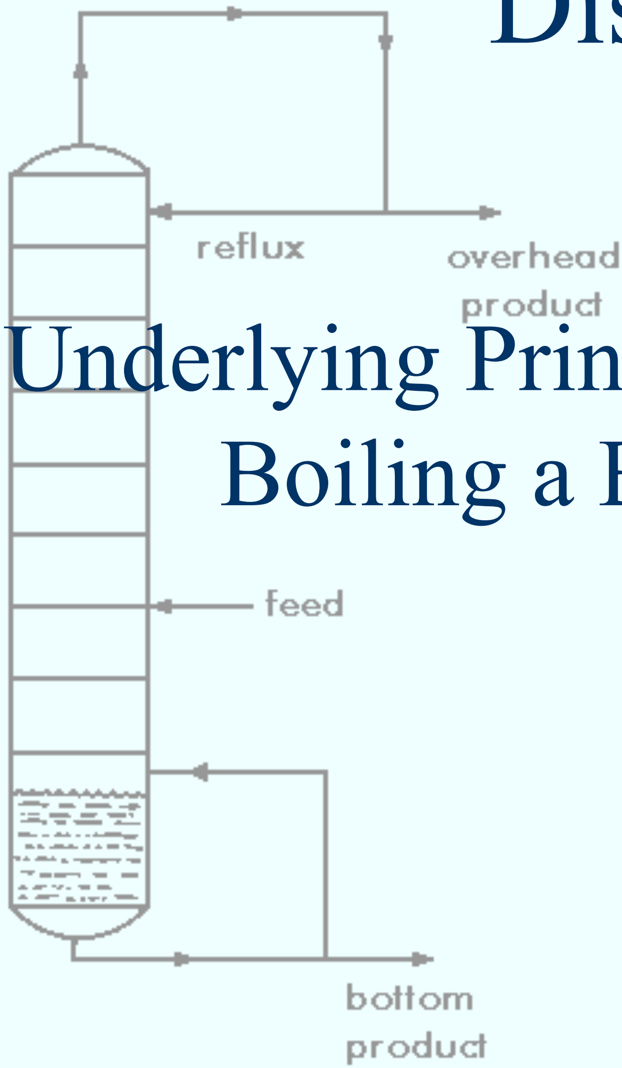
Distillation



Underlying Principles of Distillation

Boiling a Binary Mixture

Learning Outcomes

After this lecture you should be able to ….

- Explain boiling
- Understand the relationship between boiling point, vapour pressure and volatility
- Understand what happens when a binary mixture is boiled
- Understand what happens when a binary mixture is condensed
- Explain the Temperature-X-Y diagram
- Explain the X-Y diagram
- Define an azeotrope
- Develop an equilibrium curve

Vapour Pressure

Vapour pressure is the pressure exerted by the vapour - when dynamic equilibrium between vapour and liquid exists

Water in an open dish will slowly vaporise. Eventually the dish will be dry.

If the dish is sealed, water will still vaporise. However, vapour will condense at an equal rate – dynamic equilibrium

The pressure in the sealed dish is the vapour pressure.

Vapour pressure changes with temperature – it increases

Different substances have different vapour pressures

Boiling

Boiling occurs when the vapour pressure equals the surrounding atmospheric pressure

Water, at atmospheric pressure, will boil at 100 °C

Water, at a temperature of 82 °C, will boil if the pressure is reduced to 0.5 of an atmosphere.

Water, at a temperature of 25 °C, has a vapour pressure of 0.03 atmospheres

What is the VP of water at 50 °C
What is the boiling point of water at the top of Everest?

(Source for data: Table 2-5 in Perry)

Variation of atm pressure with height

- What is the atmospheric pressure at the top of Mount Everest?
- The following empirical formula can be used to calculate this pressure
- $P = P_o(1 + H.k/T_o)^{gM/-Rk}$
  - P_o = atmoshperic pressure (101,325 Pa)
  - g = acceleration due to gravity (9.81 m/s^2)
  - M = molecular weight of air (0.029 kg/mol)
  - R = universal gas constant (8.314 J/mol K)
  - H = height (m)
  - k = temp gradient over height = -0.0065 K/m
  - T_o = Temp at ground level (298 K)

- Aside - To calculate the temperature of air at this elevation so we use another empirical formula:
- $T = T_o + H.k$
  - T_o , H and k = same as above
  - Source – wikipedia.

