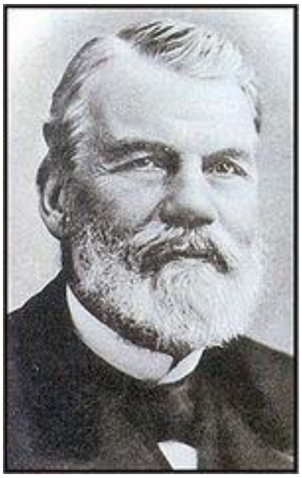
CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)
03. RAOULT'S LAW AND APPLICATIONS

ALI KH. AL-MATAR (aalmatar@ju.edu.jo)

Chemical Engineering Department
University of Jordan' nb
hjui
Amman 11942, Jordan

Outline

- *K* Values & Relative Volatility
- Representation of VLE Data
- Interpretation of Deviations From Raoult's Law
- Azeotropic Mixtures
- Types of VLE Calculations: Ideal Solutions
  - Bubble P and Dew P
  - Bubble T and Dew T
  - Flash Calculations



François-Marie Raoult (10 May 1830 – 1 April 1901) was a French chemist who conducted research into the behavior of solutions, especially their physical properties.

K Values & Relative Volatility

- The *K* value is a **distribution coefficient** between two different phases for a certain component

$$\boxed{K_i = \frac{y_i}{x_i}}$$

- The **relative volatility** is a measure of the **selectivity** of getting one species in a phase preferentially;

$$\boxed{\alpha_{1,2} = \frac{K_1}{K_2} = \frac{(y_1/x_1)}{(y_2/x_2)}}$$

  - Measure of the selectivity of separation of two components

Relative Volatility

- Relative volatility is a criterion to determine whether normal distillation is a viable choice to separate the more volatile species from the less volatile species in a mixture.
- **Exclude using** ordinary distillation if

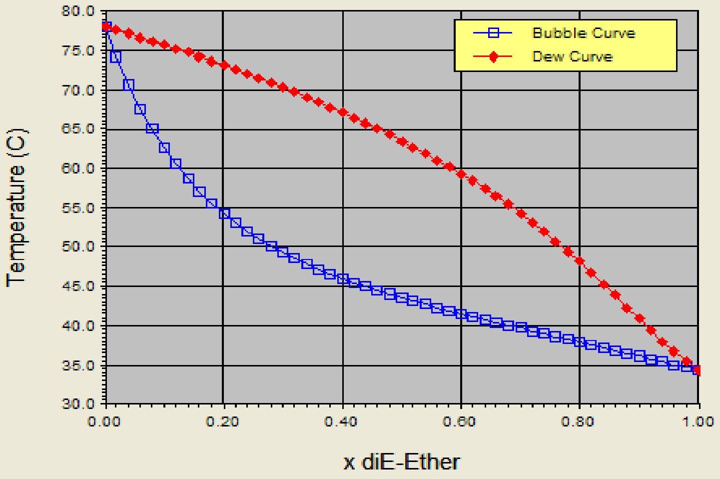
$$\boxed{0.95 \le \alpha_{1,2} \le 1.05}$$

  - Due to the large number of trays required when α is in this range.
  - Does not exclude the use of "**super-fractionators**".

Representation of VLE Data

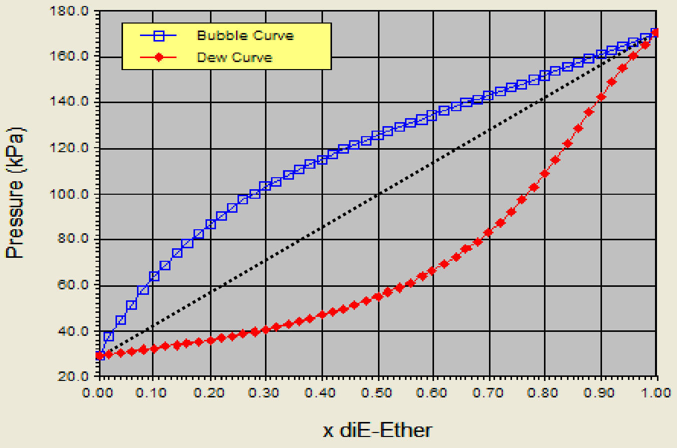
- There are three equivalent ways of representing the VLE data:
  - *Pxy*,
  - *Txy*,
  - *xy*.
- The information contained in any of the methods of representing the data is the same.
- Some representations are more useful in certain situations e.g., *Pxy* is more practical for petroleum refineries' atmospheric distillation.

