Faculty of Engineering and Technology
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Thermodynamics II

Lec 1: Vapor Liquid Equilibrium-part 1

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Content

- Introduction
- The nature of equilibrium
- Phase Rule in VLE
- Raoult’s law
- Bubble and dew points calculations

VLE Calculations

Purpose of this lecture:

- To demonstrate how Raoult’s law can be used in the prediction of the VLE behavior of ideal mixtures

Highlights

- Phase rules gives the number of variables we need in order to determine the intensive state of a system at equilibrium
- Raoult’s law can be used for constructing Pxy, Txy diagrams and performing dew point and bubble point calculations

Introduction

- Composition changes are the desired outcome, not only of chemical reactions, but of a number of industrially important mass-transfer operations
- Processes such as distillation, absorption, and extraction bring phases of different composition into contact, and when the phases are not in equilibrium, mass transfer between the phases alters their compositions.
- Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium.
- Thus, for quantitative treatment of mass transfer the equilibrium T, P, and phase compositions must be known
- The most commonly encountered coexisting phases in industrial practice are vapor and liquid, although liquid/liquid, vapor/liquid, and liquid/solid systems are also found

Introduction

Flash distillation

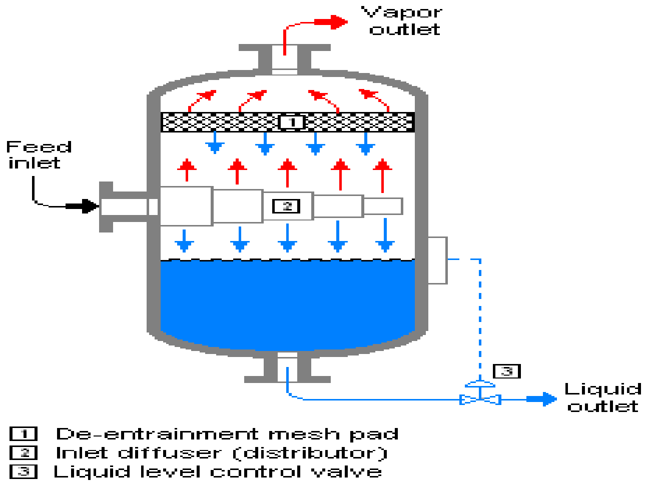
- Flash distillation is a single stage separation technique.
- A liquid mixture feed is pumped through a heater to raise the temperature and enthalpy of the mixture.
- It then flows through a valve and the pressure is reduced, causing the liquid to partially vaporize.
- Once the mixture enters a big enough volume the liquid and vapor separate.
- Because the vapor and liquid are in such close contact up until the "flash" occurs, the product liquid and vapor phases approach equilibrium.

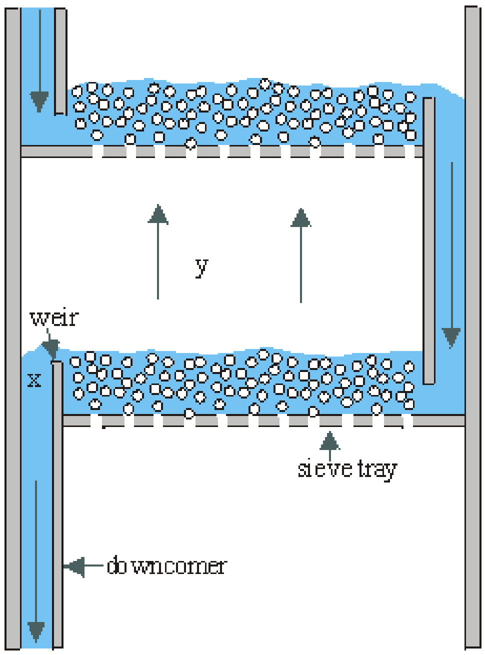
Introduction

Flash (or partial) evaporation

- Is the partial vaporization that occurs when a saturated liquid stream undergoes a reduction in pressure by passing through a throttling valve or other throttling device.
- This process is one of the simplest unit operations.
- If the throttling valve or device is located at the entry into a pressure vessel so that the flash evaporation occurs within the vessel, then the vessel is often referred to as a flash drum.

Introduction





The nature of equilibrium

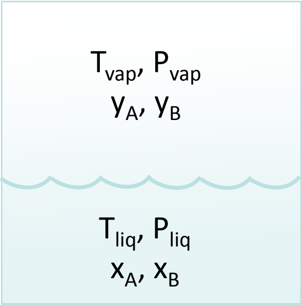
- Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time.
- This implies a balance of all potentials that may cause change.

Example

- An isolated system consisting of liquid and vapor phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system.
- The temperature, pressure, and phase compositions reach final values which thereafter remain fixed

Vapor-liquid equilibrium (VLE)

Consider a binary (i.e., 2-component) system with 2-phases:



What do we know?

$y_A + y_B = 1$ $x_A + x_B = 1$

$y_A \neq x_A$

At equilibrium: $T_{vap} = T_{liq}$
$P_{vap} = P_{liq}$

Gibbs' Phase Rule:

degrees of freedom = # components (C) - # phases (P) + 2

For a binary, 2-phase system: 2 – 2 + 2 = 2

We can specify only 2 intensive variables (all others are fixed, by VLE)

Phase Rule for Intensive Variables

- For a system of π phases and N species, the degree of freedom is:

$$F = 2 - \pi + N$$

  - # variables that must be specified to fix the intensive state of the system at equilibrium

Phase Rule Variables:

- The system is characterized by T, P and (N-1) mole fractions for each phase
  - Requires knowledge of 2 + (N-1)π variables

Phase Rule Equations:

- At equilibrium $\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\pi}$ for all N species
  - These relations provide (π-1)N equations

The difference is $F = 2 + (N-1)\pi - (\pi-1)N$

$= 2 - \pi + N$

- Phase rules gives the number of variables we need in order to determine the intensive state of a system at equilibrium

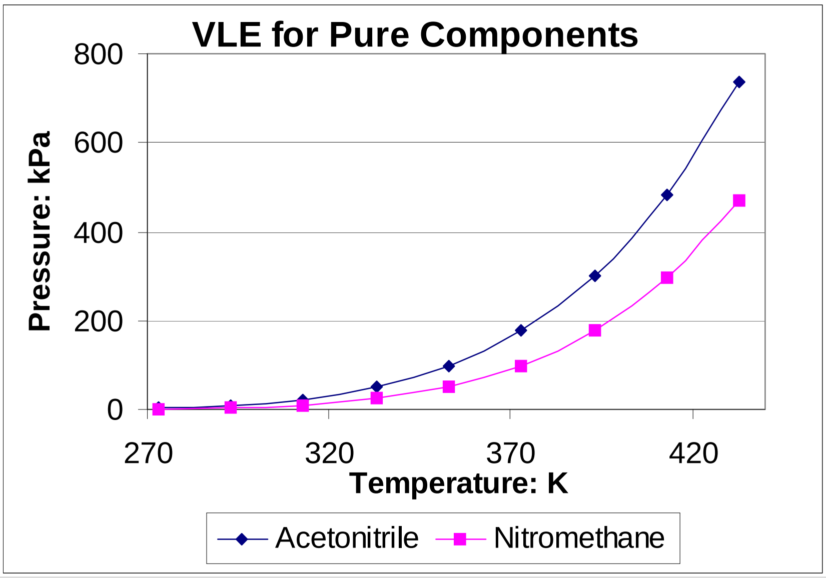
Phase Rule in VLE: Single Component Systems

