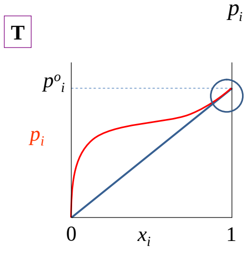
Binary Liquid-Vapor Phase Diagram

Tetrachloroethane-cyclohexanone
Binary System

Background:

Raoult's Law: At a *given temperature* for an *ideal* solution of miscible solvents the vapor pressure, p_i of a constituent i above the solution is *proportional* to the vapor pressure of the pure solvent p^o_i at the same temperature and is *scaled* by the mole fraction of the solvent, x_i of i in the solution.

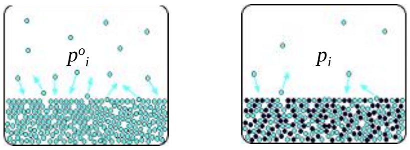
$$p_i = x_i P_i^o$$



For a binary mixture one component is considered the solvent (x_i larger) and the other is the solute.

Non-ideal solutions deviates from the Raoult's Law.

Ideal solutions are dilute solutions, practically.



Gas phase molecules of (only) *i* shown.

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions_and_Mixtures/Ideal_Solutions/Changes_In_Vapor_Pressure,_Raoult's_Law

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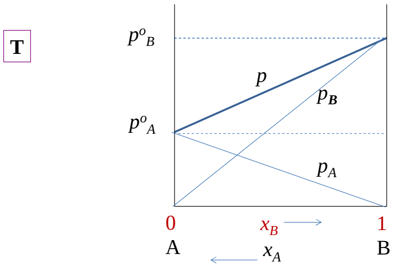
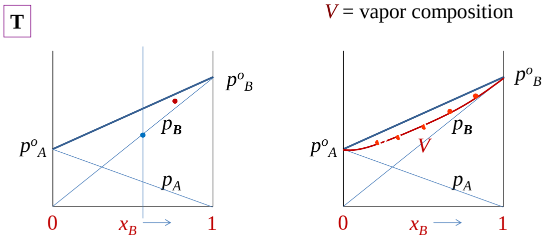
For a binary ideal single phase system *p (total v.p.)* and x_i's follows;

$$p = p_A + p_B$$

$$p_i = x_i P_i^o \qquad p = x_A\, p^o_A + x_B\, p^o_B$$



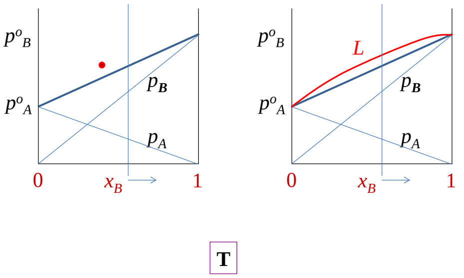
For a binary solutions for mole fractions are not closer to unity of a component could be different than that predicted by Raoult's Law. *If actual* p_B > *ideal* p_B (predicted), it is termed a *positive deviation*. The composition of B in vapor phase is greater than x_B.

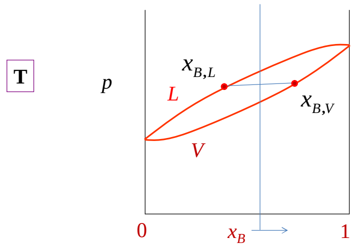


V = vapor composition

The composition of B in the liquid phase has to be less than the starting x_B.

L = liquid composition





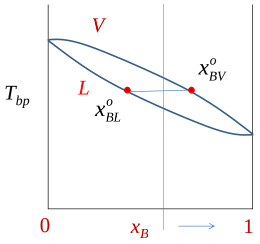
$x_{B,V}$ $x_{B,L}$ mole fractions of B at equilibrium in vapor and liquid phases

If the temperature is increased the pressure of both components would increase.

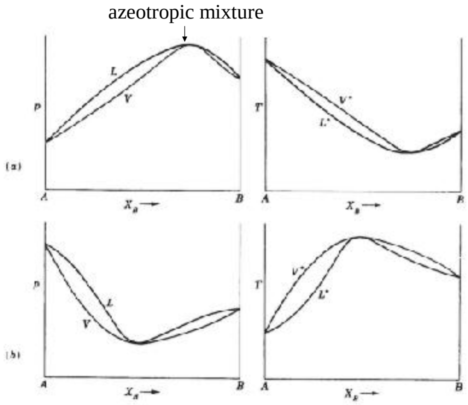
At one point when the total pressure p equals the atmospheric pressure the solution boils.

The boiling temperature in inversely related to vapor pressure.

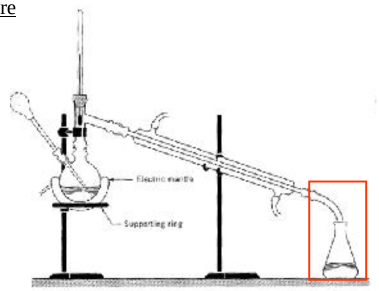
The boiling temperature vs. x_B plot there would look as follows.



For solutions which are far away from ideality the p vs x_i produces a solution which will be in equilibrium with a vapor of the same composition = azeotropic mixture.



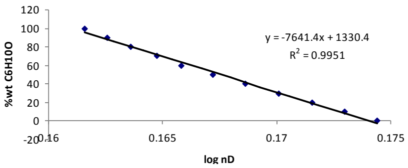
Set up and procedure (in brief)



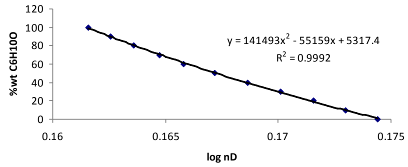
Obtain samples from the solution and the condensed vapor at different temperatures for various compositions of solution (see lab text).
Measure the refractive index of each sample ASAP.
Use the calibration plot to determine the composition of the samples..

log nD	%wt C6H10O
0.17441	0
0.17298	10
0.17155	20
0.1701	30
0.16864	40
0.16719	50
0.16582	60
0.16473	70
0.1636	80
0.16256	90
0.16158	100

Calibration Plot of nD



Calibration Plot of nD



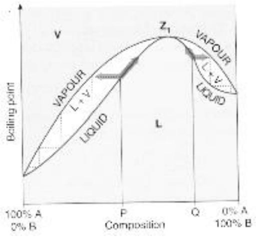
Collect a series of samples from the boiling liquid and the vapor (condensed) in equilibrium with the liquid different boiling temperatures.

Measure the refractive index of the liquids.

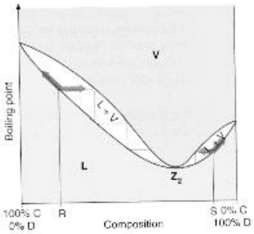
1. Use calibration curve to find the wt% of $C_6H_{10}O$.
2. Convert to mole fraction of $C_6H_{10}O$ (both liquids).
3. Calculate the mole fraction of $C_2H_2Cl_4$.
4. Plot T (boling point) vs mole fraction for the two phases (liquid and vapor).
5. Determine azeotropic composiyion and it’s boiling point.

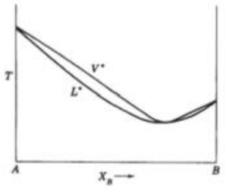
For the azeotropic mixture (azeotrope) the composition of the vapor is equal to the composition of the liquid left (definition of the azeotrope).

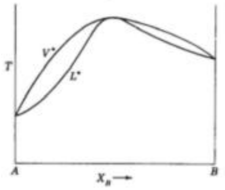
negative deviation



positive deviation







Plot T vs x_B.

Determine the composition and the boiling temperature of the azeotropic mixture.