Positive Deviations from Raoult's Law



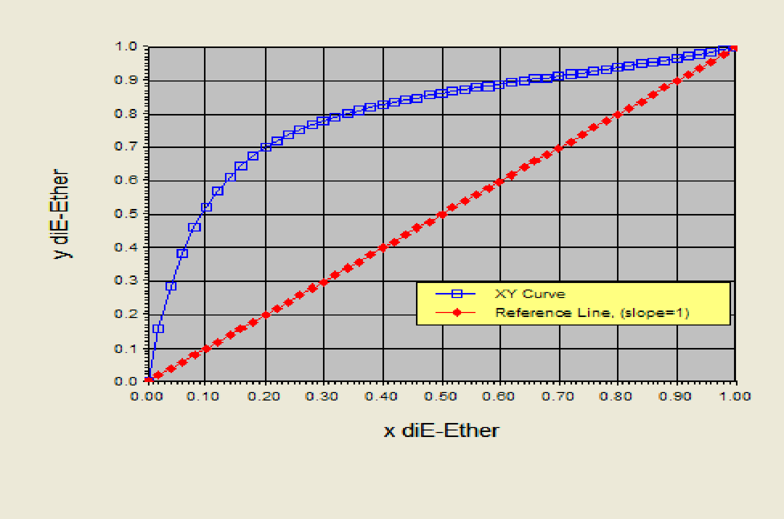
Phase behavior of the diethyl ether (1) – ethanol (2) system. (*Txy*) at 101.325 kPa. This system features **positive deviations** from Raoult's law since the bubble curve (*Pxy*) is above the Raoult's law line.

Positive Deviations from Raoult's Law



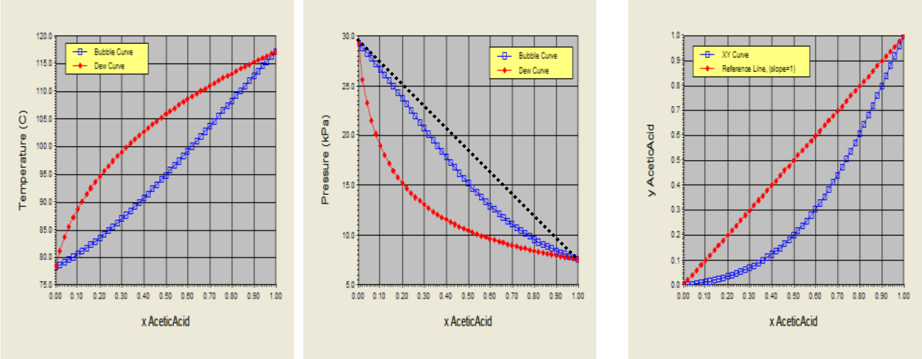
Phase behavior of the diethyl ether (1) – ethanol (2) system. *Pxy*at 50 °C. This system features **positive deviations** from Raoult's law since the bubble curve (*Pxy*) is above the Raoult's law line.

Positive Deviations from Raoult’s Law



Phase behavior of the diethyl ether (1) – ethanol (2) system. (*xy*) at 101.325 kPa. This system features **positive deviations** from Raoult’s law since the bubble curve (*Pxy*) is above the Raoult’s law line.

Negative Deviations from Raoult’s Law



Phase behavior of the acetic acid (1) – ethanol (2) system. Left figure (*Txy*) at 101.325 kPa, middle figure (*Pxy*) at 50 °C, and right figure (*xy*) at 101.325 kPa.

This system features **negative deviations** from Raoult’s law since the bubble curve (*Pxy*) is below the Raoult’s law line.

