Physical Chemistry I. practice

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V.: Ideal mixtures

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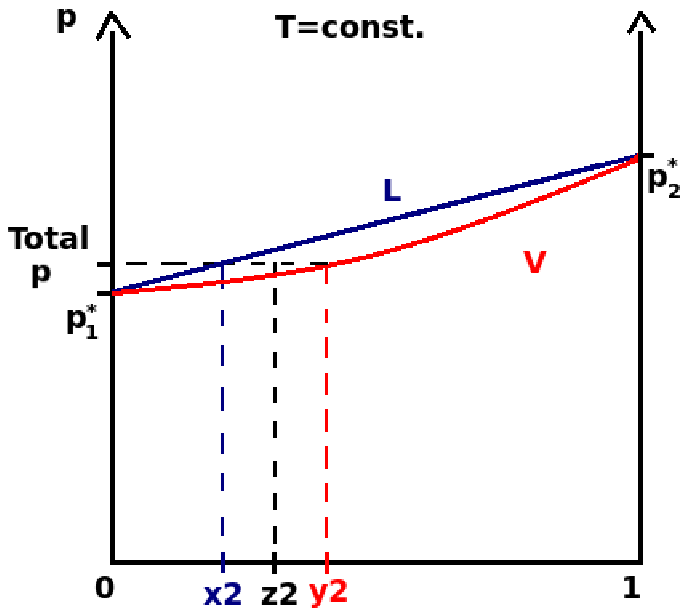
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Requirements.pdf
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Important_dates.pdf

Pressure-composition diagram

2 components, 2 phases
Miscible components, ideal solution, vapor is ideal gas



z_2: molar fraction of comp. 2 in the total system
x_2: molar fraction of comp. 2 in the liquid phase (solution)
y_2: molar fraction of comp. 2 in the gas phase (vapor)

Dalton's law:
$p = p_1 + p_2$, $p_1 = y_1 \cdot p$, $p_2 = y_2 \cdot p$

Raoult's law:
$p_1 = x_1 \cdot p_1^*$, $p_2 = x_2 \cdot p_2^*$

p_1^*, p_2^*: eq. vapor pressure of comp. 1 and 2

$y_2 = \frac{p_2}{p} = \frac{x_2 \cdot p_2^*}{p}$

$z_1 + z_2 = x_1 + x_2 = y_1 + y_2 = 1$

Konovalov's first law, lever rule

$y_2 = \frac{p_2}{p} = \frac{x_2 \cdot p_2^*}{p}$

Konovalov's first law for ideal mixtures:

if $p_1^* < p_2^*$: $p_1^* < p < p_2^* \quad \rightarrow \quad \frac{p_2^*}{p} > 1,\ y_2 > x_2$

$n_1 = (n_g + n_l) \cdot z_1 = n_g \cdot y_1 + n_l \cdot x_1$

$n_g \cdot (z_1 - y_1) = n_l \cdot (x_1 - z_1)$

Lever rule: $\frac{n_l}{n_g} = \frac{z_1 - y_1}{x_1 - z_1}$

We can also calculate n_g and n_l directly

$n_1 = n_g \cdot y_1 + n_l \cdot x_1 = n_g \cdot y_1 + (n - n_g) \cdot x_1 = n \cdot x_1 + n_g \cdot (y_1 - x_1)$

$\rightarrow \qquad n_g = \frac{n_1 - n \cdot x_1}{y_1 - x_1} \qquad n_l = \frac{n_1 - n \cdot y_1}{x_1 - y_1}$

Vapor composition

We have an ideal mixture of acetone (Ac) and acetonitrile (An)

$log(p^*_{Ac}) = 9,36457 - \frac{1279{,}87}{237{,}50+T}$

$log(p^*_{An}) = 9,36789 - \frac{1397{,}93}{238{,}89+T}$

(p in Pa, T in $°C$; but no dimensions inside log!)

$T = 20°C \qquad x_{Ac} = 0,2$

What is the vapor pressure? What is the composition of the vapor?

$$p = p_{Ac} + p_{An} = x_{Ac} \cdot p^*_{Ac} + (1 - x_{Ac}) \cdot p^*_{An}$$

$$y_{Ac} = \frac{p_{Ac}}{p} = \frac{x_{Ac} \cdot p^*_{Ac}}{p} \qquad y_{An} = \frac{p_{An}}{p} = \frac{(1-x_{Ac}) \cdot p^*_{An}}{p}$$

Vapor composition

$$log(p^*_{Ac}) = 9,36457 - \frac{1279,87}{237,50+20} = 4,39420$$

$$\rightarrow p^*_{Ac} = 10^{4,39420} Pa = 24786\ Pa$$

$$log(p^*_{An}) = 9,36789 - \frac{1397,93}{238,89+20} = 3,96818$$

$$\rightarrow p^*_{An} = 10^{3,96818} Pa = 9294\ Pa$$

$$p = 0,2 \cdot 24786\ Pa + 0,8 \cdot 9294\ Pa = 12392\ Pa$$

$$y_{Ac} = \frac{0,2 \cdot 24786\ Pa}{12392\ Pa} = 0,4$$

$$y_{An} = \frac{0,8 \cdot 9294\ Pa\ Pa}{12392\ Pa} = 0,6$$

Solution composition

Reverse example: we know that

$y_{Ac} = 0,4, \quad p^*_{Ac} = 24786\ Pa, \quad$ and $p^*_{An} = 9294\ Pa$

What is the composition of the solution?