Volatility

Liquids with high vapour pressures are said to be volatile. It is *the degree to which it tends to transfer from the liquid to vapour state*

Water, at a temperature of 25 °C, has a vapour pressure of 0.03 atmospheres

Methanol, at the same temperature, has a vapour pressure of 0.16 atmospheres

Methanol is more volatile than water => more likely to be found as vapour. Vapour pressure is a measure of volatility.

Methanol has a lower boiling point (65 °C) than water

Volatile liquids have low boiling points

Volatility = P_a/x_a (P_a = partial pressure, x_a = mole fraction)

Relative Volatility

Relative volatility is the ratio of the volatilities of two components

It indicates how easy or difficult a particular separation by distillation will be

P_a = partial pressure of MVC
x_a = mole fraction of a in the liquid
MVC = more volatile component

$$\alpha_{ab} = \frac{P_a / x_a}{P_b / x_b}$$

Relative Volatility

If α is equal to 1, separation is not possible

If α is close to 1, separation is difficult.

If α is large, separation is easy

α is a function of temperature. It can change throughout the column. It is fairly steady for most systems (see C&R Vol 6 p434 for more).

For example, for Benzene-Toluene, α rises as the temperature falls. Therefore, reduce the temperature to ease the separation. To reduce T, decrease the pressure in the column.

Activity – define basic terms

Think, pair, share the following concepts:

- Define vapour pressure
- What is volatility?
- When does a liquid boil?
- Explain why you can’t get a hot cup of tea at the top of Mount Everest!
- Why do pressure cookers cook food faster?

Binary Mixtures

Mix two components, e.g. Methanol and Water

b.p. of Meth = 65 °C, b.p. of H_2O = 100 °C

b.p. of mixture = somewhere in between (not always so!)