Interpretation of Deviations From Raoult's Law

- **Negative deviations** indicates that adhesive forces between different components (cross interactions) are stronger than the average cohesive forces between like components (pure interactions).
  - Each component is retained in the liquid phase by attractive forces that are stronger than in the pure liquid so that its partial vapor pressure is lower.
  - Leads to maximum boiling azeotropes (HCl-H2O).
- **Positive Deviations** indicates that the cohesive forces (pure interactions) are greater than the adhesive forces (cross interactions).
  - The dissimilarities of polarity leads both components to escape solution more easily. Therefore, the vapor pressure is greater than expected from the Raoult's law, showing positive deviation.
  - Leads to minimum boiling azeotropes (benzene and methanol, carbon disulfide and acetone, and chloroform and ethanol.)

Azeotropic Mixtures

- Derived from the Greek words ζέειν (boil) and τρόπος (turning) combined with the prefix α- (no) to give the overall meaning, "no change on boiling"
- An azeotrope is a mixture for which $x_i = y_i$ i.e., the dew-point and bubble-point curves are tangent to the same horizontal line.
  - Azeotropes are important; since no separation can be achieved of a constant-boiling solution by distillation.
  - At low pressure, the liquid phase activity coefficient may be obtained from azeotropic composition from

$$\boxed{\gamma_i(\mathbf{x}^{AZ}) = \frac{P}{P_i^{vap}}}$$

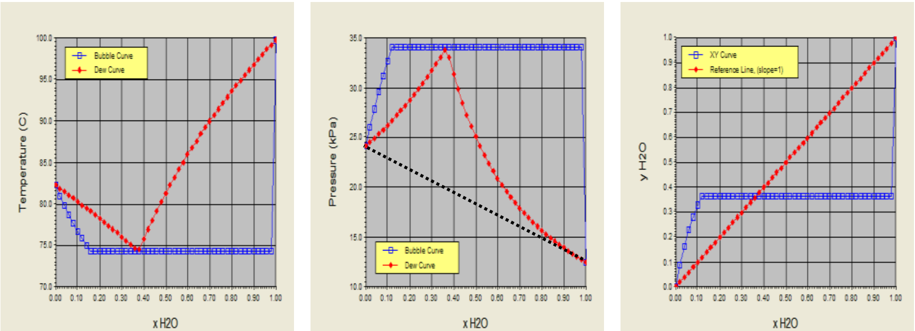
  - The relative volatility for an azeotropic mixture is unity

$$\boxed{\alpha^{AZ} = 1}$$

Types of Azeotropes

- Maximum boiling azeotrope
  - Has a maximum in the *Txy* plane, or a minimum in the *Pxy* plane, or is approaching the *x*=*y* line from below in an *xy* plane.
  - Occurs when there are negative deviations from Raoult's law i.e., when the activity coefficients of one or more species is less than one.
- Minimum boiling azeotrope
  - Has a minimum in the *Txy* plane, or a maximum in the *Pxy* plane, or is approaching the *x*=*y* line from above in an *xy* plane.
  - Occurs when there are positive deviations from Raoult's law i.e., when the activity coefficients of at least one species in the mixture is greater than one.
- Complex
  - Saddle
  - Double

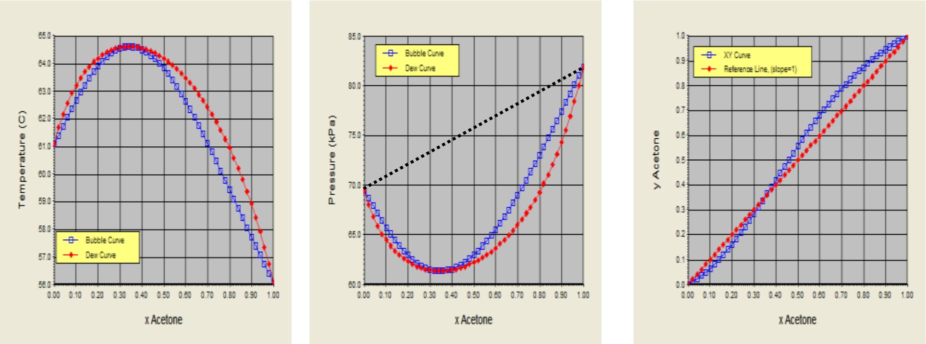
Minimum Boiling Azeotrope



Phase behavior of the water (1) – 2-propanol (2) system. Left figure (*Txy*) at 101.325 kPa, middle figure (*Pxy*) at 50 °C, and right figure (*xy*) at 101.325 kPa.

