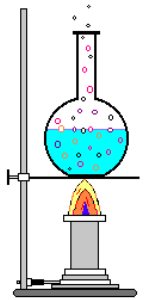
CHAPTER 6

MULTIPHASE SYSTEMS



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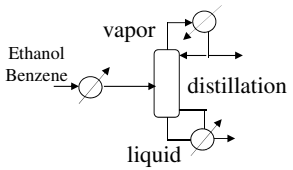
Course Learning Outcomes

At the end of this course students will be able to

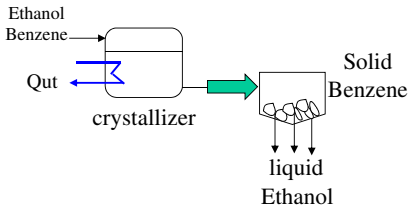
- Apply Raoult's Law for a single condensable species
- Explain the meaning of Ideal solution and the applicability of Henry's Law and Raoult's Law
- Use Txy and Pxy diagram to determine the Bubble and Dew point temperatures and pressures, compositions and relative amounts of each phase in a two phase mixture
- The effects of varying temperature and pressure on Bubble point, Dew Points, and phase amounts and compositions.

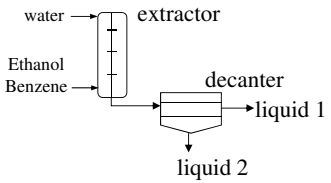
Multiphase Systems

Process 1



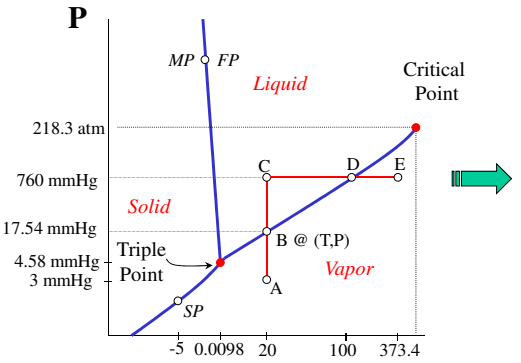
Process 2





Process 3

Single Component Phase Equilibrium - Phase Diagrams for H_2O



Important concepts:

- Vapor Pressure
- Boiling Point (b.p.)
- b.p. temperature
- Normal b.p.
- Sublimation Point (SP)
- Melting Point (MP)
- Freezing Point (FP)
- Triple Point

Vapor Pressure (p*)

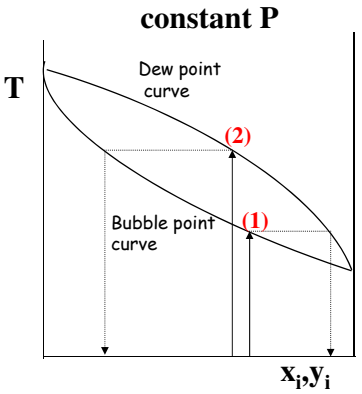
- Volatility of a species is the degree to which the species tends to transfer from the liquid or solid state to the vapor state
  - ✓ Highly volatile species tends to be more likely in vapor phase
- Vapor pressure (p*) - a measure of species volatility
  - ✓ The higher the vapor pressure for a given temperature the greater the volatility of species.
  - ✓ Vapor pressure is related to boiling - liquids with high vapor pressures (volatile liquids) will boil at lower temperatures.
  - ✓ The vapor pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture.

Vapor Pressure (*p**) – Applications in Chemical Engineering

p* is used in :

(1) *Bubble P calculations* - T-xy diagram.
(given T, x_i, calculate P, y_i)

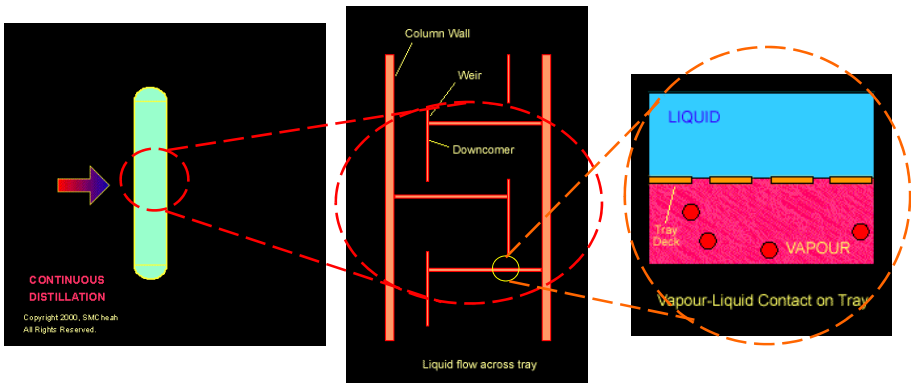
(2) *Dew P calculations* - T-xy diagram.
(given y_i, T, calculate x_i, P)



In general, *p** is crucial (among others) for **VLE** calculations…….