- For a two phase (p=2) system of a single component (N=1):

$$F = 2 - \pi + N$$

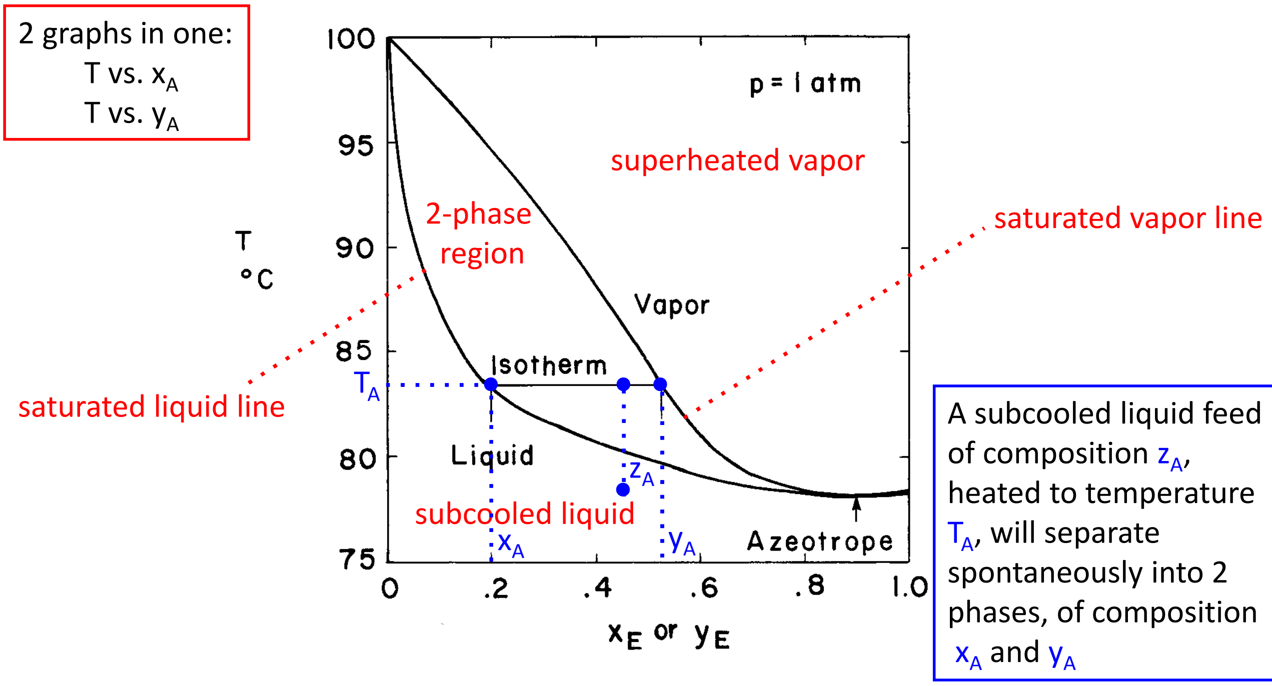
$$F = 2 - 2 + 1 = 1$$

- Therefore, for the single component system, specifying either T or P fixes all intensive variables.



Specify P and T

2 graphs in one:
T vs. x_A
T vs. y_A

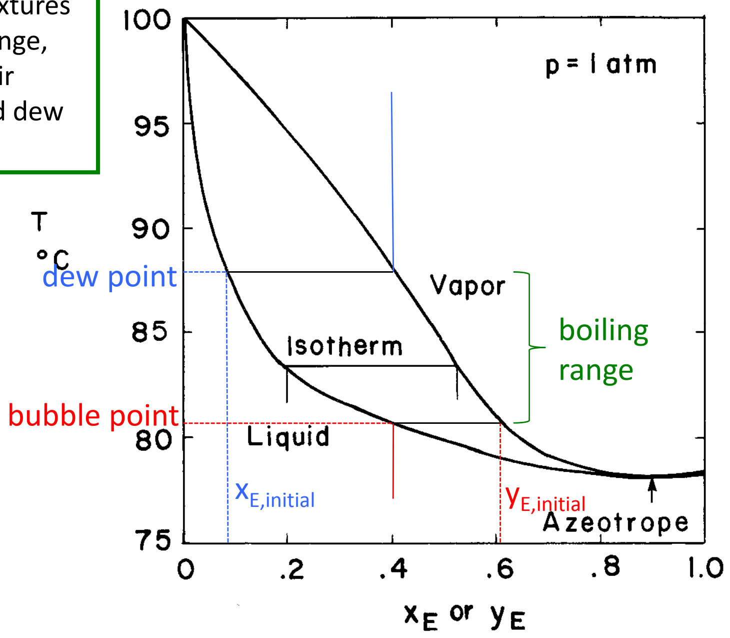


A subcooled liquid feed of composition z_A, heated to temperature T_A, will separate spontaneously into 2 phases, of composition x_A and y_A

Temperature-composition diagram for ethanol-water

Boiling point, dew point, bubble point

Pure liquids have a boiling point; mixtures have a boiling range, delimited by their bubble point and dew point.



1. Consider a sub-cooled binary liquid that is 40 mol% ethanol.
What is its bubble point?
What is the composition of the first bubble?

2. Consider a superheated binary vapor that is 40 mol% ethanol.
What is its dew point?
What is the composition of the first drop?

3. *What is the boiling range of this mixture?*

Figure 2-3 Temperature-composition diagram for ethanol-water1

Useful definitions

- Boiling/bubble point T_{bp}: temperature at which the average liquid molecule has just enough kinetic energy to escape from the surface of the liquid into the gas phase
  - Recall that kinetic energy follows a *Boltzmann distribution,* so molecules with higher than average kinetic energy can still escape from the surface at $T < T_{bp}$, by evaporation
- Saturated liquid: a liquid at its boiling/bubble point
- Dew point T_{dp}: temperature at which the average vapor molecule has just enough kinetic energy to condense
- Saturated vapor: a vapor at its dew point
- Vapor pressure: pressure at which the liquid and vapor phase are in equilibrium at a given temperature
- Azeotrope: a constant-boiling mixture, i.e., a mixture that behaves like a single component

Useful definitions

Saturated liquid and Subcooled liquid

- If a substance exists as a liquid at the saturation temperature, it is called a saturated liquid.
- If the temperature of the liquid is lower than the saturation temperature, it is called a subcooled liquid.

Saturated vapor and Superheated vapor

- If a substance exists entirely as vapor at the saturation temperature, it is called a saturated vapor.
- When the vapor is at a temperature greater than the saturation temperature, it is said to exist as superheated vapor.

Correlations for Vapor Pressures

Antoine Equation:

The Antoine equation may have slightly different forms:

$$\ln P_i^{sat} = A - \frac{B}{T + C}$$

where A, B, and C are experimentally derived parameters.

temperature and pressure are in the following units: T [=]°C and P^* [=] mm Hg.

- The Antoine equation is generally reasonably good over a moderate range of temperatures. It doesn't do very well near the critical poin

Correlations for Vapor Pressures

- P_i^{sat}, or the vapour pressure of component i, is commonly represented by Antoine Equation

$$\ln P_i^{sat} = A - \frac{B}{T + C}$$

- For acetonitrile (Component 1):

$$\ln P_1^{sat} / \text{kPa} = 14.2724 - \frac{2945.47}{T/°C + 224}$$

- For nitromethane (Component 2):

$$\ln P_2^{sat} / \text{kPa} = 14.2043 - \frac{2972.64}{T/°C + 209}$$

- These functions are the only component properties needed to characterize ideal VLE behaviour

Correlations for Vapor Pressures

DIPPR Correlation:

More accurate yet is the DIPPR correlation of vapor pressures:

$$\ln P^* = A + B/T + C\ln T + DT^E$$

where the constants A, B, C, D and E are contained in the DIPPR database for each compound.

- Ordinarily, $E = 6$. The DIPPR database also has a calculator package to do the interpolation at any desired temperature so that the coefficients don't need to be copied down.