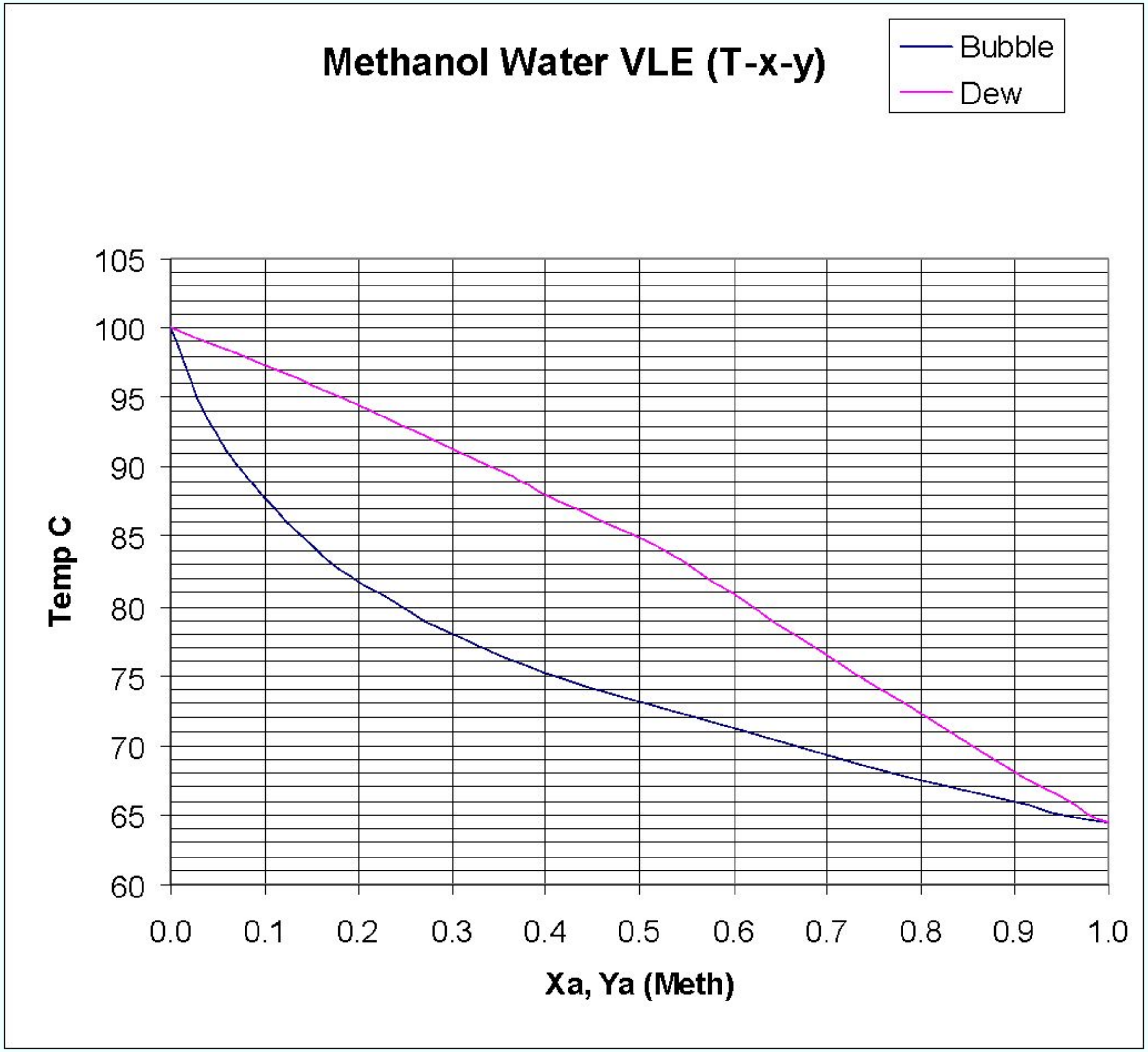
Boiling point of the mixture depends on the relative amounts of the two components present

A mixture containing 30% Meth, 70% H_2O has a b.p. of 78 °C. We call this the 'bubble point'.

The composition of this bubble is different to the composition of the liquid!

That's how distillation works!

A T-x-y Diagram – Meth H_2O



The T-x-y Diagram

Rules

The more volatile component (MVC) is labeled a

x is the liquid phase concentration and y is the vapour

x_a = mole fraction of a in liquid, etc.

