

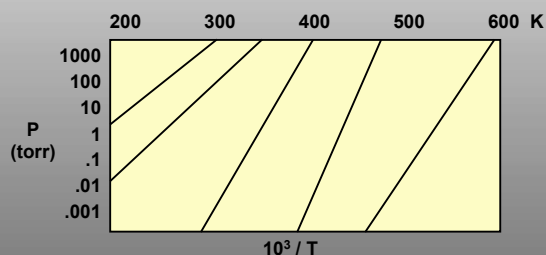
## Distillation

- A non-instrumental method of separation based on relative vapor pressures.
- One of the first separation methods.
- Significant approach for solvent preparation and purification.
- Not considered an analytical technique but theory relates to chromatographic methods.

## Distillation

### Basis of separation:

Variation in the saturation vapor pressure of a material versus temperature.



### Clausius-Clapeyron Equation

Gives the relationship between temperature and VP.

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

- R = 1.987 cal/mol K  
 $\Delta H_{vap}$  = enthalpy of vaporization  
 T = temperature, K  
 C = compound specific constant

Can be used to determine the  $\Delta H_{vap}$  from the P of a liquid at two temperatures.

## Trouton's rule

Trouton's rule can be used to estimate for the  $\Delta H_{vap}$ , so only the boiling point must be known.

$$\frac{\Delta H_{vap}}{T_b} \approx 23.3 \frac{\text{cal}}{\text{mol K}}$$

It yields a poor estimate for highly polar solvents. Works best for hydrocarbons.

## Trouton's rule example

An example of how accurate Trouton's rule using some known solvents.

Solvent	BP, °C	$\Delta H_{vap}$ , cal/mol
water	100	9717
methyl acetate	56.3	7270
n-heptane	98.43	7575

## Trouton's rule example

Solvent	$\Delta H_{vap}$ , cal/mol	
	estimated	actual
water	8694	9717
methyl acetate	7676	7270
n-heptane	8657	7575

Solvent	calculated constant	
water	26.04	(+11.8%)
methyl acetate	22.07	(-5.3%)
n-heptane	20.39	(-12.5%)

Only need to know the BP if you can accept 15% error.

## Raoult's law

Really concerned about separating components.

We need a way to deal with the vapor pressures of binary mixtures.

Raoult's law can be used.

$$P_A = X_A P_A^o$$

where  $P_A$  = vapor pressure of A in mixture  
 $X_A$  = mole fraction of A in liquid  
 $P_A^o$  = vapor pressure of pure A

## Raoult's law

When dealing with mixtures:

$$\frac{P_A}{P_B} = \frac{X_A P_A^o}{X_B P_B^o}$$

$$\frac{P_A}{P_B} = \frac{Y_A}{Y_B}$$

where Y = molar ratio of the vapors.

## Raoult's law

Each substance will have its own vapor pressure at any given temperature.

The molar ratio of A and B in the vapor phase can be defined by:

$$\frac{Y_A}{Y_B} = \alpha \frac{X_A}{X_B}$$

Relative amount of each vapor is a function of their VP at a specific temperature and the amount of each substance in the liquid phase.

where  $\alpha = P_A^o / P_B^o$

(relative volatility for an ideal solution)

## Raoult's law

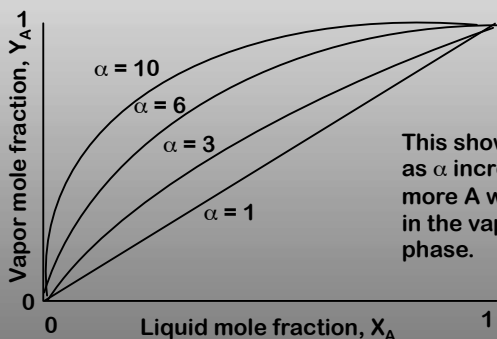
If A is always the more volatile of the two solvents, then  $\alpha > 1$ .

Therefore: 
$$\frac{Y_A}{1 - Y_A} = \alpha \frac{X_A}{1 - X_A}$$

Where 
$$X_B = 1 - X_A$$
$$Y_B = 1 - Y_A$$

We can plot  $Y_A$  as a function of  $X_A$  and  $\alpha$ .

## $Y_A$ vs $X_A$ for various $\alpha$ values



This shows that as  $\alpha$  increases, more A will be in the vapor phase.

## Raoult's law

Overall, if two solvents have different vapor pressures, we can enrich the more volatile component in the vapor phase.

As  $\alpha$  increases, the greater the degree of enrichment.

We still need a way to separate them and determine how effective the equipment must be.