Application of vapor pressure in distillation process

Distillation occurs because of the differences in the vapor pressure (volatility) of the components in the liquid mixture



Vapor Pressure (p*) Estimation

i. **Claussius-Clapeyron equation**
ii. **Cox Chart**
iii. **Antoine equation**

Antoine Equation

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

- Antoine constants (A, B and C) for many compounds are available in the literature Table B.3 for water only (pg. 638-639) and Table B.4 (pg. 640-641) in the textbook

Calculate the vapor pressure of benzene at 50°C using the Antoine Equation. Also estimate the normal boiling point of benzene (the vapor pressure at 1 atm)

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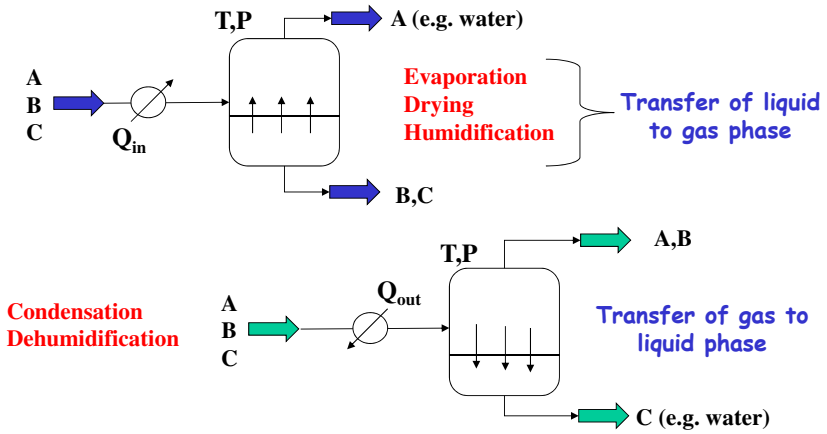
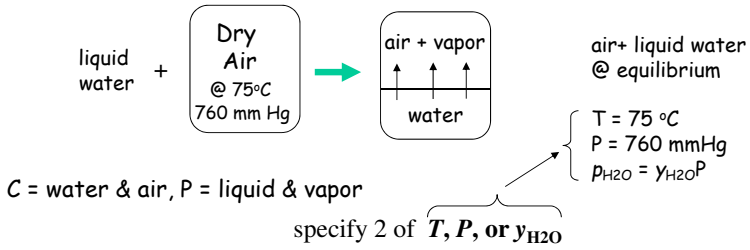




If a gas at temperature T and pressure P contains a saturated vapor whose mole fraction is y_i and if this vapor is the only species that would condense if the temperature were slightly lowered, the partial pressure of the vapor in the gas equals the pure-component vapor pressure $p^*_i(T)$ at the system temperature.

Raoult's Law, single condensable species : $p_i = y_i P = p_i^*(T)$

Example II

Air and liquid water are contained at equilibrium in closed container at 75 °C and 760 mmHg. Calculate the molar composition of the gas phase

- A gas in equilibrium with a liquid must be saturated with the volatile component of that liquid.
- Partial pressure of a vapor at equilibrium in a gas mixture containing a single condensable component **cannot exceed** the vapor pressure of the pure component in the system ;
  $p_i (= y_i P) \leq p^*$
  - ✓ For a given temperature, a vapor (vapor pressure) present in a gas is less than its saturation amount, $p_i < p^*$, is called superheated vapor
  - ✓ If a superheated vapor is cooled down at constant pressure, the temperature at which $p_i = p^*$ (saturated vapor) is known as the dew point of the gas
- Any attempt to increase p_i by either adding more vapor or increasing total pressure, would lead to condensation.

