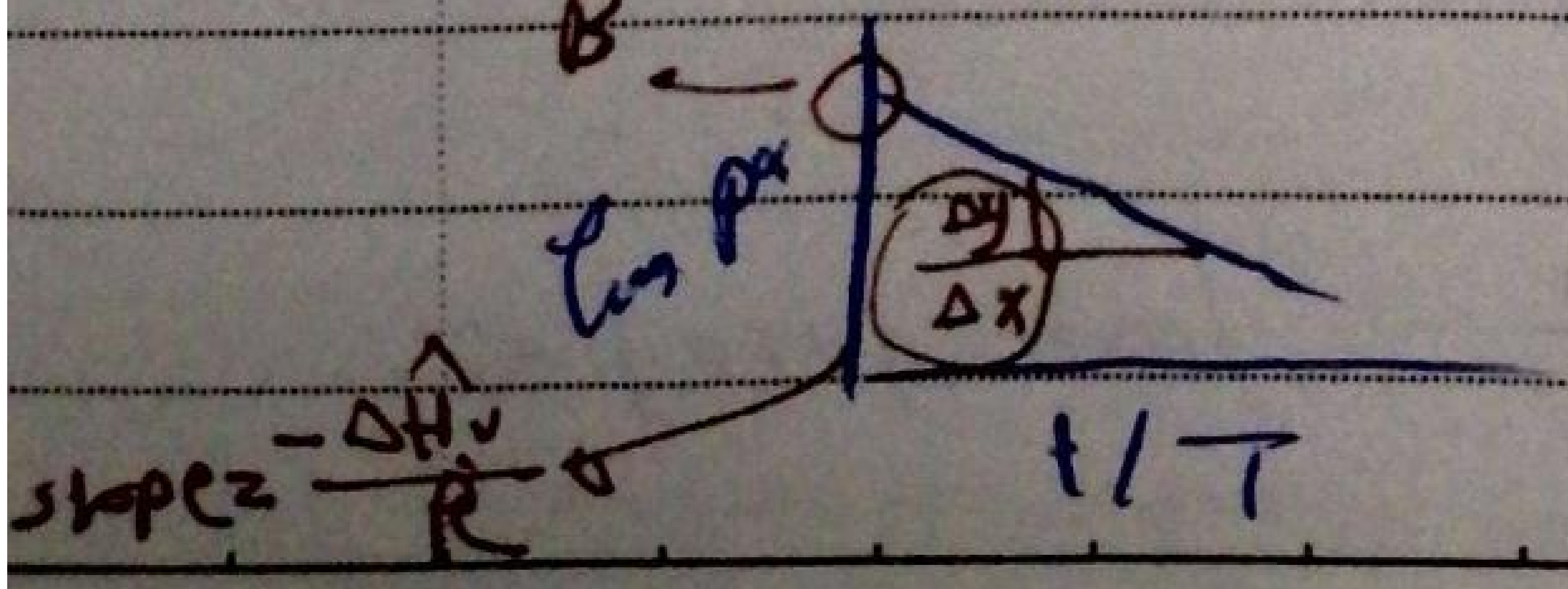
$$\Rightarrow \frac{d(\ln p^*)}{d(1/T)} = \frac{-\Delta\hat{H}_v}{R}$$