Bubble point curve and Dew point curve are both shown

Bubble = Dew for pure components only

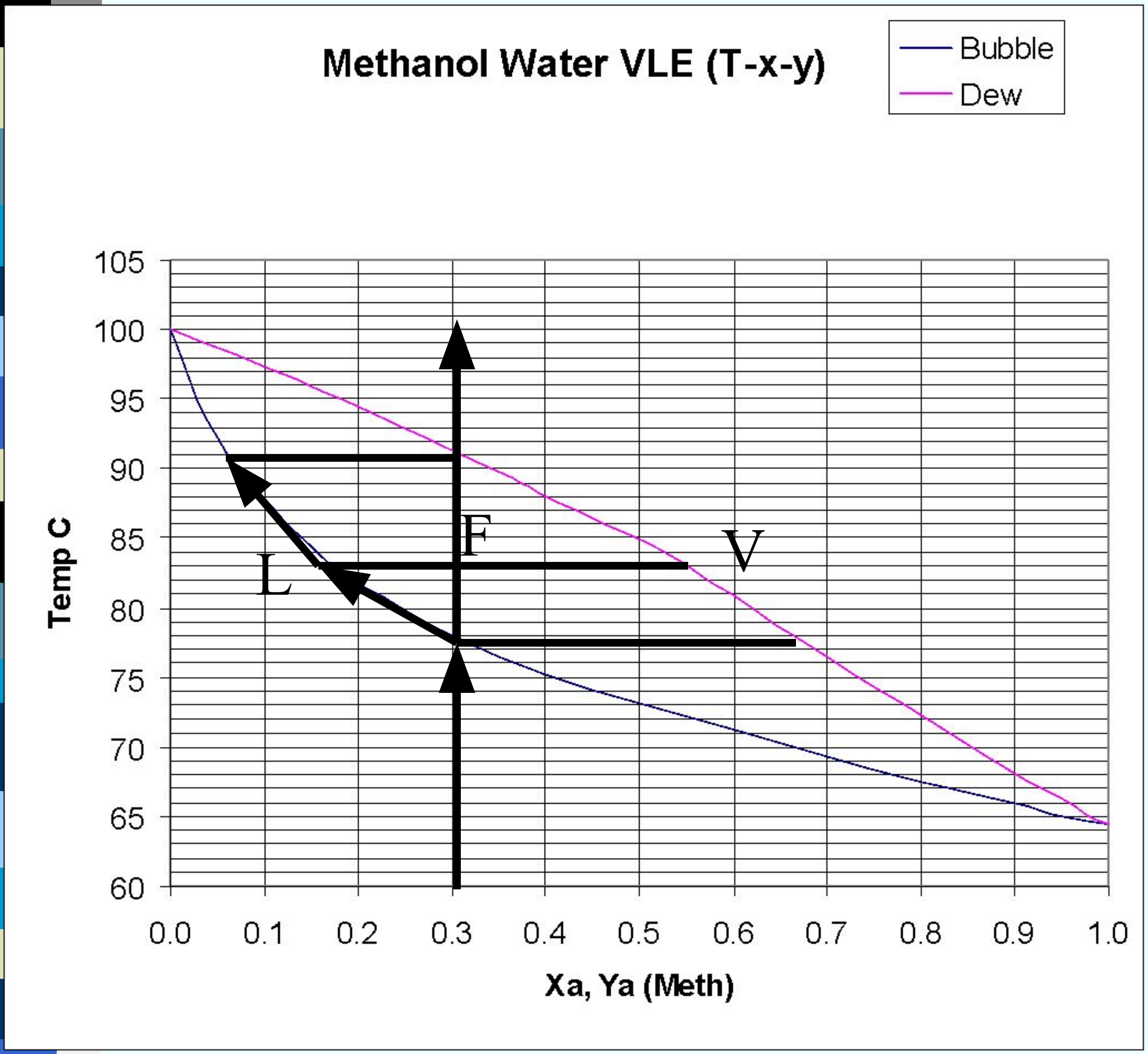
Subcooled liquid beneath bubble point curve

Super heated vapour above dew point curve

Both liquid and vapour phases exist in between

Would the diagram look different if the pressure was changed?