Example IV

A stream of air at 100°C and 5260 mm Hg contains 10% water by volume.

a. Calculate the dew point of the air

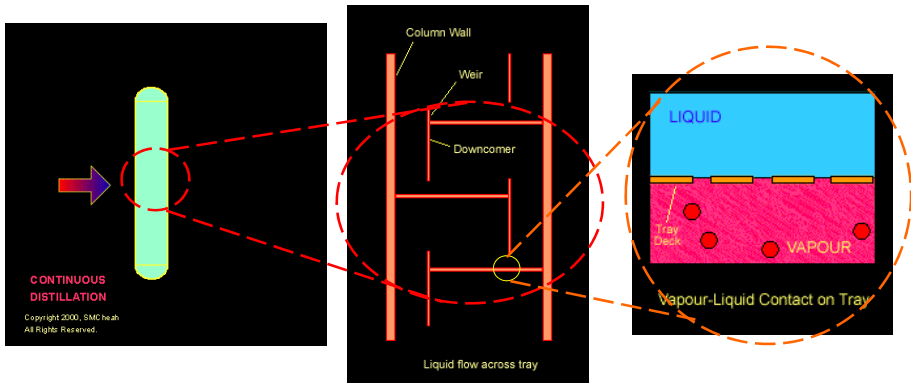
b. Calculate the percentage of vapor that condenses and the final composition of the gas phase if the gas is cooled to 80°C at constant pressure.

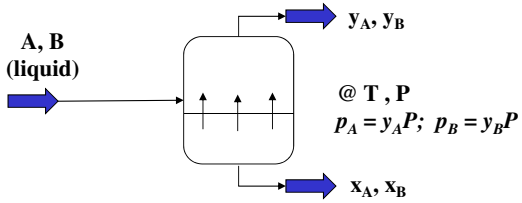
Saturation condition at outlet:

c. Calculate the percentage of vapor that condenses and the final gas phase composition if instead of being cooled at constant pressure the gas is compressed isothermally (at constant temperature) to 8500 mm Hg.

Initially, $y_{H2O}\,P < p_{H2O}^*(100^oC)$. Saturation occurs when P is high enough.

Saturation condition





F = 2 + C - P = 2 ⟹ specify 2 of T,P, y_{H2O}

Raoult's Law $p_A = y_A P = x_A p_A^*(T)$ $p_B = y_B P = x_B p_B^*(T)$ .... .. Ideal solution

Valid

- when x_i ==> 1.0 (liquid is almost pure i); *when x_i = 1 (single condensable species)*
- for the entire range of compositions for mixtures of similar substances, e.g. paraffinic hydrocarbon of similar molecular weight

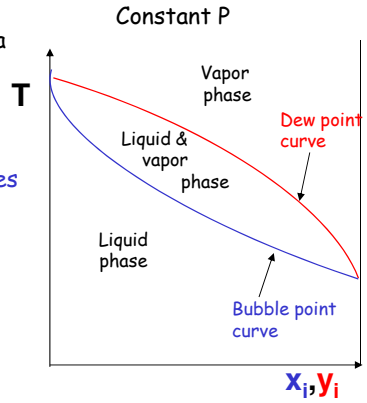
i. A benzene-toluene mixture containing 30mole% benzene vapor is placed a closed container at 1 atm and 115°C. Is the vapor mixture is in equilibrium with liquid mixture ?

ii. An equal-molar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapors at 50°C. What is the system pressure and composition of the vapor?

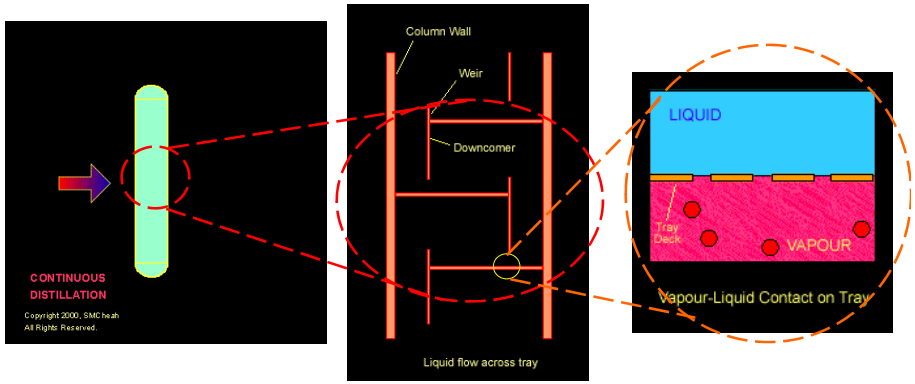
A benzene-toluene mixture containing 30 mole% benzene vapor is placed a closed container at 1 atm and 115°C. Is the vapor mixture is in equilibrium with liquid mixture

An equal-molar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapors at 50°C. What is the system pressure and composition of the vapor?