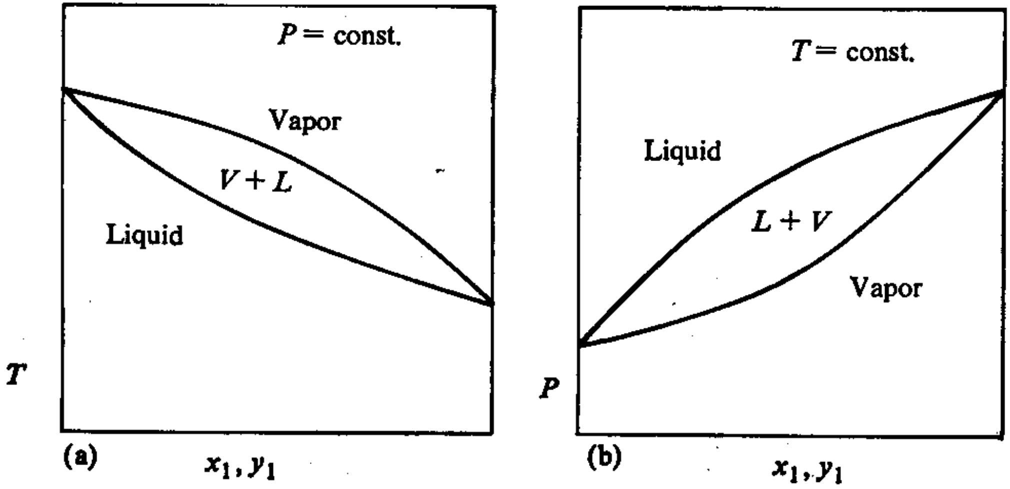
Phase Rule in VLE: Ideal Binary Mixtures

(General Case)

- For a two phase (π=2), binary system (N=2):

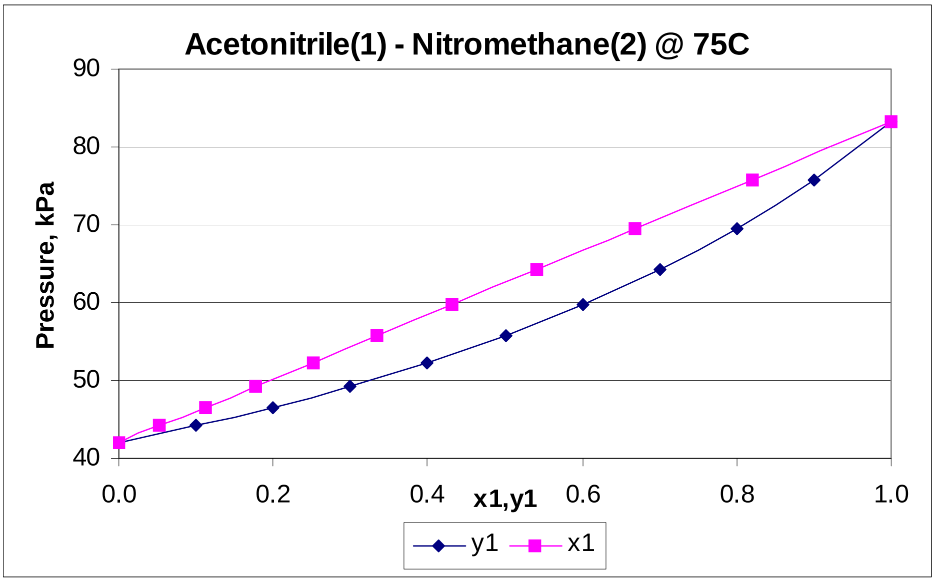
$$F = 2 - 2 + 2 = 2$$

- Therefore, for the binary case, two intensive variables must be specified to fix the state of the system.



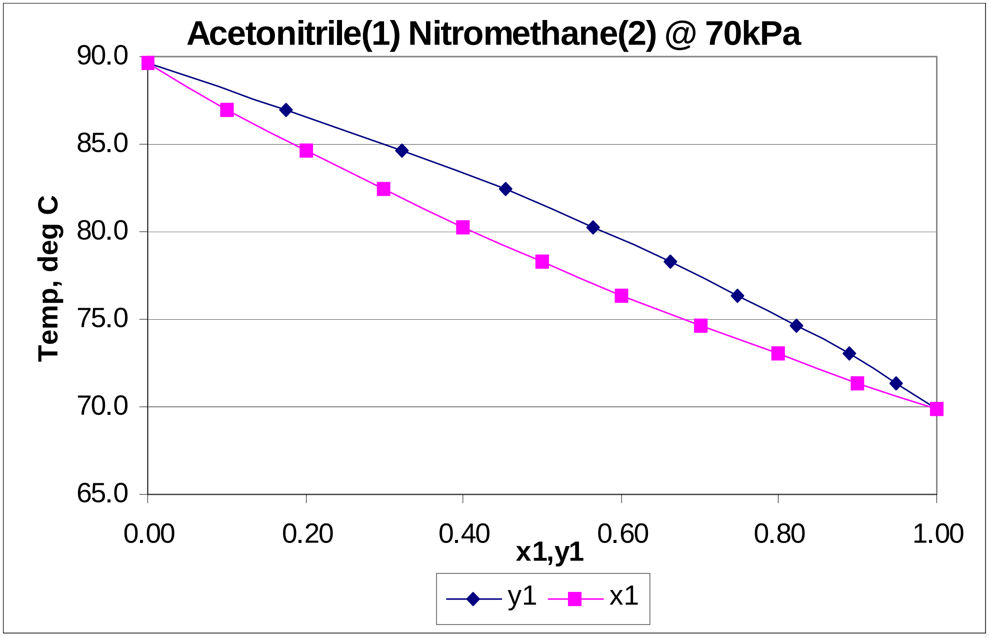
Phase Rule in VLE: Binary Systems (Pxy diagrams)

- Example: Acetonitrile (1) / Nitromethane (2) system

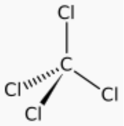


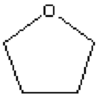
Phase Rule in VLE: Binary Systems (Txy diagrams)

- Alternatively, we can specify a system pressure and examine the VLE behavior as a function of temperature and composition.

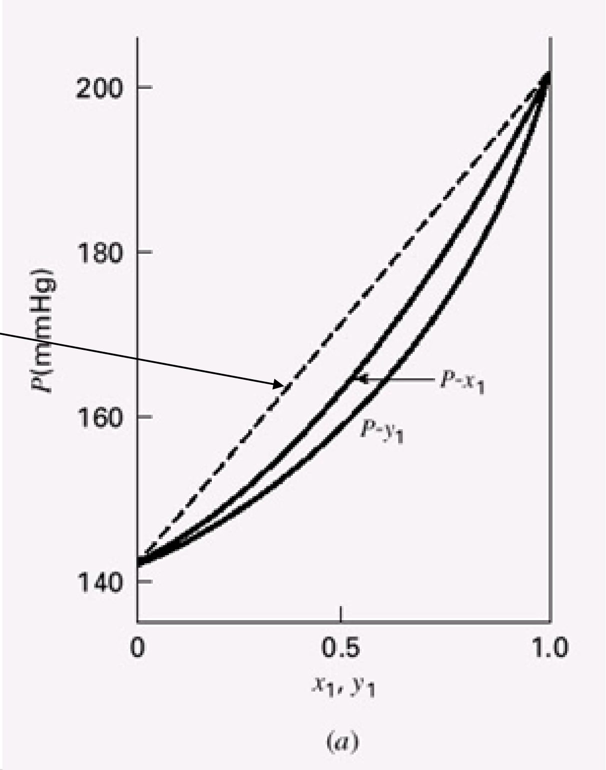


Tetrahydrofuran (THF) / Carbon tetrachloride

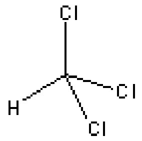


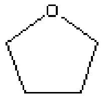


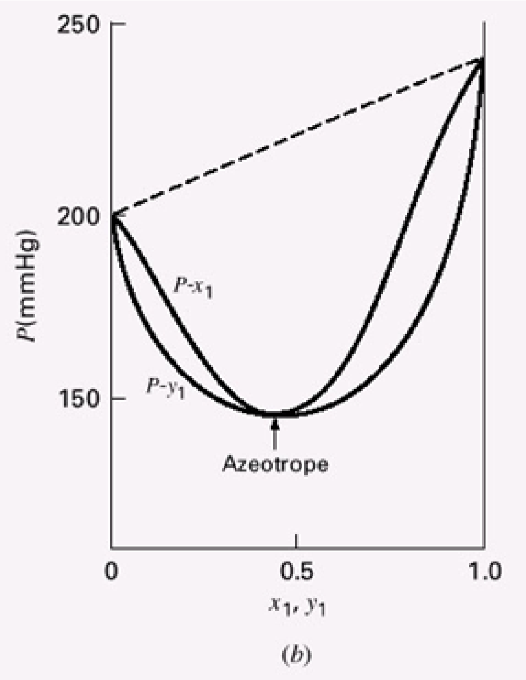
- ➢ **Negative deviation from Raoult's law (dotted line)**
- ➢ **Intermolecular (attractive) forces between**
- ➢ **unlike molecules are stronger than like molecules**
- ➢ **Unlike molecules like each other !**



Chloroform / Tetrahydrofuran







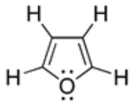
Minimum-pressure **or** ***negative*** **azeotrope**