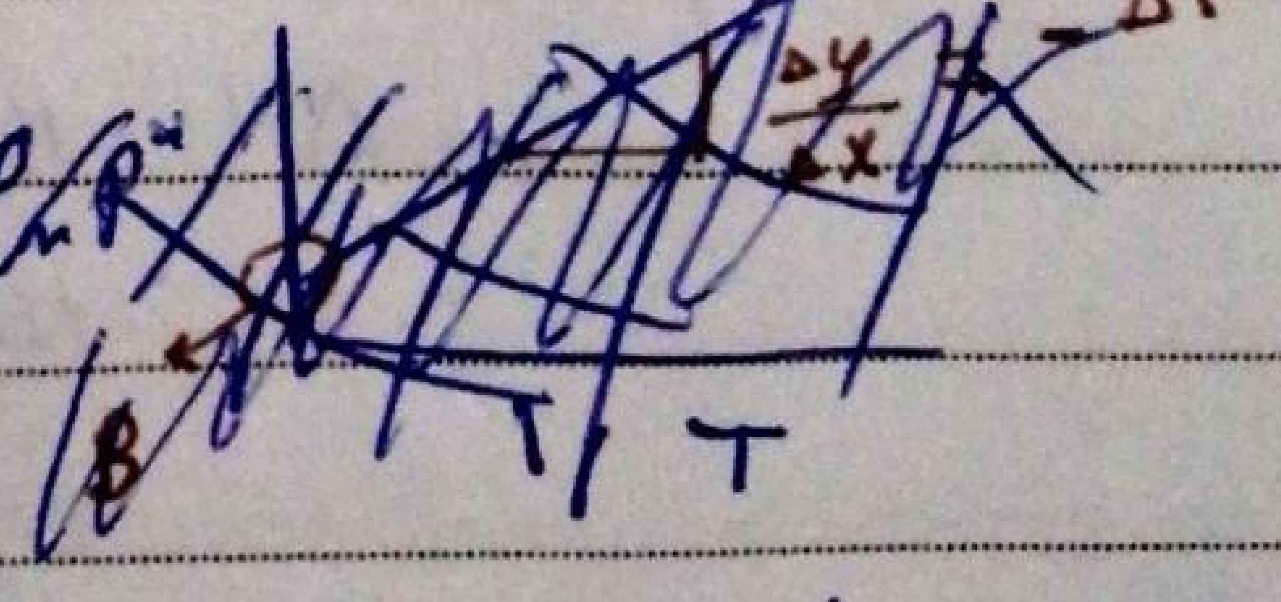


if $\Delta\hat{H}_v$ constant

- Clausius - Clapeyron equation

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$





- if only two point is available divide two equations or (−)

$$\frac{\ln p^*}{\ln p^*} = -\Delta\hat{H}_v$$

No.

↳ Antoine equation

$$\log_{10} p^{*} = A - \frac{B}{C+T}$$

T : in absolute T

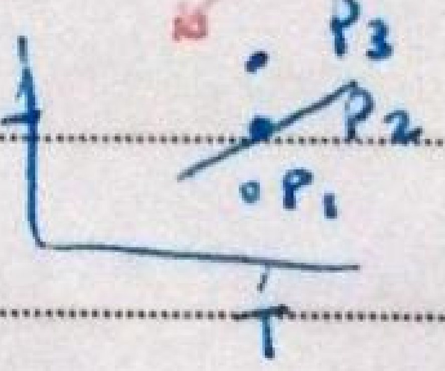
A, B, C : Constant for each Component.

Also Charts may be used.

for Liquid vapor system : $p^{*}_{(T)} = P$ → boiling material P_2 when T is absolute

$p^{*}(T) < P$ → Liquid P_1 →

$p^{*}(T) > P$ → vapor P_3



6.2 : The Gibbs phase rule :

↳ The degrees of freedom for multiphase system

$$DF = 2 + C - \pi$$

where

C : number of Chemical species

π : number of phase in a system at equilibrium

if DF = 0 All intensive property of the System can be obtained.

intensive property : properties that does not depend on the size of the system.

6.3: Gas-liquid systems: one Condensable Component:

B: gas phase. (vapor phase)

A: liquid phase

if only ~~A~~ w can transfer between two phases then: $P_w = y_w P = P^*_w(T)$

partial pressure of w

vapor fraction of w

total pressure

$\boxed{P = P_w + P_{air}}$

Notes:

- Saturation: the gas phase contain the maximum amount of condensable material (w)

- At equilibrium $P_i = P_i^* = y_i P$ → Saturati

if we try to increase p_i by → $y_i \uparrow$, → $p \uparrow$ } → both lead to Condensed

$P_i^*(T) = \downarrow y_i P_{tot} \uparrow$ ← why

↳ constant for given (T) ↑ or ↓ must

- Quantity of w in gas phase maybe bellow saturation $P_i = y_i P < P_i^*(T)$ → under Saturati

↳ This case: Superheated vapor

No.