- In a vaporization process of liquid mixture containing several components at constant pressure, the vapor composition will have a composition different from that of the liquid.
- As vaporization proceeds the composition of the remaining liquid continuously changes and hence does so its vaporization temperature.
- A similar phenomenon occurs if a mixture of vapors is subjected to condensation at constant pressure – the composition of vapor and the condensation temperature both change.



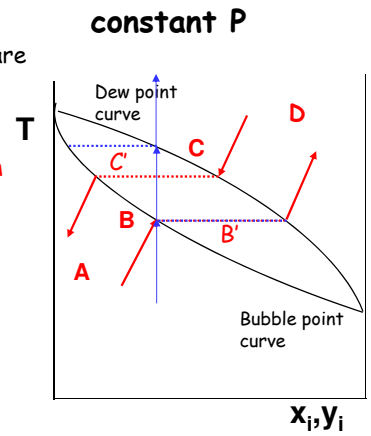
Distillation occurs because of the differences in the vapor pressure (volatility) of the components in the liquid mixture



Ideal solutions – Raoult's and Henry's law are obeyed & the gas vapor can be considered as ideal gas

Constant P heating path on a T-x-y diagram

A – subcooled liquid
B - saturated liquid (Bubble Point Temp.)
C - saturated vapor (Dew Point Temp.)
D - superheated vapor
B' - vapor composition in equilibrium with liquid at bubble point. temp.
C' - liquid composition in equilibrium with vapor at dew point. temp.



Bubble-point temperature (T_{bp}) of the liquid - the temperature at which the first bubble vapor forms when the liquid is heated at given pressure

Raoult's law :

$$p_i = y_i P = x_i p_i^*(T_{bp}) \quad \text{hence,} \quad \sum y_i = 1 = \frac{\sum_i x_i p_i^*(T_{bp})}{P} \quad \text{(trial \& error)}$$

and Bubble-point pressure (P_{bp}) of the liquid - the pressure at which the first bubble vapor forms when the liquid is heated at given temperature

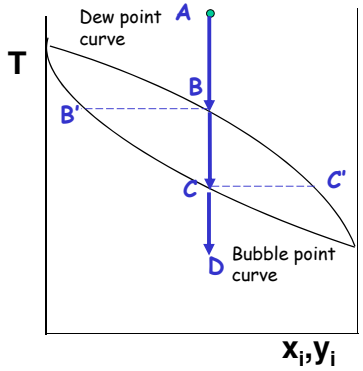
$$p_i = y_i P_{bp} = x_i p_i^*(T)$$

$$\sum y_i = 1 = \frac{\sum_i x_i p_i^*(T)}{P_{bp}} \qquad \text{hence,} \quad P_{bp} = \sum_i x_i p_i^*(T)$$

constant P

Constant P cooling path on a T-x-y diagram

A – superheated vapor
B - saturated vapor (Dew point Temp.)
C - saturated liquid (Bubble Point Temp.)
D - subcooled liquid
B' – liquid composition in equilibrium with vapor at dew point. temp.
C' - vapor composition in equilibrium with liquid at bubble point. temp.



Dew-point temperature (T_{dp}) of the vapor – temperature at which the first drop of liquid forms when the vapor is cooled at given pressure

Raoult's law :

$$p_i = y_i P = x_i p_i^*(T_{dp}) \quad \text{hence,} \quad \sum x_i = 1 = \frac{y_i P}{p_i^*(T_{dp})} \text{ (trial \& error)}$$

Dew-point pressure (P_{dp}) of the vapor – pressure at which the first drop of liquid forms when the vapor is cooled at given temperature

$$\sum_i x_i = 1 = P_{dp} \sum_i \frac{y_i}{p_i^*(T)} \quad \text{hence,} \quad P_{dp} = \frac{1}{\sum_i \frac{y_i}{p_i^*(T)}}$$

A vapor mixture containing 30 mole% benzene and 70% toluene at 1 atm is cooled isobarically a closed container from an initial temperature of 115°C.

a. At what temperature does the first drop of condensate form? What is its composition?

b. At one point during the process the system temperature is 100°C. Determine the mole fraction of benzene in the vapor and liquid phases.

c. Calculate the ratio of total moles in vapor to total moles liquid at the system of 100°C

a. At what temperature does the first drop of condensate form? What is its composition?

b. At one point during the process the system temperature is 100°C. Determine the mole fraction of benzene and toluene in the vapor and liquid phases

c. The ratio (total moles in vapor/total moles liquid) at the system temperature is 100°C

Basis : F = 1 mol feed

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