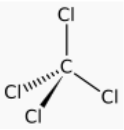
- **Strong negative deviation from Raoult's law due to hydrogen bonding**

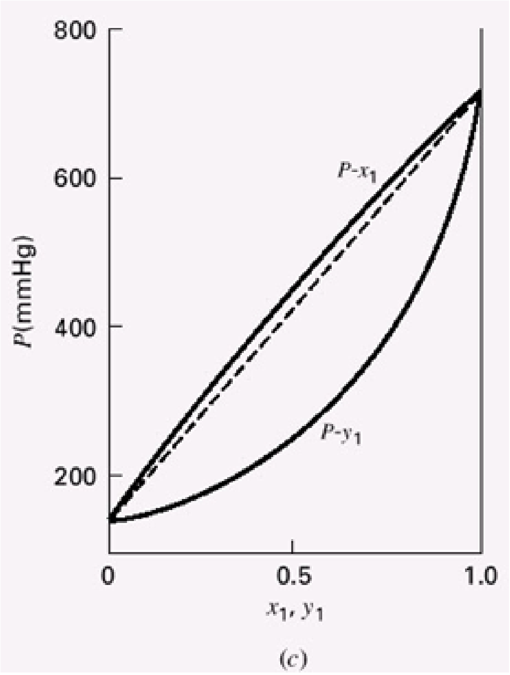
Azeotrope (constant boiling mixtures):

- **A boiling liquid at this composition produces a vapor of exactly the same composition**
- **No separation is possible by distillation at azeotropic composition diagram**

Furan / Carbon tetrachloride



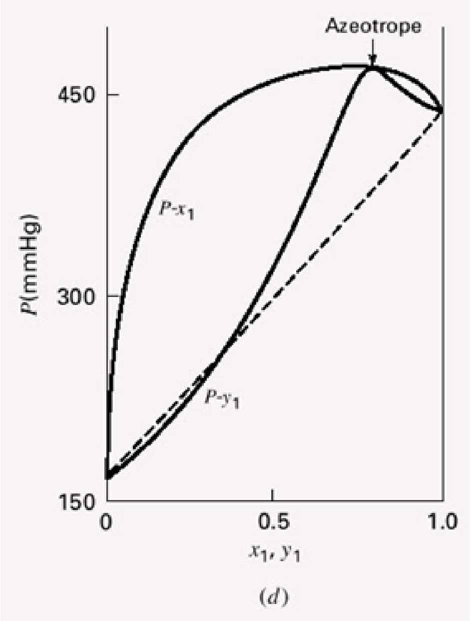




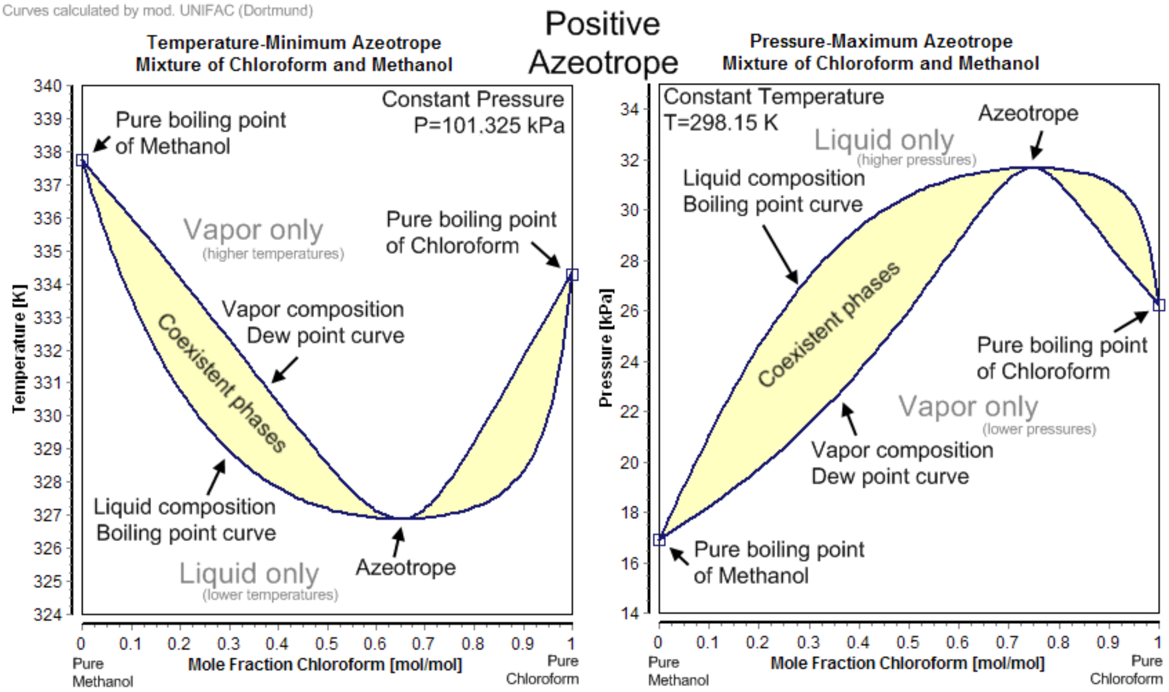
- **A slightly positive deviation**

Ethanol / toluene

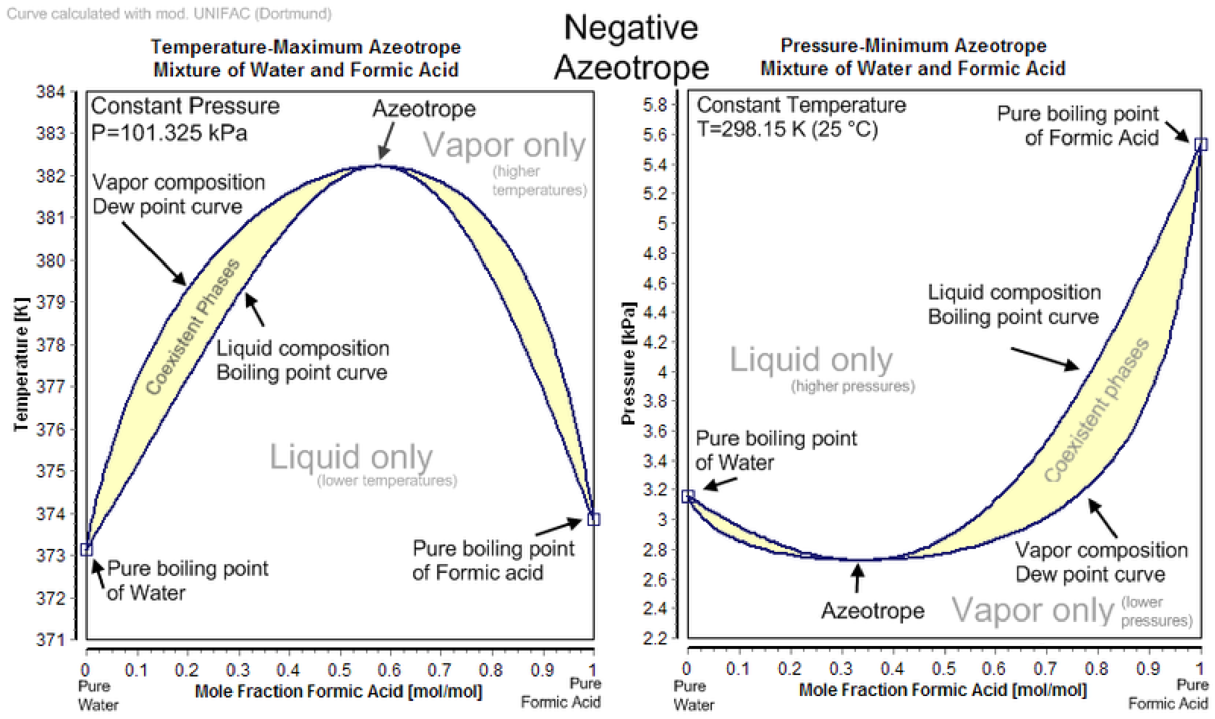
- Strong positive deviation with a maximum pressure azeotrope Intermolecular forces between like molecules are stronger than unlike molecules
- Unlike molecules don’t like each other !