Boiling a Mixture – Methanol Water



Heat a 30%Meth 70%H_2O mixture so vapour can't escape but Pressure is constant

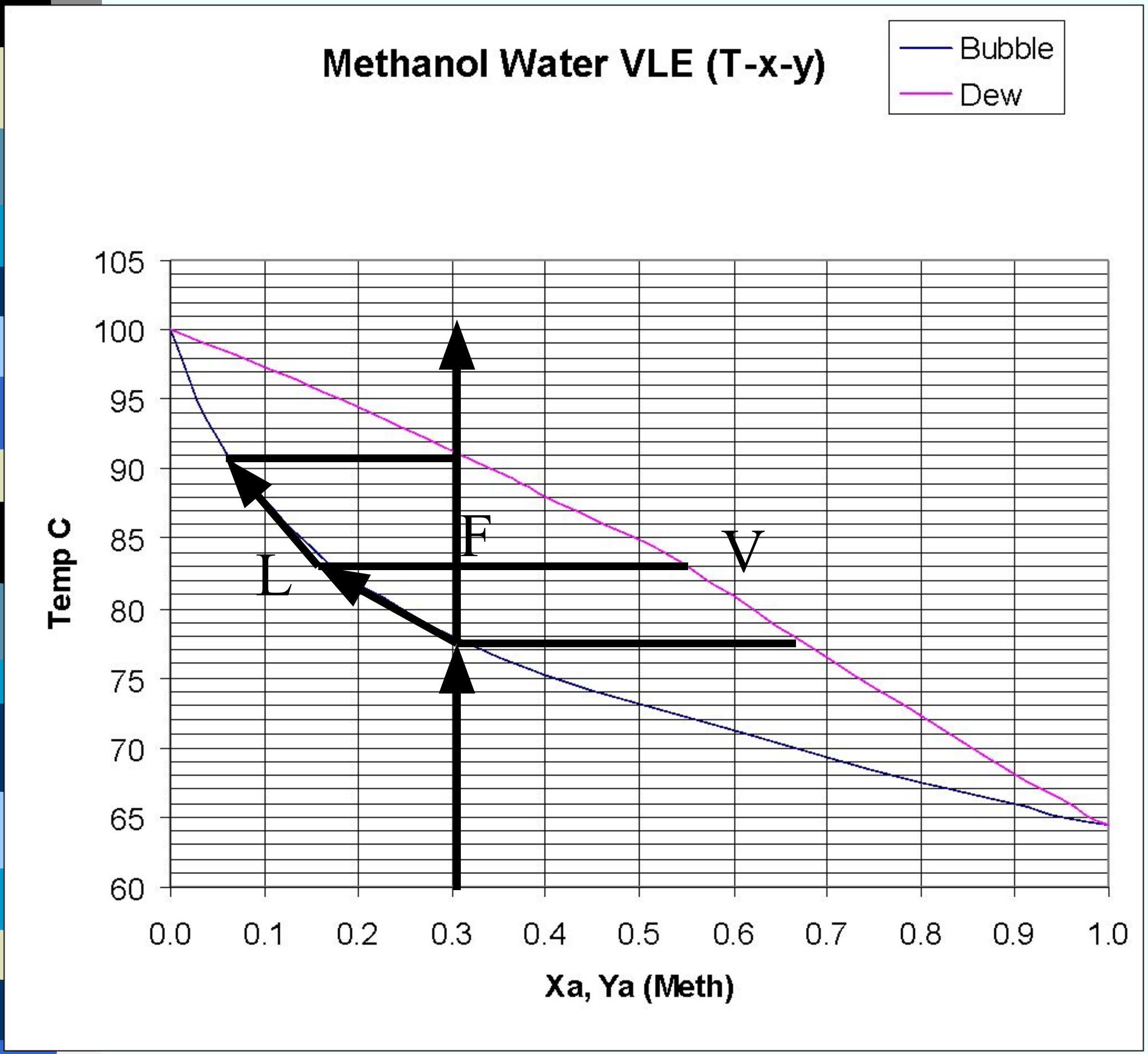
1st bubble of vapour formed at 78°C

Bubble composition is 65%Meth 35%H_2O

Liquid becomes less conc in Meth so BP increases

At 83°C liquid is 15% Meth, vapour is 55%