- Dew point: The temprature that Saturated vapor start to Condensate.

P.251, P. 252, P. 253.

EXAM

A stream of air at 100°C and 5260 mm Hg contains 10.0% water by

1. Calculate the dew point and degrees of superheat of the air.
2. Calculate the percentage of the vapor that condenses and the final composition of the gas phase if the air is cooled to 80°C at constant pressure.
3. Calculate the percentage condensation and the final gas-phase composition if, instead of being cooled, the air is compressed isothermally to 8500 mm Hg.
4. Suppose the process of part 2 is run, the product gas is analyzed, and the mole fraction of wate differs considerably from the calculated value. What could be responsible for the disparit between calculated and measured values? (List several possibilities.)

* even that

$P_{H_2O} = P_i^*(100°C) = 760$

$\equiv (\le) P^*_{H_2O}(100°C)$

$P_{H_2O} = y_{H_2O} P_{tot}$ always

SOLUTION

1. $p_{H_2O} = y_{H_2O}P = (0.100)(5260 \text{ mm Hg}) = 526 \text{ mm Hg}$
   $p^*_{H_2O}(100°C) = 760 \text{ mm Hg} > p_{H_2O} \Longrightarrow$ the vapor is superheated (see Inequality 6.3-2)

   From Equation 6.3-3

$$p_{H_2O} = p^*_{H_2O}(T_{dp}) = 526 \text{ mm Hg}$$

$$\Big\Downarrow \text{Table B.3}$$

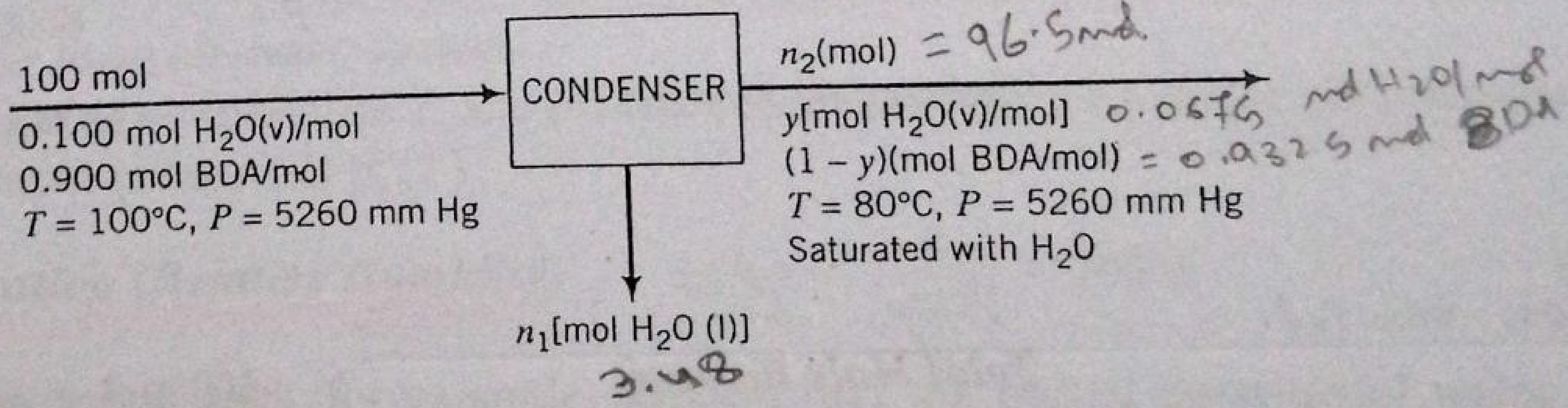
$$\boxed{T_{dp} = 90°C}$$

and the air has $100°C - 90°C = \boxed{10°C \text{ of superheat}}$

2. Since the air becomes saturated at 90°C, further cooling must lead to condensation. Since t products are liquid water in equilibrium with a gas phase, the water vapor in the gas m remain saturated.