Positive Azeotrope



Negative Azeotrope



Simple Models For VLE: Raoult's Law

- Applied to vapor/liquid equilibrium, to find by calculation the temperatures, pressures, and compositions of phases in equilibrium
- The two major assumptions are:
  - The vapor phase is an ideal gas.
  - The liquid phase is an ideal solution
- The first assumption means that Raoult's law can apply only for low to moderate pressures.
- The second implies that it can have approximate validity only when the species that comprise the system are chemically similar
- The ideal solution represents a standard to which real-solution behavior may be compared.
- Ideal-solution behavior is often approximated by liquid phases wherein the molecular species are not too different in size and are of the same chemical nature.

Simple Models For VLE: Raoult's Law

- Raoult’s Law for ideal phase behavior relates the composition of liquid and vapor phases at equilibrium through the component vapor pressure, P_i^{sat}.

$$\boxed{y_i P = x_i P_i^{\,sat} \qquad (i = 1, 2, \ldots, N)}$$

or

$$\frac{y_i}{x_i} = \frac{P_i^{sat}}{P}$$

- Where x_i is a liquid phase mole fraction, y_i is a vapor phase mole fraction, and P_i^{sat} is the vapor pressure of pure species *i* at the temperature of the system.
- The product $y_i P$ is known as the partial pressure of species *i*.
- If experimental data are not available, estimation of VLE can still be done.
- The simplest method assumes ideal vapor and ideal liquid phases.
- It is not very accurate for some mixtures, but is a good first approximation, and the only method that we will deal with in this introductory course.

Simple Models For VLE: Raoult's Law

- The Raoult’s law, simple model for VLE, provides a realistic description of actual behavior for a relatively small class of systems.
- Nevertheless, it is useful for displaying VLE calculations in their simplest form, and it also serves as a standard of comparison for more complex systems.
- A limitation of Raoult’s law is that it can be applied only to species of known vapor pressure, and this requires the species to be “subcritical,” i.e., to be at a temperature below its critical temperature.
- Raoult’s Law – feature for species with mole fraction approaching unity
  - An important and useful feature of Raoult’s law is that it is valid for any species present at a mole fraction approaching unity, i.e. one provided only that the vapor phase is an ideal gas.
  - Chemical similarity of the constituent species is not here a requirement.

Simple Models For VLE: Raoult's Law

- Raoult's Law can be applied to each component that distributes between the two phases in the system.
- For example, if we have a binary mixture of *A* and *B*, then we can write Raoult's Law for both components.
- If we do that and then add the two equations together, we obtain a convenient relationship between the liquid mole fractions and the total pressure:

$y_A P = x_A P_A^*(T)$ Raoult's Law for component A

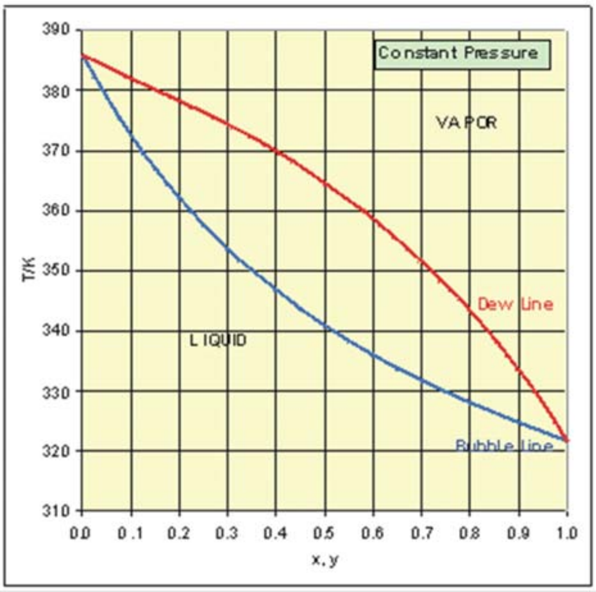
$y_B P = x_B P_B^*(T)$ Raoult's Law for component B

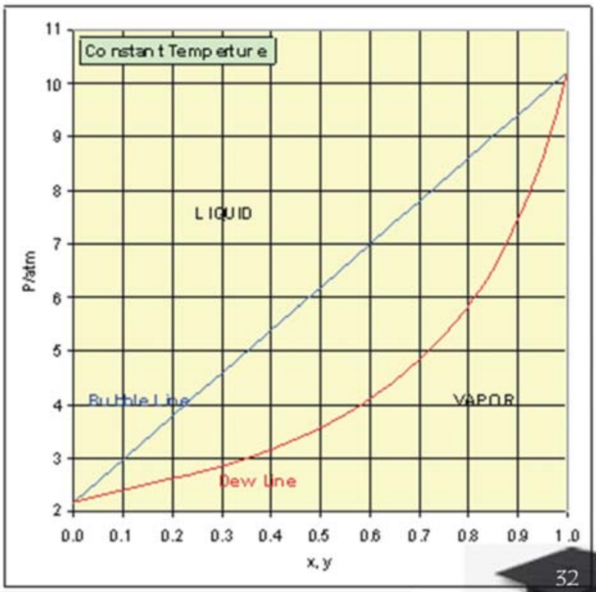
$P = x_A P_A^*(T) + (1 - x_A) P_B^*(T)$ **The above two equations added together**

where we have made use of the fact that $y_A + y_B = 1$ and $x_A + x_B = 1$.

Simple Models For VLE: Raoult's Law

- Raoult's law can be used to solve VLE problems in place of the *Txy* and *Pxy* diagrams or to generate *Txy* and *Pxy* .





Dew point and Bubble point Calculations

Dew Point Pressure:

Given a vapour composition at a specified temperature, find the composition of the liquid in equilibrium

Given T, $y_1, y_2, \dots y_n$ find P, $x_1, x_2, \dots x_n$

Dew Point Temperature:

Given a vapour composition at a specified pressure, find the composition of the liquid in equilibrium

Given P, $y_1, y_2, \dots y_n$ find T, $x_1, x_2, \dots x_n$

Bubble Point Pressure:

Given a liquid composition at a specified temperature, find the composition of the vapour in equilibrium

Given T, $x_1, x_2, \dots x_n$ find P, $y_1, y_2, \dots y_n$

Bubble Point Temperature:

Given a vapour composition at a specified pressure, find the composition of the liquid in equilibrium

Given P, $x_1, x_2, \dots x_n$ find T, $y_1, y_2, \dots y_n$

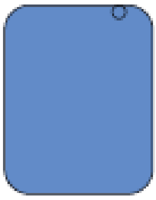
Dew point and Bubble point Calculations

BUBL P: Calculate $\{y_i\}$ and P, given $\{x_i\}$ and T

To calculate the P when the 1st bubble appear as a result of decrease in P at constant T. Also calculate the bubble's composition $\{y_i\}$.

or

To calculate the P when the last bubble disappear as a result of increase in P at constant T. Also calculate the composition $\{y_i\}$ of this bubble.

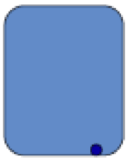


Dew point and Bubble point Calculations

DEW P: Calculate $\{x_i\}$ and P, given $\{y_i\}$ and T

To calculate the P when the 1st dew (a drop of liquid) appear as a result of increase in P at constant T. Also calculate the composition $\{x_i\}$ of this dew.

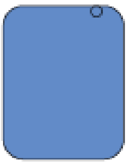
or



To calculate the P when the last dew disappear as a result of decrease in P at constant T. Also calculate the composition $\{x_i\}$ of this dew.

Dew point and Bubble point Calculations

BUBL T: Calculate $\{y_i\}$ and T, given $\{x_i\}$ and P



To calculate the T when the 1st bubble appear as a result of increase in T at constant P. Also calculate the composition $\{y_i\}$ of this bubble.

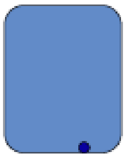
or

To calculate the T when the last bubble disappear as a result of decrease in T at constant P. Also calculate the composition $\{y_i\}$ of this bubble.

Dew point and Bubble point Calculations

DEW T: Calculate $\{x_i\}$ and T, given $\{y_i\}$ and P

To calculate the T when the 1st dew (a drop of liquid) appear as a result of decrease in T at constant P. Also calculate the composition $\{x_i\}$ of this dew.



or

To calculate the T when the last dew disappear as a result of increase in T at constant P. Also calculate the composition $\{x_i\}$ of this dew.