This system features a **minimum boiling azeotrope**.

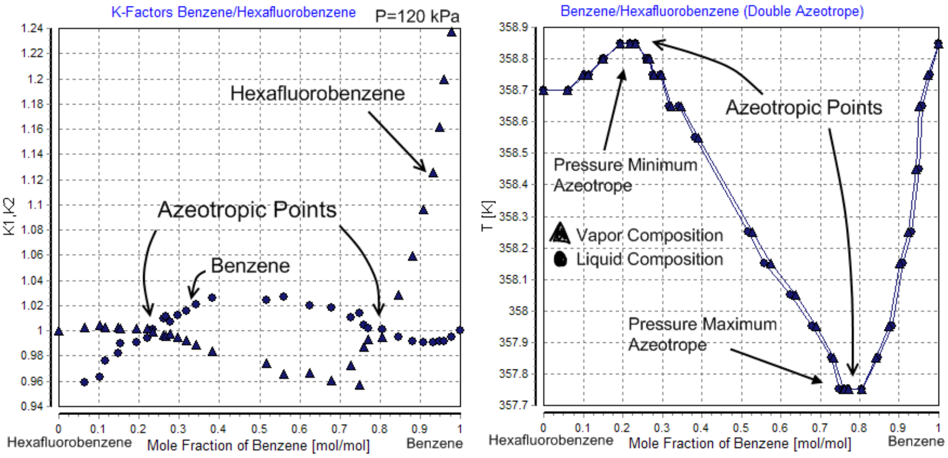
Maximum Boiling Azeotrope



Phase behavior of the acetone (1) – chloroform (2) system. Left figure (*Txy*) at 101.325 kPa, middle figure (*Pxy*) at 50 °C, and right figure (*xy*) at 101.325 kPa.

This system features a **maximum boiling azeotrope**.

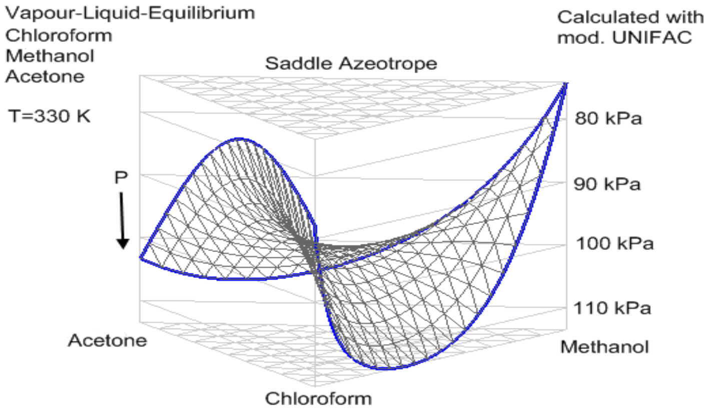
Double Boiling Azeotrope



A rare type of complex binary azeotrope is one where the boiling point and condensation point curves touch at two points in the phase diagram. Such a system is called a double azeotrope, and will have two azeotropic compositions and boiling points. An example is water and *N*-methylethylenediamine.

Olson, John D. "Thermodynamics of Hydrogen Bonding Mixtures ."

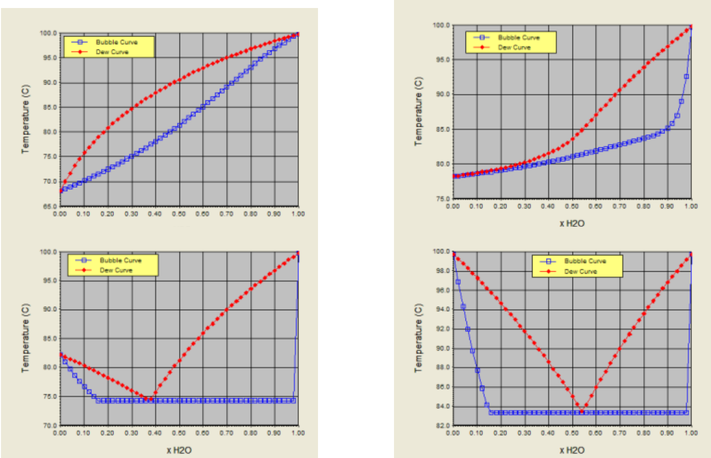
Saddle Azeotrope (ternary Mixture)