   On the following flowchart, the symbol BDA stands for **bone-dry air**, a term used to sig the water–free component of an air-water vapor mixture.

   Basis: 100 mol Feed Gas



   Let us first do the degree-of-freedom analysis. Three unknown variables appear on the ch n_1, n_2, and y. Since only two species are involved in the process, we can only write two pendent material balances, leaving us one equation short. If we fail to observe that th at the condenser outlet is saturated with water, solution of the problem would be impos however, the saturation condition supplies the needed third equation, Raoult's law.

   The solution outline is as follows: apply Raoult's law at the outlet to determine y, the fraction of water in the outlet gas; then use a dry air balance to determine n_2 and a total balance or a water balance to determine the final unknown, n_1.

   Raoult's Law at Outlet $\quad yP = p^*_{H_2O}(T)$

$$\Big\Downarrow$$

$$y = \frac{p^*_{H_2O}(80°C)}{P} = \frac{355 \text{ mm Hg}}{5260 \text{ mm Hg}} = \boxed{0.0675 \frac{\text{mol } H_2O}{\text{mol}}}$$

Balance on Dry Air

$$\frac{100\text{ mol} \;\Big|\; 0.900\text{ mol BDA}}{\quad \Big|\; \text{mol}} = n_2(1-y)$$

$$\Big\Downarrow \; y = 0.0675$$

$$n_2 = 96.5\text{ mol}$$

Total Mole Balance

$$100\text{ mol} = n_1 + n_2$$

$$\Big\Downarrow \; n_2 = 96.5\text{ mol}$$

$$n_1 = 3.5\text{ mol H}_2\text{O condensed}$$

Percentage Condensation

$$\frac{3.5\text{ mol H}_2\text{O condensed}}{(0.100 \times 100)\text{ mol H}_2\text{O fed}} \times 100\% = \boxed{35\%}$$

occurs when P is high enough for the in

The mechanism of evaporation of a liquid depends on the relative values of the vapor pressure of the liquid and the total system pressure. If evaporation takes place at a temperature such that $p^* < P$, the process involves transfer of molecules from the surface of the liquid to the gas above the surface, while if $p^* = P$, vapor bubbles form throughout the entire liquid, but predominantly at the heated container walls: that is, the liquid *boils*. The temperature at which $p^* = P$ is the **boiling point** of the liquid at the given pressure.

↳ only for one condensible pt

T
RSELF

1. If water vapor is in equilibrium with liquid water, must the vapor be saturated? yes Can a vapor be saturated if there is no liquid present in the system? yes
2. The vapor pressure of acetone is 200 mm Hg at 22.7°C. Liquid acetone is kept in a sealed flask at 22.7°C, and the gas above the liquid contains air and acetone vapor at a pressure of 960 mm Hg. What is (a) the partial pressure of acetone in the gas, (b) the partial pressure of N_2, and (c) the mole fraction of acetone in the gas? What assumption have you made in answering the preceding question? How would you determine the boiling point of the acetone, assuming a constant total pressure of 960 mm Hg?
3. Suppose you have a curve of $p^*_{H_2O}$ versus T, and you are given the temperature and pressure (T_0 and P_0) of a mixture of water and noncondensable gases.
    - **a.** Define the dew point of the gas. Would the vapor be saturated or superheated if $T_0 > T_{dp}$? If $T_0 = T_{dp}$?
    - **b.** If you are told that the gas is saturated, how would you calculate the mole fraction of water in it? What would happen to the vapor if you (i) heated the gas isobarically (at constant pressure), (ii) cooled the gas isobarically, (iii) compressed the gas isothermally (at constant temperature), and (iv) expanded the gas isothermally? $\uparrow y_{H_2O}P_{tot} = p^*_i(T_0)$
    - **c.** If you are given the mole fraction of water in the gas, how would you calculate the dew point of the gas?
    - **d.** If you are given the degrees of superheat of the gas, how would you calculate the mole fraction of water in the gas?