Dew point and Bubble point Calculations

- **For bubble point calculations**

$$\sum_i y_i = 1 \qquad \sum_i \left(x_i P_i^{sat} / P\right) = 1$$

$$P = \sum_i x_i P_i^{sat}$$

P-x **curve is linear to composition**

Characteristic of ideal solution

- For a binary system: $x_2 = 1 - x_1,$ $\quad P = P_2^{sat} + (P_1^{sat} - P_2^{sat})x_1$

For dew point calculations

$$\sum_i x_i = 1 \qquad \sum_i \left(y_i P / P_i^{sat}\right) = 1$$

$$P = \frac{1}{\sum_i y_i / P_i^{sat}}$$

VLE Calculations

- For now, we are going to employ these calculations only for identifying the state and composition of binary and ideal mixtures
- As we are going to see later in the course, the aforementioned VLE calculations are also applicable to non-ideal or/and multi-component mixtures
- The calculations revolve around the use of 2 key equations:

1) Raoult's law for ideal phase behaviour:

$$P_i = y_i * P = x_i * P_i^{sat} \qquad (1)$$

2) Antoine's Equation

$$ln(P_i^{sat}) = A_i - \frac{B_i}{T + C_i} \qquad (2)$$

BUBL P Calculation (T, x1 known)

- Calculate P_1^{sat} and P_2^{sat} from Antoine's Equation
- For the vapour-phase composition (bubble) we can write:

$$y_1 + y_2 = 1 \qquad (3)$$

- Substitute y_1 and y_2 in Eqn (3) by using Raoult's law:

$$\frac{x_1 * P_1^{sat}}{P} + \frac{x_2 * P_2^{sat}}{P} = \frac{x_1 * P_1^{sat}}{P} + \frac{(1 - x_1) * P_2^{sat}}{P} = 1 \qquad (4)$$

- Re-arrange and solve Eqn. (4) for P
- Now you can obtain y_1 from Eqn (1)
- Finally, $y_2 = 1 - y_1$

DEW P Calculation (T, y1 known)

- Calculate P_1^{sat} and P_2^{sat} from Antoine's Equation
- For the liquid-phase composition (dew) we can write:

$$x_1+x_2=1 \qquad (5)$$

- Substitute x_1 and x_2 in Eqn (5) by using Raoult's law:

$$\frac{y_1 * P}{P_1^{sat}} + \frac{y_2 * P}{P_2^{sat}} = \frac{y_1 * P}{P_1^{sat}} + \frac{(1-y_1) * P}{P_2^{sat}} = 1 \qquad (6)$$

- Re-arrange and solve Eqn. (6) for P
- Now you can obtain x_1 from Eqn (1)
- Finally, $x_2 = 1-x_1$

BUBL T Calculation (P, x1 known)

Since T is an unknown, the saturation pressures for the mixture components cannot be calculated directly. Therefore, calculation of T, y_1 requires an iterative approach, as follows:

- Re-arrange Antoine's equation so that the saturation temperatures of the components at pressure P can be calculated:

$$T_i^{sat} = \frac{B_i}{A_i - ln(P)} - C_i \qquad (7)$$

- Select a temperature T' so that $T_1^{sat} < T' < T_2^{sat}$
- Calculate $P_1^{sat}(T')$ and $P_2^{sat}(T')$
- Solve Eqn. (4) for pressure P'
- If $|P-P'| < \varepsilon$, then P'=P; If not, try another T'-value
- Calculate y_1 from Raoult's law

DEW T Calculation (P, y1 known)

Same as before, calculation of T, x_1 requires an iterative approach:

- Re-arrange Antoine's equation so that the saturation temperatures of the components at pressure P can be calculated from Eqn. (7):
- Select a temperature T' so that $T_1^{sat} < T' < T_2^{sat}$
- Calculate $P_1^{sat}(T')$ and $P_2^{sat}(T')$ from Antoine's Eqn.
- Solve Eqn. (6) for pressure P'
- If $|P - P'| < \varepsilon$, then P'=P; If not, try another T'-value
- Calculate x_1 from Raoult's law

P, T Flash Calculation

- Calculate P_1^{sat} and P_2^{sat} from Antoine's Equation
- Use Raoult's law in the following form:

$$\sum y_i = \frac{x_1 * P_1^{sat}}{P} + \frac{(1 - x_1) * P_2^{sat}}{P} = 1 \qquad (8)$$

- Re-arrange and solve Eqn. (8) for x_1
- Now you can obtain y_1 from Eqn (1), i.e.,

$$y_1 = \frac{x_1 * P_1^{sat}}{P}$$

Example

Bubble-Point Calculation: What is the composition of the initial vapor formed when a mixture of 40 mol% *n*-hexane and 60 mol% *n*-octane is heated to the bubble point at 121°C? At what pressure does this occur?

Example

- **Dew-Point Calculation:** What is the dew point pressure of a mixture containing 40 mol% *n*-pentane and 60 mol% *n*-hexane at 121°C and what is the composition of the first droplets of liquid that begin to condense?

Example

Assuming Raoult's Law to be valid, prepare

(a) a Pxy diagram for T=90°C, and

(b) a Txy diagram for P=90 kPa

for a mixture of 1-chlorobutane (1) /chlorobenzene (2)

Antoine Coefficients:

	A	B	C
1-chlorobutane (1)	13.9600	2826.26	224.10
Chlorobenzene (2)	13.9926	3295.12	217.55

Construction of Pxy diagrams

- The construction of Pxy diagram requires multiple P, T Flash calculations, where T is held constant and P is varied from P_2^{sat} to P_1^{sat}.
- The results can be tabulated as shown below:

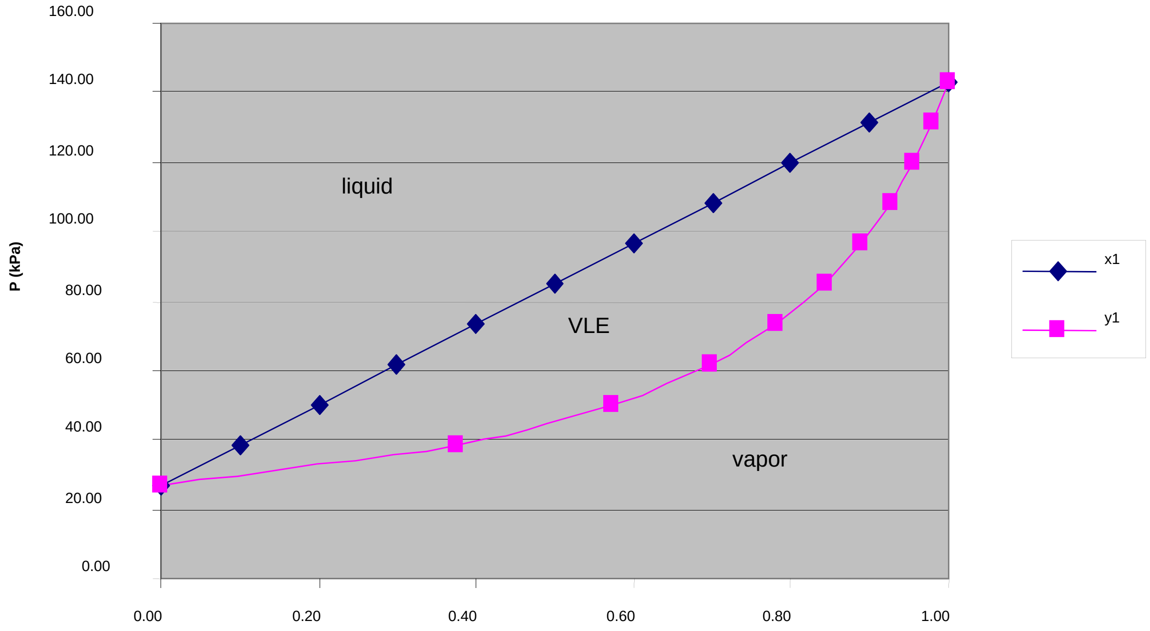
P (kPa)	$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$	$y_1 = \frac{x_1 * P_1^{sat}}{P}$
P_2^{sat}	0.0	0.0
…	…	…
P_1^{sat}	1.0	1.0