Boiling a Mixture contd



The relative amounts of liquid, vapour and feed are given by

$$\frac{Liquid}{Feed} = \frac{FV}{LV} = \frac{55-30}{55-15} = 62.5\%$$

$$\frac{Vapour}{Feed} = \frac{LF}{LV} = \frac{30-15}{55-15} = 37.5\%$$

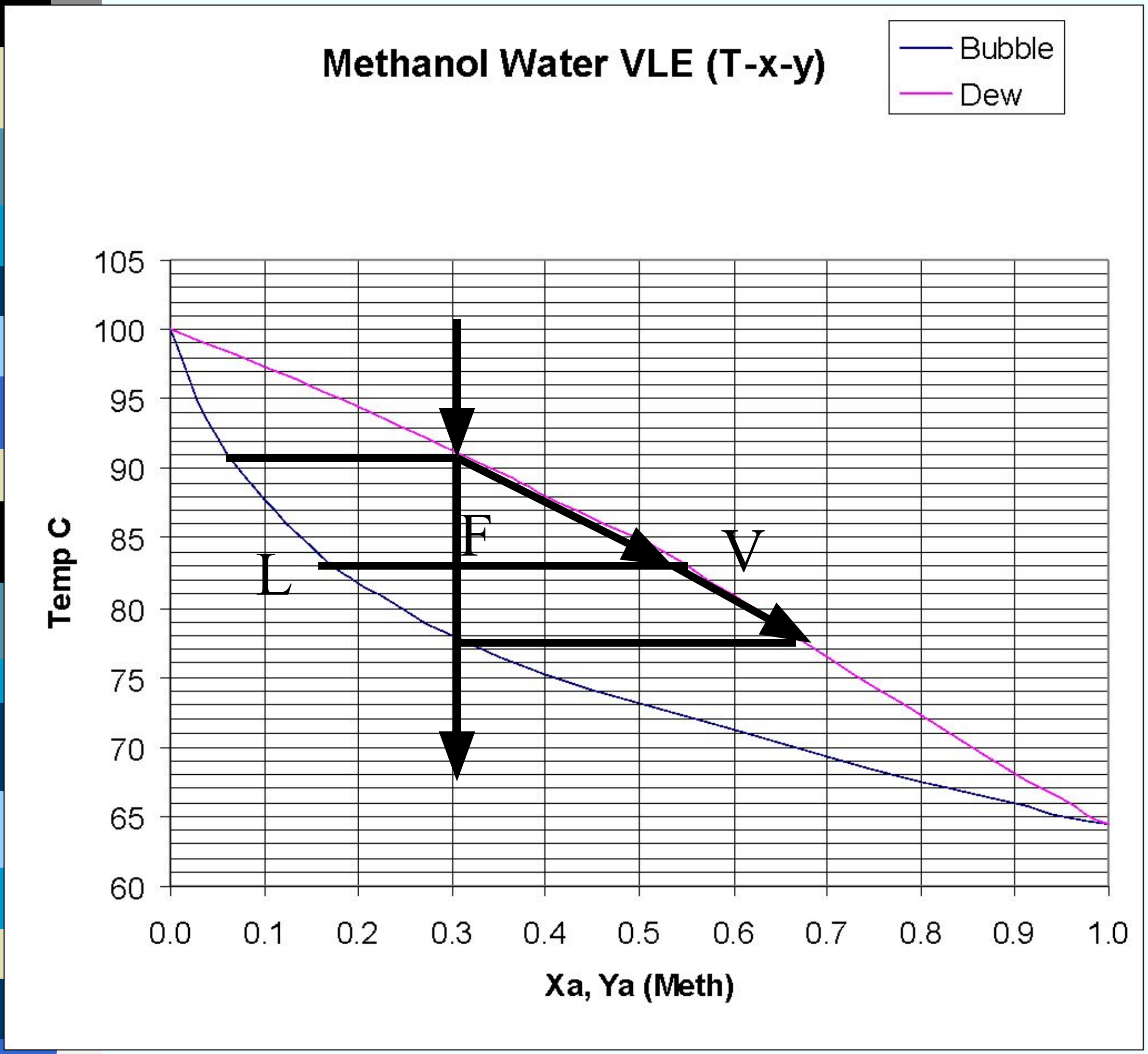
Liquid continues to boil

At 92 °C, conc of vapour is 30% Meth.