Several quantities besides those introduced in the previous section are commonly used to describe the state and composition of a gas containing a single condensable vapor. *In the definitions to be given, the term "saturation" refers to any gas–vapor combination, while "humidity" refers specifically to an air–water system.*

Suppose a gas at temperature T and pressure P contains a vapor whose partial pressure is p_i and whose vapor pressure is $p_i^*(T)$.

Relative Saturation (Relative Humidity)
$$s_r(h_r) = \frac{p_i}{p_i^*(T)} \times 100\% \tag{6.3-4}$$

if it was 100% → sat

A relative humidity of 40%, for example, signifies that the partial pressure of water vapor equals $\frac{4}{10}$ of the vapor pressure of water at the system temperature.

Molal Saturation (Molal Humidity)

$$s_m(h_m) = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry) gas}} \tag{6.3-5}$$

(Can you prove the second equality?)

Absolute Saturation (Absolute Humidity)

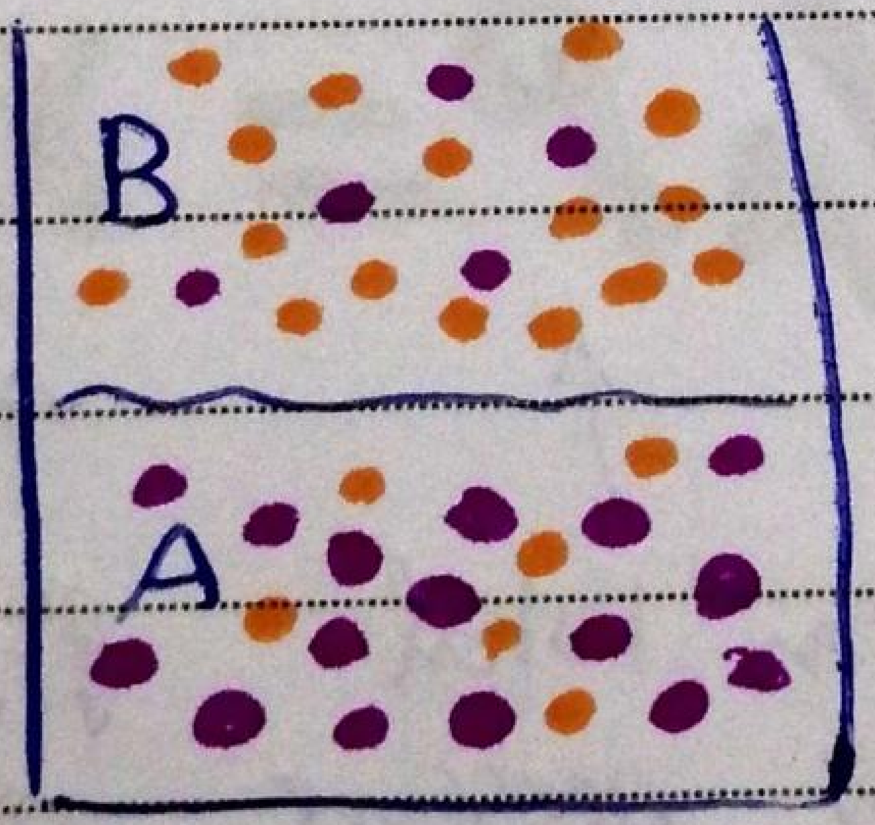
$$s_a(h_a) = \frac{p_i M_i}{(P - p_i)M_{dry}} = \frac{\text{mass of vapor}}{\text{mass of dry gas}} \tag{6.3-6}$$

where M_i is the molecular weight of the vapor and M_{dry} is the average molecular weight of the dry (vapor-free) gas.