This type of calculations can also be performed by keeping T constant and varying x_1 or y_1 from 0.0 to 1.0

Example* – (a) Generation of Pxy Data

P1sat	142.88	kPa		
P2sat	26.54	kPa		
x1	**x2**	**P (kPa)**	**y1**	**y2**
0.00	1.00	26.54	0.00	1.00
0.10	0.90	38.17	0.37	0.63
0.20	0.80	49.81	0.57	0.43
0.30	0.70	61.44	0.70	0.30
0.40	0.60	73.08	0.78	0.22
0.50	0.50	84.71	0.84	0.16
0.60	0.40	96.34	0.89	0.11
0.70	0.30	107.98	0.93	0.07
0.80	0.20	119.61	0.96	0.04
0.90	0.10	131.25	0.98	0.02
1.00	0.00	142.88	1.00	0.00

Example – (a) Construction of a Pxy Plot



Construction of Txy diagrams

- The construction of Txy, diagram requires multiple P, T, Flash calculations, each one of which provides a set of equilibrium y1, x1 values for a given value of temperature (**at fixed P**) The results can be tabulated as shown below:

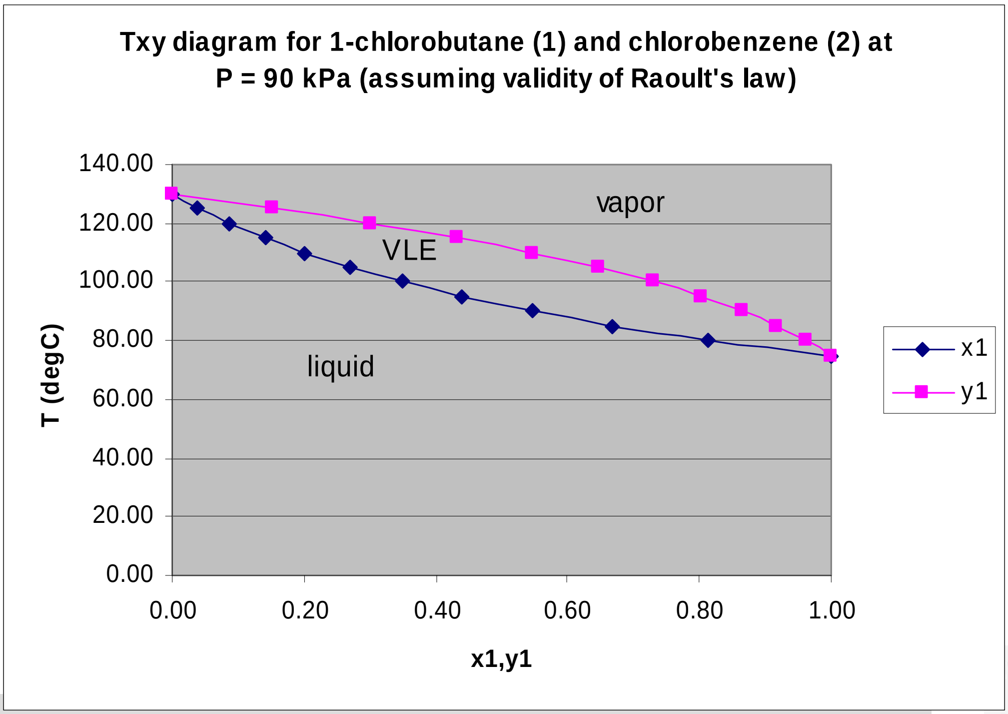
T (°C)	$x_1 = \frac{P - P_2^{sat}}{P_1^{sat} - P_2^{sat}}$	$y_1 = \frac{x_1 * P_1^{sat}}{P}$
T_2^{sat}	0	0
…	…	…
T_1^{sat}	1.0	1.0

- This type of calculations can also be performed by keeping P constant and varying x_1 or y_1 from 0.0 to 1.0

Example – (b) Generation of Txy Data

P	90.00	kPa		**A1**	13.96		**A2**	13.99
T1sat	74.65	degC		**B1**	2826.26		**B2**	3295.12
T2sat	129.57	degC		**C1**	224.10		**C2**	217.55
T (degC)	**P1sat**	**P2sat**	**x1**	**x2**	**y1**			
74.65	90.00	15.12	1.00	0.00	1.00			
80.00	106.29	18.51	0.81	0.19	0.96			
85.00	123.53	22.23	0.67	0.33	0.92			
90.00	142.88	26.54	0.55	0.45	0.87			
95.00	164.52	31.50	0.44	0.56	0.80			
100.00	188.61	37.18	0.35	0.65	0.73			
105.00	215.33	43.67	0.27	0.73	0.65			
110.00	244.86	51.04	0.20	0.80	0.55			
115.00	277.39	59.38	0.14	0.86	0.43			
120.00	313.10	68.77	0.09	0.91	0.30			
125.00	352.18	79.30	0.04	0.96	0.15			
129.57	391.01	90.00	0.00	1.00	0.00			

Example – (b) Construction of a Txy Plot


Txy diagram for 1-chlorobutane (1) and chlorobenzene (2) at P = 90 kPa (assuming validity of Raoult's law)

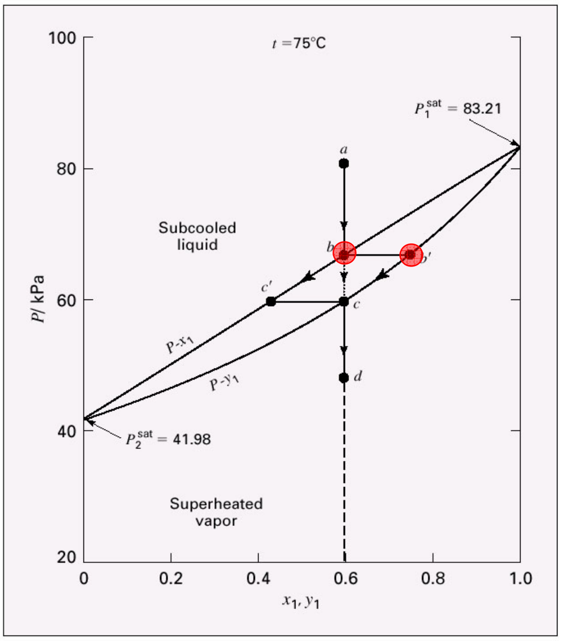
VLE Calculations - Summary

- Why? To completely identify the thermodynamic state of a mixture at equilibrium (single phase, 2 phases..?)
- How? Through the calculation of its P, T, and composition
  - The type of calculation that we need to perform is subject to the variables we are looking to evaluate
  - These calculations are classified as follows:

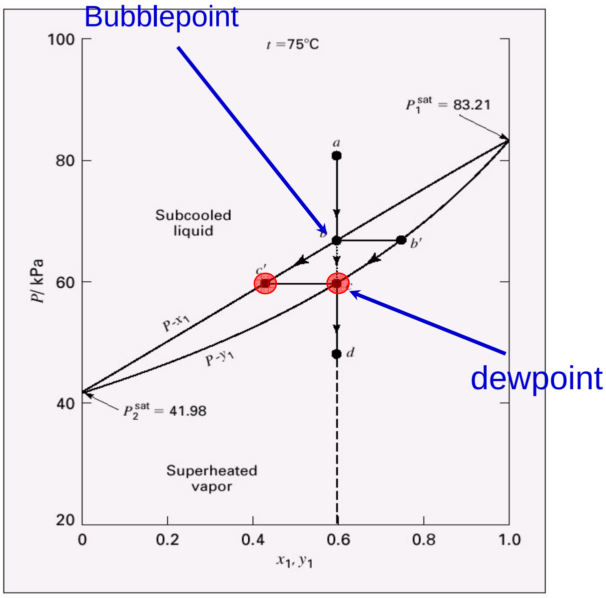
Specified/Known Variables	Unknown Variables	Calculation
T, x	**P, y**	**BUBL P**
T, y	**P, x**	**DEW P**
P, x	**T, y**	**BUBL T**
P, y	**T, x**	**DEW T**
P, T	**x, y**	**P, T Flash**

Example

Ex 10.1 acetonitrile (1) / nitromethane (2)



Example cont.



Example cont.