The best known of these is the ternary azeotrope formed by 30% acetone, 47% chloroform, and 23% methanol, which boils at 57.5°C. Each pair of these constituents forms a binary azeotrope, but chloroform/methanol and acetone/methanol both form positive azeotropes while chloroform/acetone forms a negative azeotrope. The resulting ternary azeotrope is neither positive nor negative. Its boiling point falls *between* the boiling points of acetone and chloroform, so it is neither a maximum nor a minimum boiling point. This type of system is called a saddle azeotrope.[4] Only systems of three or more constituents can form saddle azeotropes.

Hilmen, Eva-Katrine (November 2000). "Separation of Azeotropic Mixtures: Tools for Analysis and Studies on Batch Distillation Operation" . Norwegian University of Science and Technology, Dept. of Chemical Engineering.

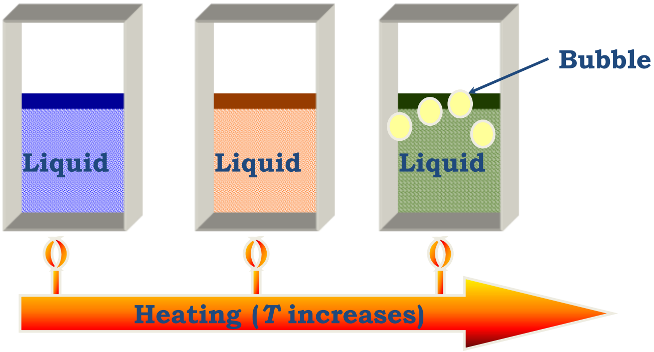
Water-Alcohol Mixtures



Phase behavior (*Txy*) of the water (1) – alcohol (2) systems at 101.325 kPa: Top left is methanol, top right is ethanol, bottom left is 2-propanol and bottom right is 2-butanol.

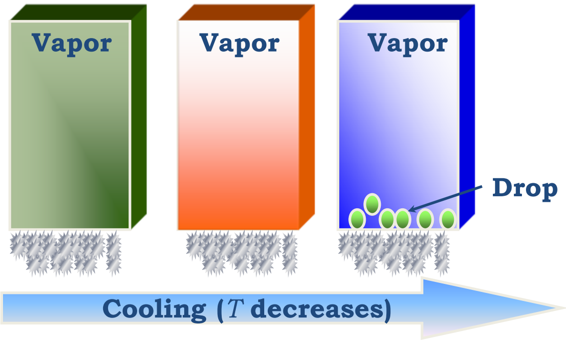
Bubble Point

- The temperature at which the first bubble of vapor forms (at a given pressure).
- Related to vaporization (from liquid phase to vapor phase).



Dew Point

- The temperature at which the first drop of liquid forms (at a given pressure).
- Related to condensation (from vapor phase to liquid phase).



Types of VLE Calculations: Ideal Solutions

- Three main types of VLE calculations are frequently encountered
  - Bubble-point calculation,
    - Bubble *P*: calculate $\{y_i\}$ and *P*, given $\{x_i\}$ and *T*,
    - Bubble *T*: calculate $\{y_i\}$ and *T*, given $\{x_i\}$ and *P*.
  - Dew-point calculation
    - Dew *P*: calculate $\{x_i\}$ and *P*, given $\{y_i\}$ and *T*,
    - Dew *T*: calculate $\{x_i\}$ and *T*, given $\{y_i\}$ and *P*.
  - Flash calculations. Many cases, the general approach will be given.