6.4: Multicomponent Gas-liquid Systems

- Raoult's Law and Henry's law:

Note: The composition of the two phases at given temperature and pressure are dependent.



B: gas phase
A: Liquid phase.

🟣 : Molecules of Tol component
🟠 : Molecules of Ben component

- Notice that there is differences in distribution of molecules of Tol, and Ben. between the two phases A and B.

↳ This is natural.
the more volatility will be in gas phase in larger quantity than in liquid phase while the less volatility would be in liquid phase more.

The more volatility • Ben.
The less volatility • Tol.

↳ The compositions of Ben. and Tol. in both phases are controlled by equilibrium relations.

- one is Raoult's law

$$\underset{\substack{\uparrow \\ \text{partial} \\ \text{pressure} \\ \text{of A} \\ \text{component}}}{P_A} = \underset{\substack{\uparrow \\ \text{fraction} \\ \text{of (A)} \\ \text{in gas} \\ \text{phase}}}{y_A} \underset{\substack{\uparrow \\ \text{total} \\ \text{pressure}}}{P} = \underset{\substack{\uparrow \\ \text{fraction} \\ \text{of A} \\ \text{in liquid} \\ \text{phase}}}{X_A} \underset{\substack{\uparrow \\ \text{vapor pressure} \\ \text{of component} \\ \text{A at} \\ \text{given T.}}}{P_A^*(T)}$$

used for similar substances $X_A \in [0, 1]$

- ملاحظة : عندما كان هناك مادة واحدة بالحالة السائلة (L)
كان القانون $P_A = y_A P = P_A^*(T)$ حيث أن

$$\boxed{X_A = 1}$$

- Another one is Henry's law.

$$\underbrace{\overset{\uparrow}{p_A} = \overset{\uparrow}{y_A} \overset{\uparrow}{P} = \overset{\uparrow}{x_A}}_{\text{at specified.}} \overset{\uparrow}{H_A}(T)$$

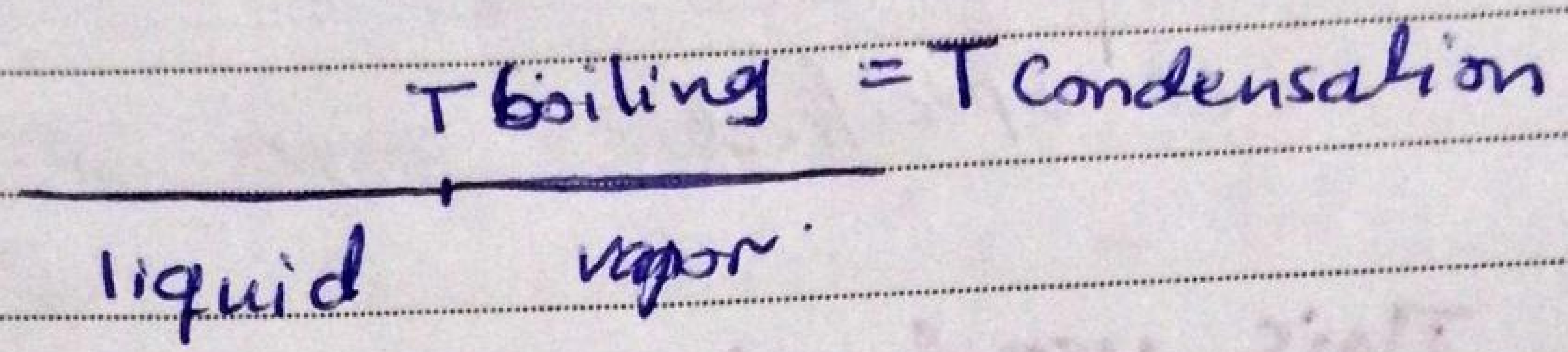
at specified.

