



By the end of today's class you will be able to describe the process of distillation and use Raoult's Law to determine the composition of vapor above a given solution.

## RAOULT'S LAW AND DISTILLATION

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### Evaporation vs. Boiling?

**Evaporation:**

- at surface
- happens at T below boiling pt.
- higher vapour pressure
- will proceed until equilibrium in closed container

**Boiling:**

- throughout
- at boiling pt.
- vapour pressure = atm. pressure

http://phet.colorado.edu/en/simulation/evaporation-and-boiling

- air molecules dissolved in water come out

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### Distillation as a Separation Process

- Liquid is relatively pure to begin with (no more than 10% contaminants).
- Solution contains a non-volatile component.
- Boiling points of components differ by at least 70 °C.

http://phet.colorado.edu/en/simulation/distillation

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## Vapor Pressure of Solutions

- The presence of a dissolved solute lowers the vapor pressure of the solvent.

- Raoult's Law:

~~partial pressure of above solution~~

$$P_A = x_A P_A^\circ$$

~~mole fraction of component in solution~~

~~vapour pressure of pure const~~

- Applies to all volatile components of ideal solutions.

- Applies reasonably well to nonideal **dilute** solutions.

## Binary Solutions

### Liquid/Liquid Solutions

$$P = P_A + P_B = x_A P_{vap,A} + x_B P_{vap,B}$$

$$= x_A P_{vap,B} + (1-x_A) P_{vap,B}$$

### Liquid/Solid Solutions

$$P = P_{solid} + P_{liquid}$$

$$= x_{solid} P_{vap,solid} + x_{liquid} P_{vap,liquid}$$

$$= x_{liquid} P_{vap,liquid}$$

Since  $P_{vap,liquid} \gg P_{vap,solid}$

## Example 1

Benzene and toluene form a nearly ideal solution. The vapor pressures of pure benzene and pure toluene at 25 °C are 95.1 and 28.4 mmHg, respectively. A solution is prepared in which the mole fractions of benzene is 0.300.

What are the partial pressures of the benzene and toluene above this solution? What is the total vapor pressure?

What is the composition of the vapor in equilibrium with the benzene toluene solution?

$\gamma = \text{mole fraction in vapour}$

$$\gamma_{benzene} = \frac{28.5}{48.4} = 0.589$$

$$\gamma_{toluene} = 1 - 0.589 = 0.411$$

$$P_A = x_A P_{vap,A}^\circ$$

$$P_{benzene} = (0.300)(95.1) = 28.5 \text{ mmHg}$$

$$P_{toluene} = (0.700)(28.4) = 19.9 \text{ mmHg}$$

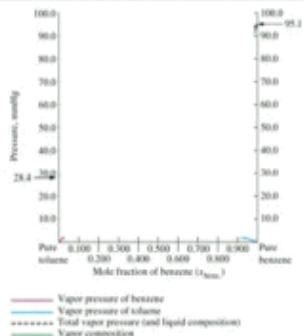
$$P_{tot} = 28.5 + 19.9$$

$$= 48.4$$

## Constructing a Vapor Pressure Diagram

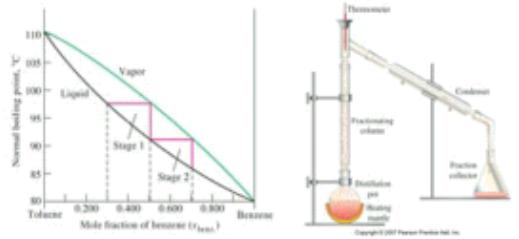
- Graph  $P_{\text{vap}}$  for benzene.
- Graph  $P_{\text{vap}}$  for toluene.
- Graph  $P_{\text{total}}$  by adding these two functions.
- Graph vapor composition by determining vapor composition at multiple pressures and connecting points.

Describe a case in which the liquid and vapour curves would converge into a single curve.

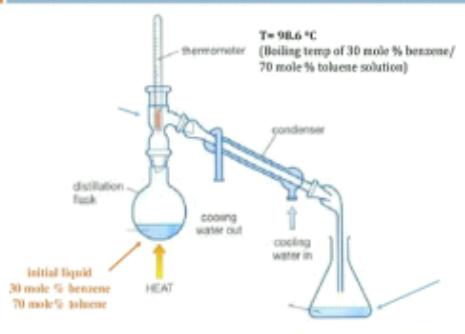


## Distillation

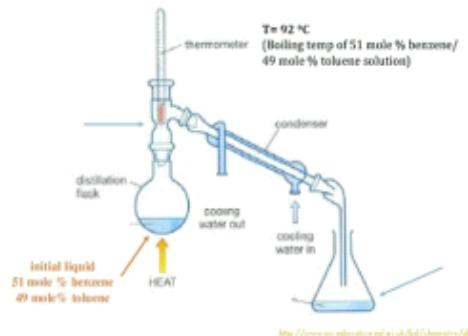
- The idea that vapor composition is different from liquid composition can be used to separate components in solution through **distillation**.



## Distillation Stage 1

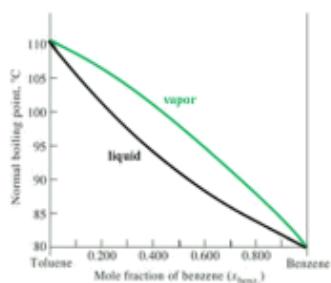


## Distillation Stage 2

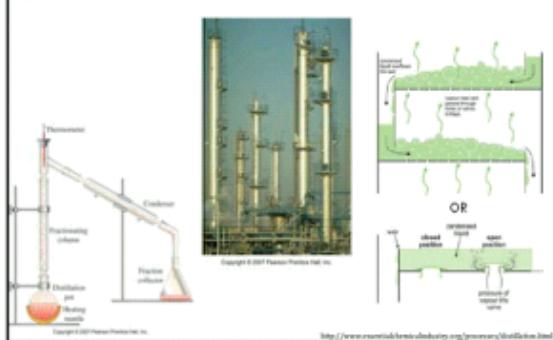


## Example 2

In theory how many stages are required to purify a liquid solution that is originally 0.100 mole % benzene to more than 0.800 mole % benzene?



## Fractional Distillation



### Example 3

Ethanol ( $C_2H_5OH$ ) and methanol ( $CH_3OH$ ) form a mainly ideal solution. At 20 °C, the vapor pressure of ethanol is 44.5 mmHg and that of methanol is 88.7 mmHg.

Calculate the partial pressures and the total vapor pressure of this solution and the mole fraction of ethanol in the vapour if  $n_{ethanol} = 1.3$  mol and  $n_{methanol} = 1.25$  mol.

Assume that you can condense the vapor phase alone. Calculate the vapor pressure of the condensed vapor phase and the mole fraction of ethanol in the vapor.

$$\gamma_{ethanol} = 22.7/66.2 = 0.34$$

$$\gamma_{methanol} = 0.66$$

$$\begin{aligned} n_{ethanol} &= 1.3 & P_{ethanol} &= 44.5 \text{ mmHg} \\ n_{methanol} &= 1.25 & P_{methanol} &= 88.7 \text{ mmHg} \\ x_{ethanol} &= \frac{1.3}{1.3+1.25} = 0.51 \\ x_{methanol} &= \frac{1.25}{1.3+1.25} = 0.49 \\ P_{ethanol} &= (0.51)(44.5) = 22.7 \\ P_{methanol} &= (0.49)(88.7) = 43.5 \\ P_{tot} &= 66.2 \text{ mmHg} \end{aligned}$$

### Suggested Readings

- 13.6 Vapor Pressures of Solutions

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