Bubble *P*: Concept and Algorithm

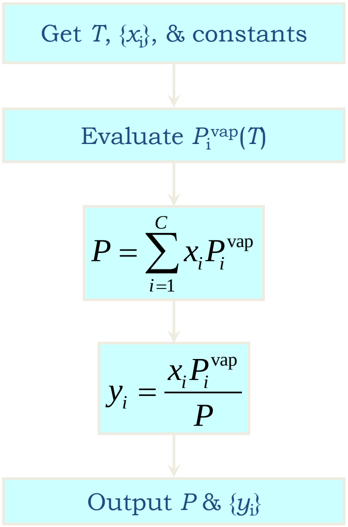
1. Given are *T* and $\{x_i\}$,
2. Wanted are *P* and $\{y_i\}$,
3. Start with the equilibrium condition

$$y_i = \frac{x_i P_i^{\text{vap}}}{P}$$

4. We know that $\{y_i\}$ must sum to one

$$P = \sum_{i=1}^{C} x_i P_i^{\text{vap}}$$

5. We have *P* that we can use to find $\{y_i\}$.



Get *T*, $\{x_i\}$, & constants

Evaluate $P_i^{\text{vap}}(T)$

$$P = \sum_{i=1}^{C} x_i P_i^{\text{vap}}$$

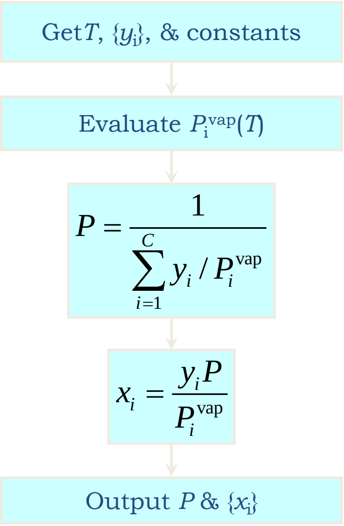
$$y_i = \frac{x_i P_i^{\text{vap}}}{P}$$

Output *P* & $\{y_i\}$

Dew *P*: Concept and Algorithm

1. Given are T and $\{y_i\}$,
2. Wanted are P and $\{x_i\}$,
3. The main difference between this algorithm and [Bubble P] is that we don't know the liquid composition.
4. Make use of

$$\sum_{i=1}^{C} x_i = 1 \Rightarrow P = \frac{1}{\sum_{i=1}^{C} y_i / P_i^{\text{vap}}}$$



Get T, $\{y_i\}$, & constants

Evaluate $P_i^{\text{vap}}(T)$

$$P = \frac{1}{\sum_{i=1}^{C} y_i / P_i^{\text{vap}}}$$

$$x_i = \frac{y_i P}{P_i^{\text{vap}}}$$

Output P & $\{x_i\}$

Bubble *T*: Concept and Algorithm

1. Given are P^{True} and $\{x_i\}$
2. Wanted are T and $\{y_i\}$
3. The T-type is different from the P-type in that the vapor pressure is a strong function of T which is initially unknown.
4. To solve this problem, trial and error is usually necessary.
    1. Obtain an initial guess of the temperature from the saturation T's obtained from Antoine equation (or any other vapor pressure model!)

       $$T_i^{sat} = \frac{B_i}{A_i - \log_{10} P^{True}} - C_i$$

    2. obtain an initial guess of T from $T = \sum_{i=1}^{C} x_i T_i^{sat}$
    3. Bubble P and find the sum of mole fractions $y_i = x_i P_i^{\text{vap}} / P^{True}$
    4. Correct the vapor pressure of a key-component (usually the first component) by **dividing** the vapor pressure of the key-component by the summation of y.
    5. Bubble P and find the sum of mole fractions.
    6. Repeat steps 3-5 until the sum of mole fraction is converged to unity.

$$\sum_{i=1}^{C} y_i = 1$$

Dew *T*: Concept and Algorithm

1. Given are P^{True} and $\{y_i\}$
2. Wanted are T and $\{x_i\}$
3. The *T*-type is different from the *P*-type in that the vapor pressure is a strong function of *T* which is initially unknown.
4. To solve this problem, trial and error is usually necessary.
    1. Obtain an initial guess of the temperature from the saturation *T*'s obtained from Antoine equation (or any other vapor pressure model!)

       $$T_i^{sat} = \frac{B_i}{A_i - \log_{10} P^{True}} - C_i$$

    2. obtain an initial guess of *T* from $T = \sum_{i=1}^{C} x_i T_i^{sat}$
    3. Dew P and find the sum of mole fractions $x_i = y_i P^{True} / P_i^{\text{vap}}$
    4. Correct the vapor pressure of a key-component (usually the first component) by **multiplying** the vapor pressure of the key-component by the summation of x.
    5. Bubble P and find the sum of mole fractions.
    6. Repeat steps 3-5 until the sum of mole fraction is converged to unity.