Henry's law constant for A Componen in specific solvent.

This used when
$x_A \rightarrow 0$ (diluted)
only

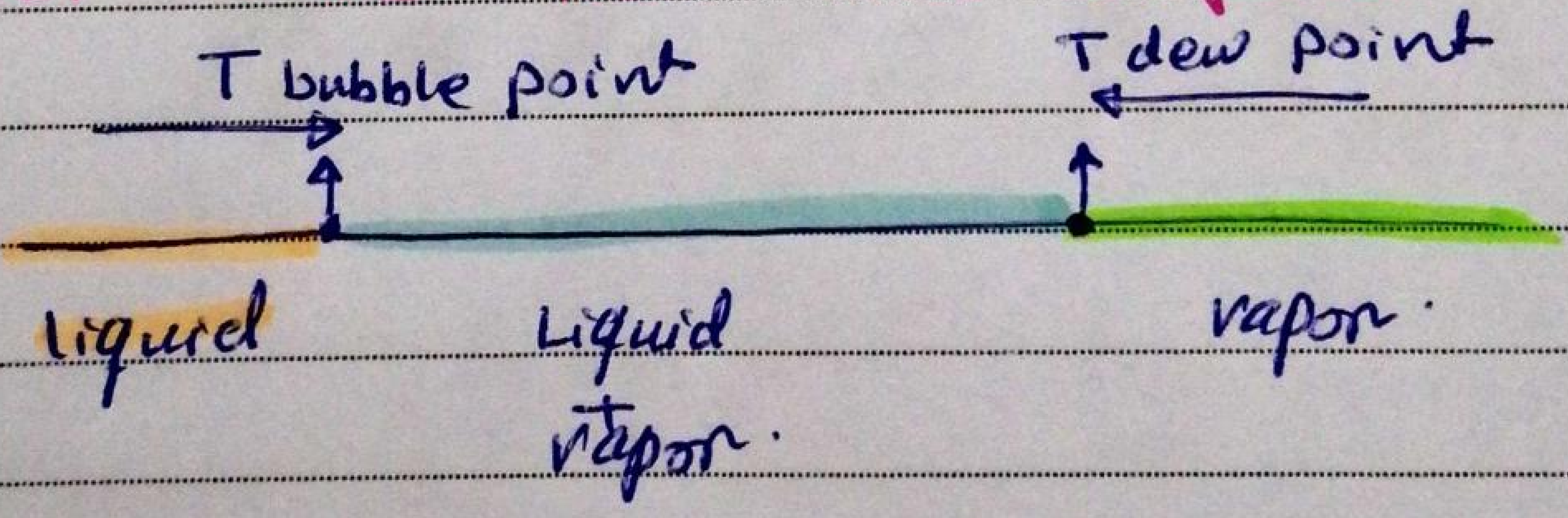
- Concept of bubble and dew point

- For one component At given p.