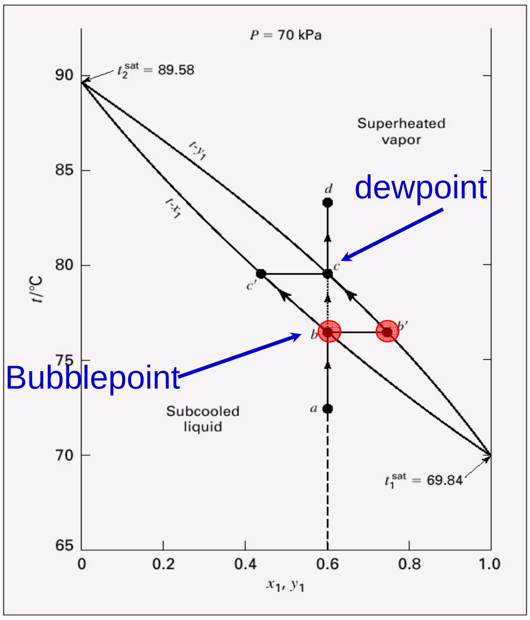
T-x-y **diagram**

BUBL T

For given *P*, $x_i \rightarrow T, y_i$

Since *T* is unknown, vapor pressures are also unknown.

Iterations are required.



Example cont.

Re-arrange Antoine's equation so that the saturation temperatures of the components at pressure P can be calculated:

$$T_i^{sat} = \frac{B_i}{A_i - ln(P)} - C_i \qquad (7)$$

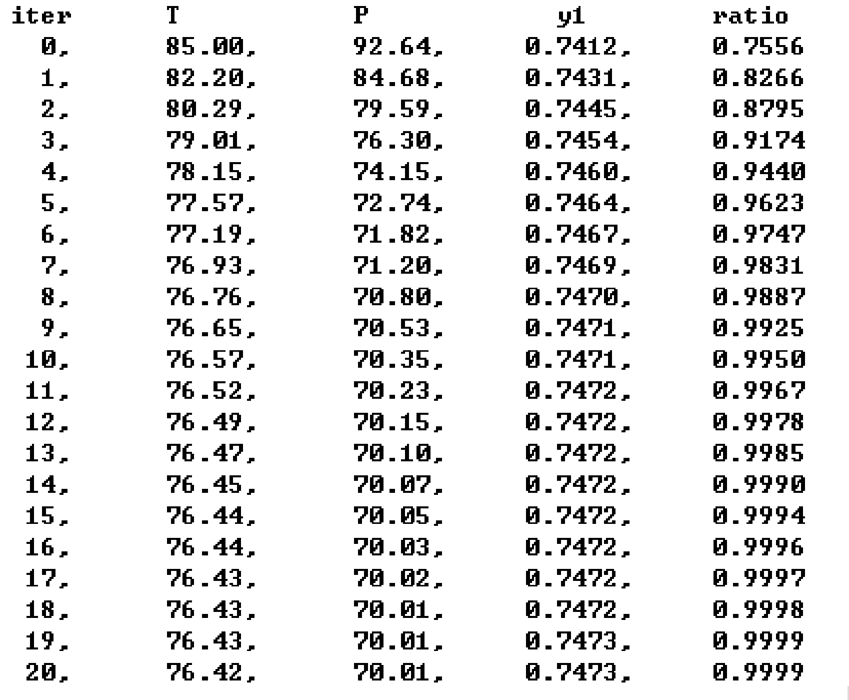
- Select a temperature T' so that $T_1^{sat} < T' < T_2^{sat}$
- Calculate $P_1^{sat}(T')$ and $P_2^{sat}(T')$
- Solve Eqn. (4) for pressure P'

$$\frac{x_1 * P_1^{sat}}{P} + \frac{x_2 * P_2^{sat}}{P} = \frac{x_1 * P_1^{sat}}{P} + \frac{(1-x_1) * P_2^{sat}}{P} = 1 \qquad (4)$$

- If $|P - P'| < \varepsilon$, then P'=P; If not, try another T'-value
- Calculate y_1 from Raoult's law

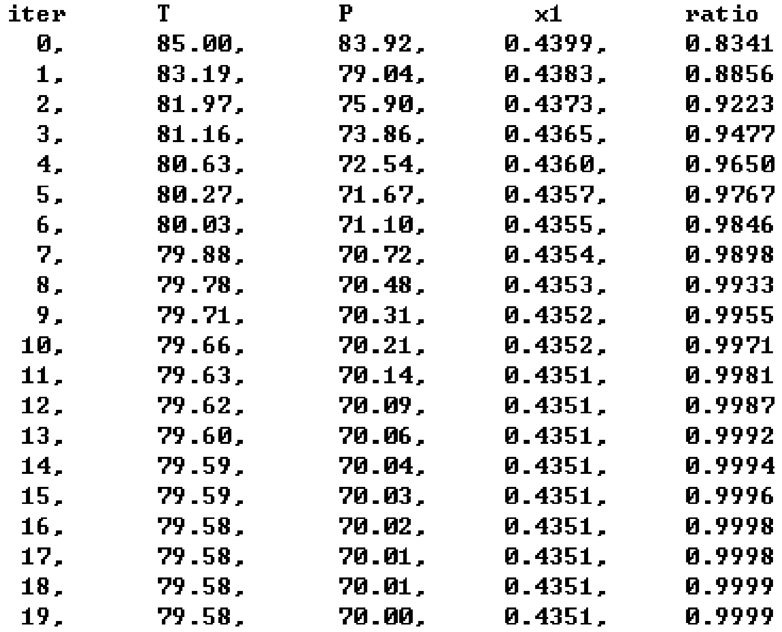
Example cont.

BUBL T results for P= 70 kPa, x_1 = 0.6



```
iter        T          P          y1        ratio
  0.      85.00.     92.64.    0.7412.     0.7556
  1.      82.20.     84.68.    0.7431.     0.8266
  2.      80.29.     79.59.    0.7445.     0.8795
  3.      79.01.     76.30.    0.7454.     0.9174
  4.      78.15.     74.15.    0.7460.     0.9440
  5.      77.57.     72.74.    0.7464.     0.9623
  6.      77.19.     71.82.    0.7467.     0.9747
  7.      76.93.     71.20.    0.7469.     0.9831
  8.      76.76.     70.80.    0.7470.     0.9887
  9.      76.65.     70.53.    0.7471.     0.9925
 10.      76.57.     70.35.    0.7471.     0.9950
 11.      76.52.     70.23.    0.7472.     0.9967
 12.      76.49.     70.15.    0.7472.     0.9978
 13.      76.47.     70.10.    0.7472.     0.9985
 14.      76.45.     70.07.    0.7472.     0.9990
 15.      76.44.     70.05.    0.7472.     0.9994
 16.      76.44.     70.03.    0.7472.     0.9996
 17.      76.43.     70.02.    0.7472.     0.9997
 18.      76.43.     70.01.    0.7472.     0.9998
 19.      76.43.     70.01.    0.7473.     0.9999
 20.      76.42.     70.01.    0.7473.     0.9999
```

DEW T results for P= 70 kPa, y_1 = 0.6



```
iter        T          P          x1        ratio
  0.      85.00.     83.92.    0.4399.     0.8341
  1.      83.19.     79.04.    0.4383.     0.8856
  2.      81.97.     75.90.    0.4373.     0.9223
  3.      81.16.     73.86.    0.4365.     0.9477
  4.      80.63.     72.54.    0.4360.     0.9650
  5.      80.27.     71.67.    0.4357.     0.9767
  6.      80.03.     71.10.    0.4355.     0.9846
  7.      79.88.     70.72.    0.4354.     0.9898
  8.      79.78.     70.48.    0.4353.     0.9933
  9.      79.71.     70.31.    0.4352.     0.9955
 10.      79.66.     70.21.    0.4352.     0.9971
 11.      79.63.     70.14.    0.4351.     0.9981
 12.      79.62.     70.09.    0.4351.     0.9987
 13.      79.60.     70.06.    0.4351.     0.9992
 14.      79.59.     70.04.    0.4351.     0.9994
 15.      79.59.     70.03.    0.4351.     0.9996
 16.      79.58.     70.02.    0.4351.     0.9998
 17.      79.58.     70.01.    0.4351.     0.9998
 18.      79.58.     70.01.    0.4351.     0.9999
 19.      79.58.     70.00.    0.4351.     0.9999
```