## Basic distillation equipment

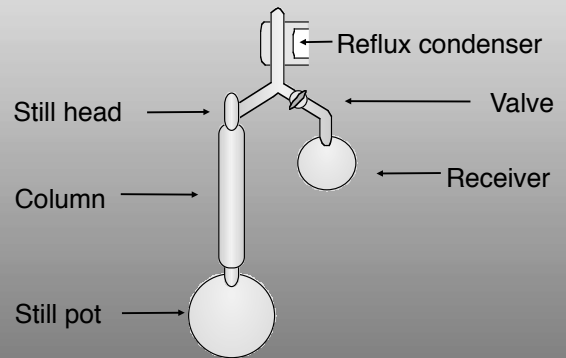
### Components

- Still pot with heat source
- Column
- Still head
- Receiver

The vapor is initially produced in the pot.

The separation occurs in the column.

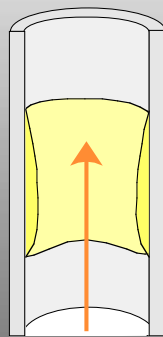
## Distillation Equipment



## The column

This is the heart of the distillation process.

The vapor will condense in a series of zones called plates. Each plate is an equilibrium between the gas and liquid phases.



## The still head

The head's function is to divide the condensate so a portion of the product can be removed (collected).

### Reflux ratio ( $R_D$ )

- the amount removed/amount returned.

If  $R_D$  is too high, you lose efficiency.

If  $R_D$  is too low, the separation could take forever.

## Estimation of plates ( $n$ ).

This can only be determined for conditions of **total reflux** - nothing is being removed.

We can estimate the  $n$  required for a 95 mole % separation of A for the first 40% of a distillation from:

$$n = \frac{2.85}{\log \alpha} = \frac{T_{bB} + T_{bA}}{3(T_{bB} - T_{bA})}$$

- useful for estimating the average number of plates during a distillation.

## Estimation of plates ( $n$ ).

If a distillation requires  $n$  plates, the column must have  $n-1$  plates. The last plate is the still head.

As  $\alpha$  increases, fewer plates are required.

$\alpha$  is not always known but can be estimated from the Clausius-Clapeyron Equation and Trouton's rule.

$$\log \alpha = 8.55 \frac{T_{bB} - T_{bA}}{T_{bB} + T_{bA}}$$

## Example

Calculate  $\alpha$  for n-hexane and n-heptane.

$$T_{BP} \text{ n-hexane} = 68.95 \text{ }^\circ\text{C}$$

$$T_{BP} \text{ n-heptane} = 98.42 \text{ }^\circ\text{C}$$

$$\log \alpha = 8.55 \frac{(371.56 - 372.12)}{(371.56 + 372.12)} = 0.3675$$

$$\alpha = 2.331$$

## Example

Now, determine the number of plates required to separate 95 mol % of n-hexane from n-heptane during the first 40% of the distillation and starting with a 1:1 mixture

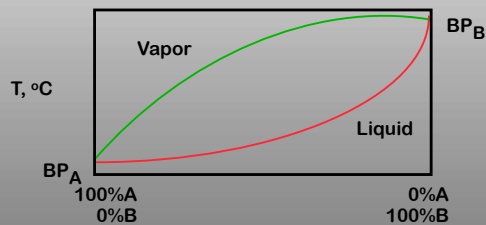
$$n = \frac{2.85}{\log \alpha} = \frac{2.85}{0.3675}$$

$$n = 7.75 = 8$$

You must always go to the next highest n.

## Boiling point changes - effect of composition

We can determine boiling point of a mixture by producing a plot of  $X_A$  vs  $Y_A$  and  $X_B$  vs  $Y_B$ .



## Variations of vapor concentration

Assume the following:

$$BP_A < BP_B$$

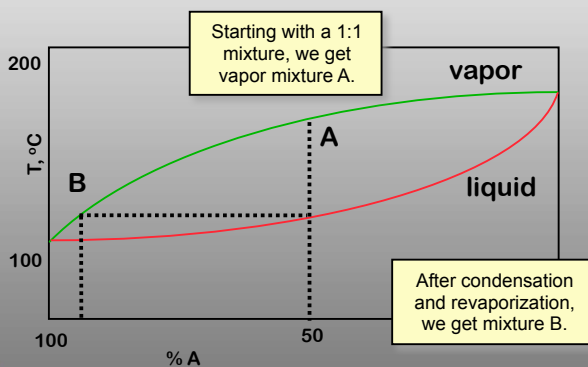
$$BP_A = 100 \text{ }^\circ\text{C}$$

$$BP_B = 200 \text{ }^\circ\text{C}$$

Start with a 1:1 mixture of A and B

We can use the  $X_A$  vs  $Y_A$  plot to determine the relative amounts of vapor for each material at any temperature.