No liquid left

Super heated vapour

Condensing a Binary Mixture



Cool the super heated vapour, 30% Meth

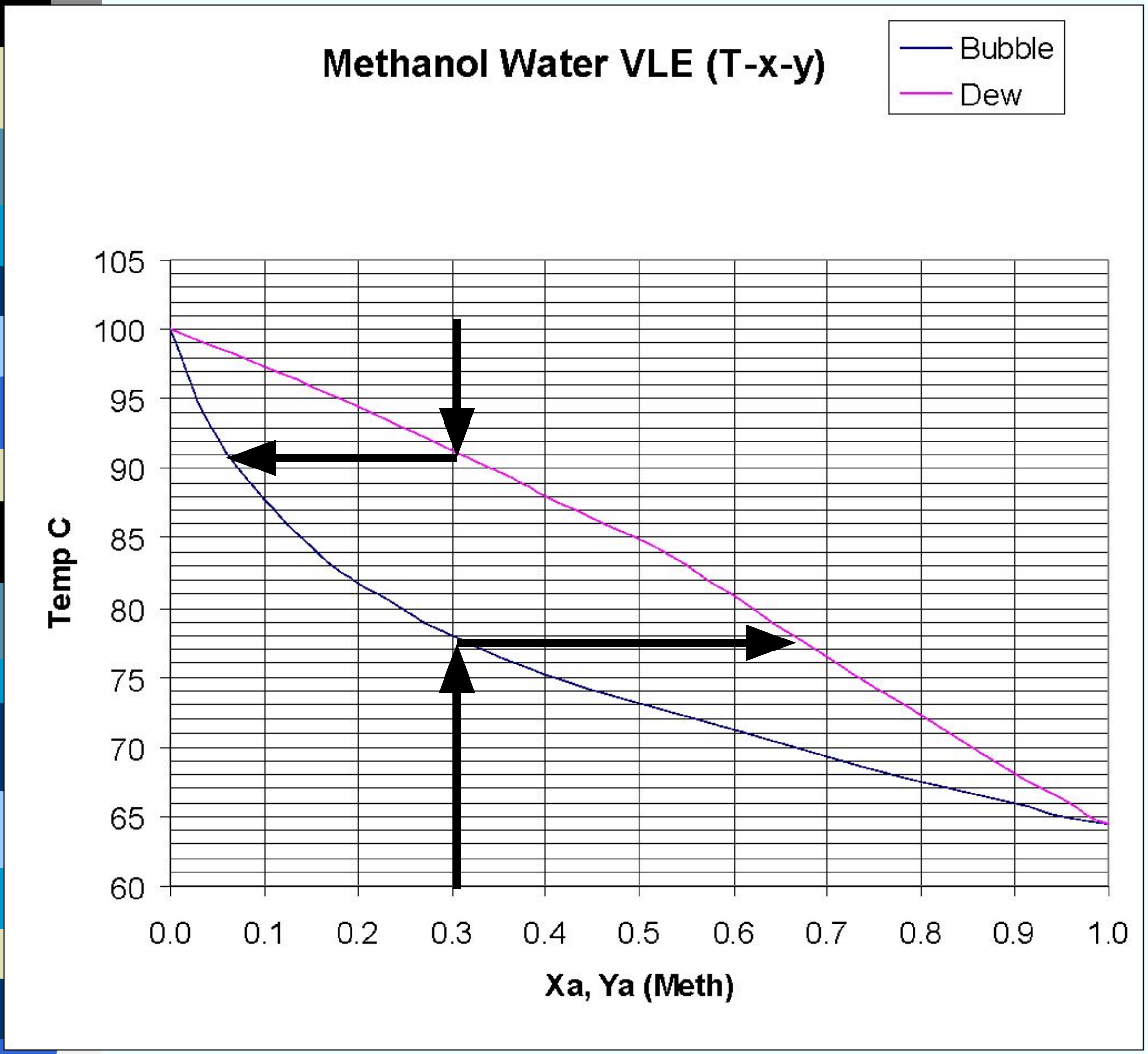
First droplet forms at the dew point - 92 °C

Drop composition = 5% Meth, 95% H_2O

Vapour becomes less conc in H_2O so dewpoint decreases

Eventually, at 78 °C, all vapour has condensed.