$x_{Ac} = \frac{p_{Ac}}{p^*_{Ac}} = \frac{y_{Ac} \cdot p}{p^*_{Ac}} \rightarrow x_{Ac}$ and p unknown:

we need another equation with p and x_{Ac}!

$$p = x_{Ac} \cdot p^*_{Ac} + (1 - x_{Ac}) \cdot p^*_{An}$$

Expressing p from the first equation: $p = \frac{x_{Ac} \cdot p^*_{Ac}}{y_{Ac}}$

From the two equations for p we have

$$\frac{x_{Ac} \cdot p^*_{Ac}}{y_{Ac}} = x_{Ac} \cdot p^*_{Ac} + (1 - x_{Ac}) \cdot p^*_{An}$$

Solution composition

$$\frac{x_{Ac} \cdot p^*_{Ac}}{y_{Ac}} = x_{Ac} \cdot p^*_{Ac} + (1 - x_{Ac}) \cdot p^*_{An}$$

$$= x_{Ac} \cdot (p^*_{Ac} - p^*_{An}) + p^*_{An}$$

$$x_{Ac} \cdot [p^*_{Ac} - y_{Ac} \cdot (p^*_{Ac} - p^*_{An})] = p^*_{An} \cdot y_{Ac}$$

$$x_{Ac} = \frac{24786 \ \ Pa \cdot 0{,}4}{[24786 \ \ Pa - 0{,}4 \cdot (24786 - 9294)]} = 0,2$$

$$x_{An} = 1 - x_{Ac} = 0,8$$

Composition of a certain boiling point

What is the composition of the ideal chlorobenzene (cb) - bromobenzene (bb) mixture that starts to boil at 100 kPa on $T = 140°C$?

$p^*_{cb} = 125,24\ \mathrm{k}Pa \qquad p^*_{bb} = 66,10\ \mathrm{k}Pa$

Start of boiling: almost all of the mixture is liquid: $z_{cb} = x_{cb}$

$$p = 100\ \mathrm{k}Pa = x_{cb} \cdot p^*_{cb} + (1 - x_{cb}) \cdot p^*_{bb}$$

$$= x_{cb}(p^*_{cb} - p^*_{bb}) + p^*_{bb}$$

$$\rightarrow \underline{x_{cb}} = \frac{p - p^*_{bb}}{p^*_{cb} - p^*_{bb}} = \frac{100\ \mathrm{k}Pa - 66{,}10\ \mathrm{k}Pa}{125{,}24\ \mathrm{k}Pa - 66{,}10\ \mathrm{k}Pa} = \underline{0,573}$$

$$\underline{x_{bb}} = 1 - x_{cb} = \underline{0,427}$$

Composition of a certain boiling point

What is the composition of the vapor phase?

$$\underline{y_{cb}} = \frac{p_{cb}}{p} = \frac{x_{cb} \cdot p^*_{cb}}{p} = \frac{0{,}573 \cdot 125{,}24\ \mathrm{k}Pa}{100\ \mathrm{k}Pa} = \underline{0,718}$$

$$\underline{y_{bb}} = 1 - y_{cb} = \underline{0,282}$$

Amount of substance in phases

Let's have $3\ mol$ of the previous mixture at $p = 95\ \mathrm{k}Pa$ with $z_{cb} = 0,63$. What is the quantity of the solution and the vapor?

$$n_l + n_g = 3\ mol \qquad \frac{n_g}{n_l} = \frac{z_{cb} - x_{cb}}{y_{cb} - z_{cb}} = \frac{n_g}{3\ mol - n_g}$$

$$x_{cb} = \frac{p - p^*_{bb}}{p^*_{cb} - p^*_{bb}} = 0,4887 \qquad y_{cb} = \frac{x_{cb} \cdot p^*_{cb}}{p} = 0,6443$$

$$\frac{n_g}{3\ mol - n_g} = \frac{0{,}63 - 0{,}4887}{0{,}6443 - 0{,}63} = 9,8811$$

$$10,8811 \cdot n_g = 29,6434\ mol$$

$$\underline{n_g} = \underline{2,7243\ mol} \rightarrow \underline{n_l} = \underline{0,2757\ mol}$$