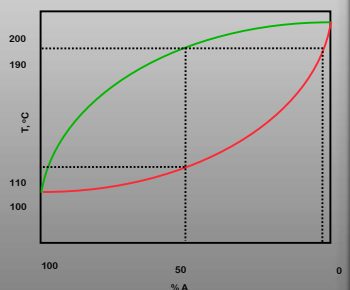
## Variations of vapor concentration



## Variations of vapor concentration

A vapor mixture produced at 190 °C would be 50% A and 50% B, or 1:1

After condensation and re-vaporization at 110 °C, the level of enrichment would be 95% A and 5% B or 19:1.



## Variations of vapor concentration

### During distillation:

A vapor mixture is initially produced in the pot and travels up into the column.

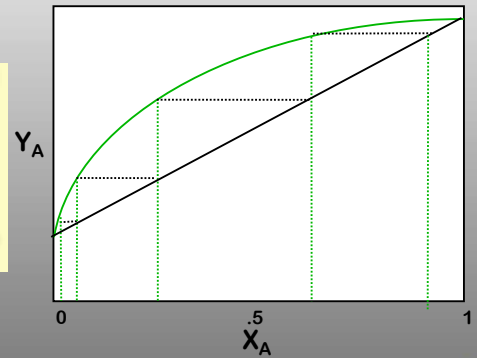
The vapor cools as it travels, causing some to condense (forming a plate).

As additional vapor travels up and reflux liquid travels down, the % A and B vary.

The relative concentration of A increases in the vapor as it travels up the column.

## Changes in concentration at each plate

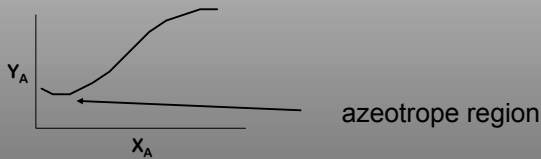
Each subsequent plate results in Further enrichment of A. We assume that the temperature of the column is decreasing as the vapor travels up.



## Some limitations.

These relationships all assume that you are dealing with an ideal solution. Non-ideal behavior such as azeotrope formation are not accounted for.

**Azeotrope** - stable mixtures that co-elute.



## More on distillation columns

For an adequate separation, the column must provide enough plates.

One way to measure its effectiveness is the height of a plate.

$$\text{plate height} = \frac{\text{column length}}{n}$$

If the height is too large, there may not be enough plates for a good separation

If its too small, the separation can take forever.

## Distillation columns

There are several types of columns available.

What you use should be based on:

- how many plates you need
- the type of through-put required

More commonly, it's based on:

- how patient you are
- what you have in the lab

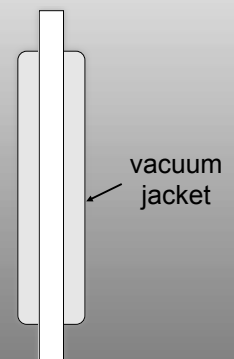
## Open tube column

Plates occur at contact between vapor and liquid drops.

Low cost and efficiency.

At ~10 ml/min throughput, plate height is ~80 cm.

ID = 6 mm

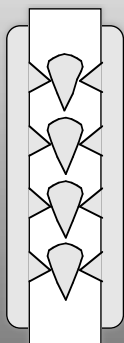


## Vigreux column

Increased contact with minimal back pressure.

At ~10 ml/min,  
plate height is ~ 12 cm

8 mm ID



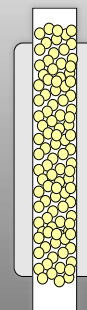
## Packed column

Open tubes can be packed with glass beads or helices.

There is increased contact and back pressure.

At ~10 ml/min,  
plate height is ~4 cm.

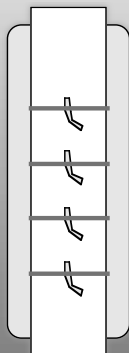
12 mm ID with 3 mm helices



## Oldershaw column

Vapor travels through perforated plates. Each is covered by a liquid layer.

If the liquid layer is > 1 mm,  
you can achieve a through-put  
of 50 ml/min with a plate height  
of 3.9 cm



## Key points

### Separation is based on:

- ✓ Variations in relative vapor as a function of mole fraction (**Raoult's law**)
- ✓ Existence of a temperature gradient in the column results in changes in relative concentration.
- ✓ Mobile phase is the more volatile solvent and the stationary phase is the less volatile solvent(s).
- ✓ Can't achieve 100% separation.
- ✓ Can only separate a single component.
- ✓ Not an analytical technique, although an important one.