Distillation = Boiling AND Condensing



Heat the mixture - partial vaporisation

Vapour has higher Xa

Remove the vapour by condensation to give liquid of higher Xa

Cool superheated vapour - partial condensation

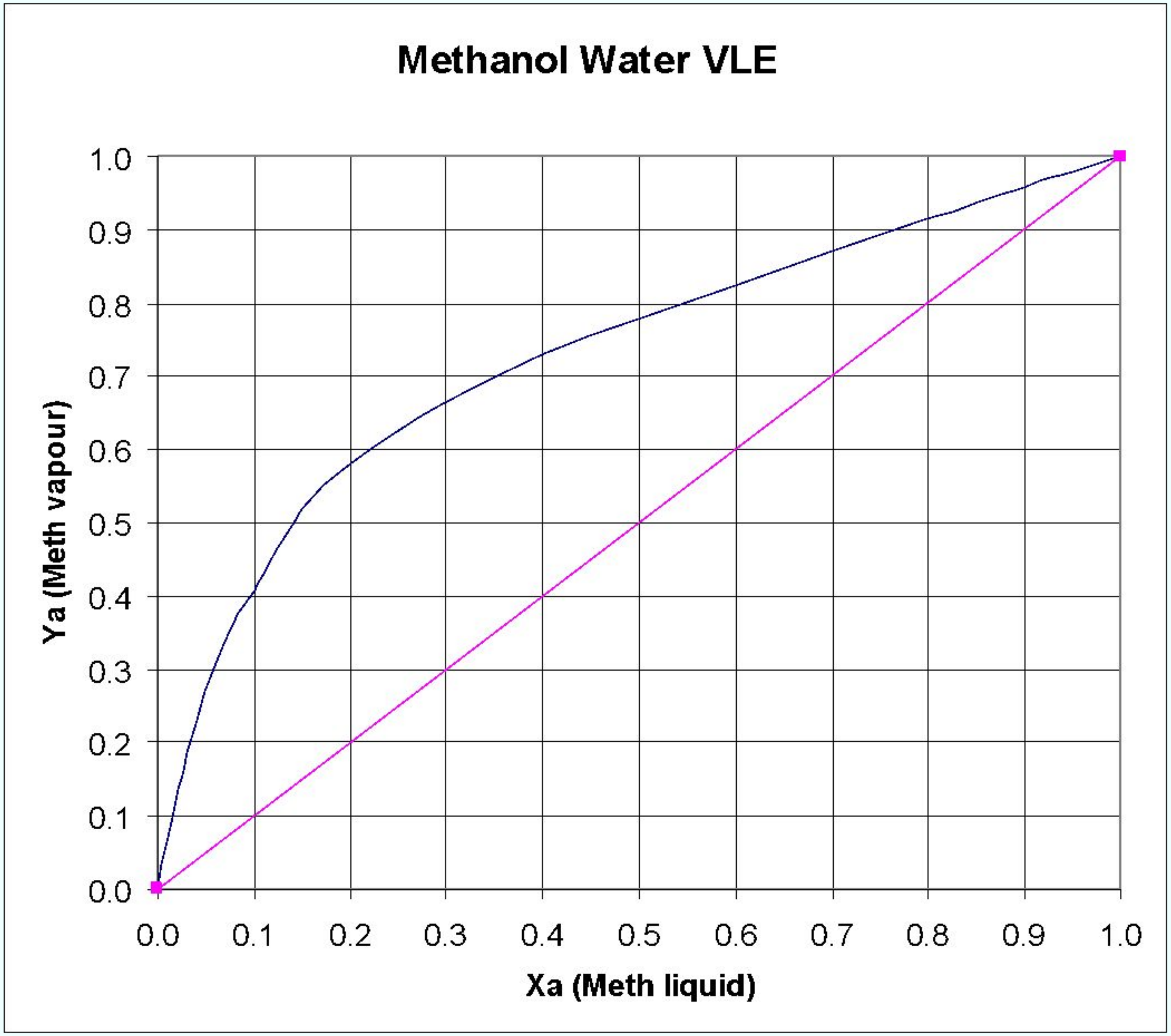
Liquid has lower Xa

Distillation column encourages repeated partial vaporisation and condensation throughout the column

The X-Y Diagram

- An alternative method of presenting Vapour Liquid Equilibrium (VLE) data
- Xa is plotted against Ya – usually a curve
- The X=Y line is also shown
- Data and plot are for a constant pressure only
- An easy way to estimate how many distillations are required to achieve a certain purity

An X-Y diagram – Meth H_2O



Activity – X-Y for Eth H_2O

Ethanol and Water are separated by distillation.

What does the X-Y curve for this binary mixture look like.

1. Find the T-x-y data. Try Perry (limited source for data)
2. Plot the curve on graph paper

Now, think about the following:

Fermentation gives an ethanol conc. of about 15 to 20%.
What happens when the mixture is boiled?