       $$\sum_{i=1}^{C} x_i = 1$$

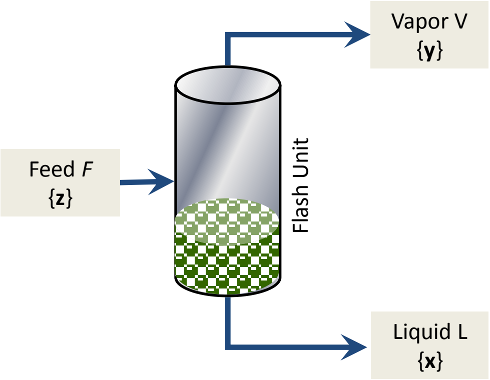
Quiz

- Determine the bubble point pressure for an equimolar binary system of components A and B. The vapor pressure of A and B are 10 and 12 kPa, respectively.
- Would you recommend ordinary distillation to separate these components? Justify your answer.

- Consider the system: ethanol/and phenol at 1 bar. Would you consider applying Raoult's law to this system? Justify your answer.

Flash Concept

- A liquid at a pressure equal to or greater than its bubble point pressure "flashes" or partially evaporates when the pressure is reduced below the bubble point pressure
- This produces a two phase system of vapor and liquid in equilibrium at known *T*, *P* and overall composition.



Flash Calculations

- Flash calculations are a combination of material, energy balances and equilibrium relations.
- In this course we are interested in isothermal flash which will avoid using energy balances.
- The flash problem is posed as:
  - Given: feed composition and flow rate.
  - Feed flow rate is assumed to be unity as a basis.
  - Wanted: $\{x_i\}$, $\{y_i\}$, and vapor and liquid flow rates.

Deriving The equations for Flash

- Overall Material balance

$$\boxed{L + V = 1}$$

- Species balance

$$\boxed{z_i = x_i L + y_i V \quad , i = 1, \cdots, C}$$

- Eliminate L from the two balance equations to obtain

$$\boxed{z_i = x_i (1 - V) + y_i V, \quad i = 1, 2, \cdots, C}$$

- Introduce the distribution coefficient $K_i = y_i / x_i$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{vap}}{P}, \quad i = 1, 2, \cdots, C \text{ or}$$

$$y_i = \frac{z_i K_i}{1 + V\,(K_i - 1)}, \quad i = 1, 2, \cdots, C \text{ or}$$

$$x_i = \frac{z_i}{1 + V\,(K_i - 1)}, \quad i = 1, 2, \cdots, C$$

- The vapor and liquid phase mole fractions must sum to unity, from which

$$F_y = \sum_{i=1}^{C} \frac{z_i K_i}{1 + V(K_i - 1)} - 1 = 0$$

$$F_x = \sum_{i=1}^{C} \frac{z_i}{1 + V(K_i - 1)} - 1 = 0$$

Rachford-Rice Equation

- Solution of any of the two last equations is dependent on the correct value of V i.e., the fraction of the feed that is vaporized.
- The distribution coefficient can be obtained from the equilibrium conditions
  - relate it to activity coefficients, vapor pressure, and vapor phase fugacity coefficients.
- A more convenient way of solving is to take the difference between the two F functions. This becomes convenient using the Newton-Raphson method due to the monotonic behavior of the derivative of this function.

Rachford-Rice equation

$$F = F_y - F_x = \sum_{i=1}^{C} \frac{z_i (K_i - 1)}{1 + V(K_i - 1)} = 0$$

$$\frac{dF}{dV} = -\sum_{i=1}^{C} \frac{z_i (K_i - 1)^2}{\left[1 + V(K_i - 1)\right]^2}$$

Precautions and Tricks

- Before carrying out a flash calculation you have to carry out a Bubble *P* and a Dew *P* calculation to check that the given pressure is indeed within the two phase region i.e., if the mixture is to flash we need to have
- Otherwise, the mixture will not flash at the given pressure.

$$\boxed{P_{\text{dew}} < P < P_{\text{bubble}}}$$

- Trial and error solution is required when using the R-R equation for more than three component systems
  - Ternary systems lead to a quadratic equation that can be solved using the discriminator.
  - Binary systems lead to linear equation.