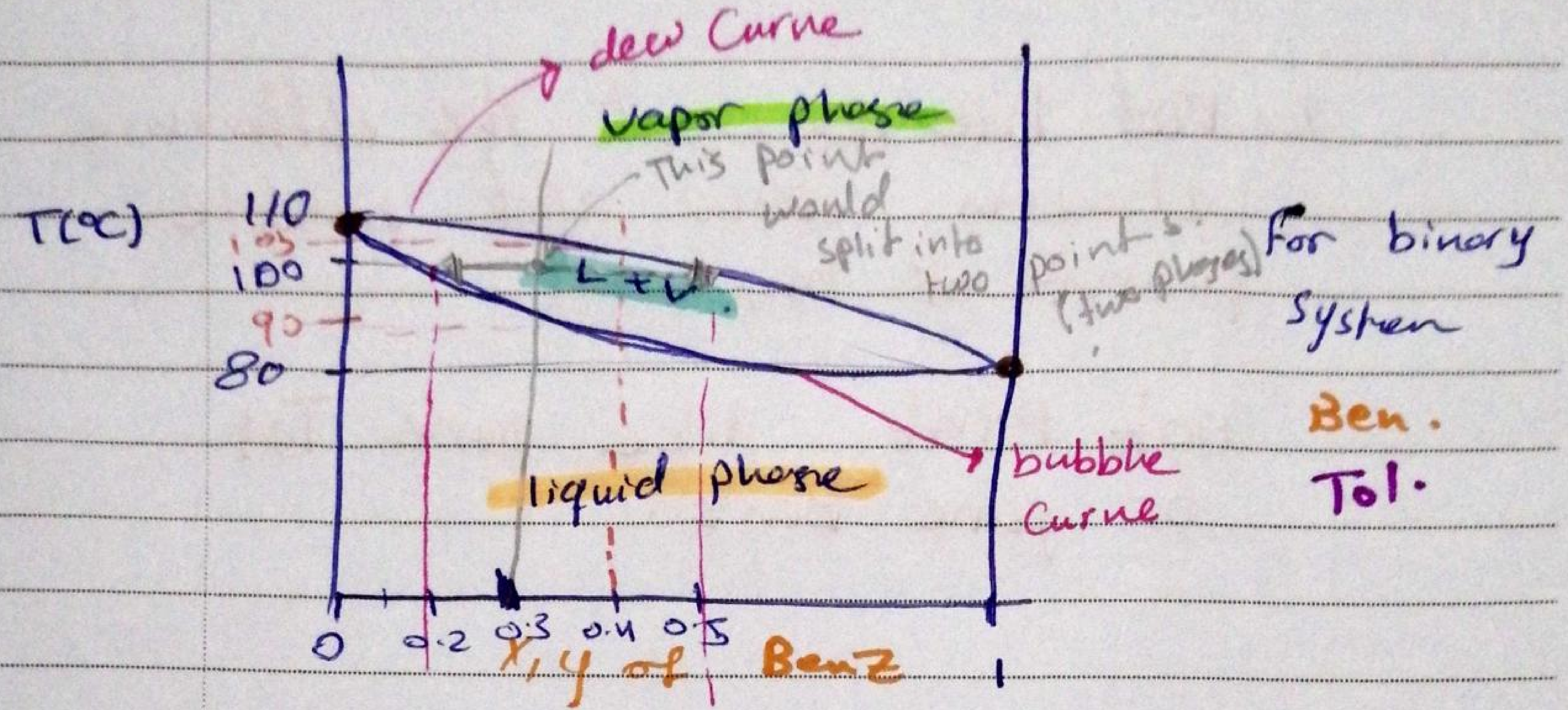
Such like water At $p = 1atm$
water transfer from Liquid → vapor
and from vapor → Liquid at
Same temperature (100°c)

- For more then one Component:



- T bubble point : The temperature at which first vapor bubble forms.

- T dew point : The temperature at which the first liquid droplet forms



At $x_{BenZ} = 0$ → T = T boiling of Tol = 110 °C

(pure Tol)

At $x_{BenZ} = 1$ → T = T boiling of BenZ = 80 °C

(pure BenZ)

(both are points only)

but Between them.

Ex: $x_{BenZ} = 0.6$ T = 70

⇒ mixture in Liquid Phase

$x_{Tol} = 1 - 0.6 = 0.4$

⇒ $Z_{BenZ} = 0.3$ T = 100 (Z both liquid and vapor composition)

from bubble curve → $x_{BenZ} = 0.2$ $x_{Tol} = 1 - 0.2 = 0.8$

from dew curve → $y_{Ben} = 0.5$ $y_{Tol} = 1 - 0.5 = 0.5$

The red line represent the difference between dew and bubble point of mixture.

not point like pure Tol or pure Benz.