Example

- The system acetone(1)/acetonitrile(2)/nitromethane (3) at 80°C and 110 kPa has the overall composition $\{z_i=0.45,0.35,0.20\}$. Assuming that Raoult's law applies for this system, determine *L*, *V*, $\{x_i\}$, $\{y_i\}$.
- The vapor pressure of the pure species at the given *T* are $\{P_i^{\text{vap}}=195.75,97.84,50.32\}$

Solution

- Carry out a Bubble P with $\{z_i\}=\{x_i\}$

$$P_{\text{bubble}} = \sum_{i=1}^{3} x_i P_i^{\text{vap}}$$

$$= (0.45)(195.75) + (0.35)(97.84) + (0.20)(50.32) = 132.4 \text{ kPa}$$

- Carry out a Dew P with $\{z_i\}=\{y_i\}$

$$P_{\text{dew}} = \frac{1}{\sum_{i=1}^{3} y_i / P_i^{\text{vap}}}$$

$$= \frac{1}{0.45/195.75 + 0.35/97.84 + 0.20/50.32} = 101.52 \text{ kPa}$$

- The given pressure falls between the bubble and dew pressures. Consequently, the solution will give flash into two vapor and liquid streams.
- Raoult's law applies which simplifies the calculations such that

$$K_i = \frac{P_i^{\text{vap}}}{P} \rightarrow \mathbf{K} = \{1.7795, 0.8895, 0.4575\}$$

- Substitute the known values into the F_y equation (arbitrarily)

$$\frac{(0.45)(1.7795)}{1+0.7795V} + \frac{(0.35)(0.8895)}{1-0.1105V} + \frac{(0.20)(0.4575)}{1-0.5425V} - 1 = 0$$

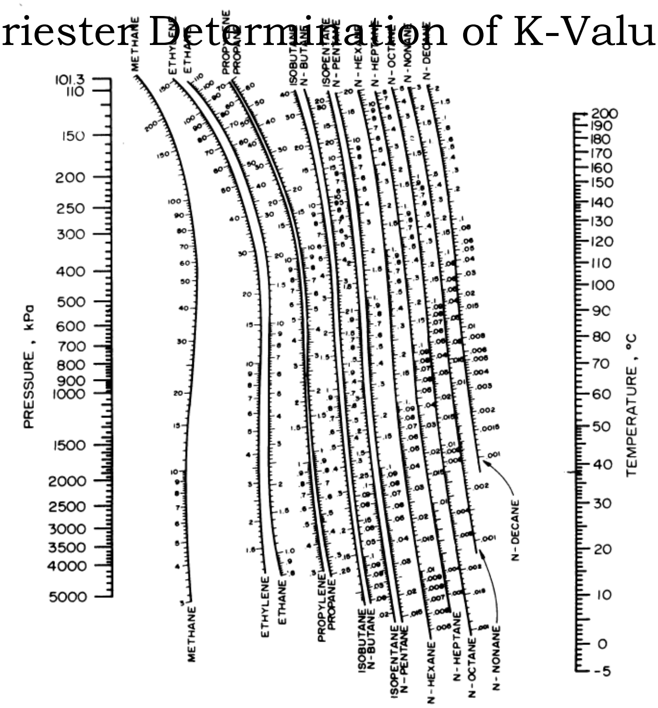
Solve this problem using R-R equation

- Solve for V to get V=0.7364. From this value of V, L=1-V=0.2636.
- Find the vapor phase, and liquid phase mole fractions from

$$y_i = \frac{z_i K_i}{1+V(K_i-1)} \quad \text{, or } x_i = \frac{z_i}{1+V(K_i-1)} \quad , i=1,\cdots,C$$

Component	z_i	x_i	y_i
Acetone	0.45	0.2859	0.5087
Acetonitrile	0.35	0.3810	0.3389
Nitromethane	0.20	0.3331	0.1524

Depriester Determination of K-Values



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