



*Department of Energy*  
*Politecnico di Milano*  
Via Lambruschini 4 - 20156 MILANO

## Exercises of "Fundamentals of Chemical Processes"

Prof. Gianpiero Groppi

### Exercise 9

Estimation of the bubble temperature and of the dew temperature of a n-butane/n-hexane mixture

A mixture, composed of 50% v/v n-butane and 50% v/v n-hexane, is maintained at 4.85 bar. Estimate its bubble temperature and dew temperature in the following cases:

- Ideal gas and ideal mixture
- Real gas and ideal mixture
- Real gas and real mixture

Assume the RKS equation of state.

**Data:**

	$A_{\text{ANTOINE}}$	$B_{\text{ANTOINE}}$	$C_{\text{ANTOINE}}$	$T_c$ [K]	$P_c$ [bar]	$\omega$
n-C <sub>4</sub> H <sub>10</sub>	13.6608	2154.700	238.789	425.10	37.96	0.200
n-C <sub>6</sub> H <sub>14</sub>	13.8193	2696.040	224.317	507.60	30.25	0.301

Antoine's equation: P is kPa, T is °C

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i}$$

The Antoine's Equation for  $P_i^{\text{sat}}$  is taken from J.M. Smith, H.C. Van Ness, M. M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th edition, McGraw Hill (2005).

## RKS parameters

$$a = \frac{0.42748 \cdot \alpha \cdot (R_{gas} \cdot T_C)^2}{P_C}$$

$$b = \frac{0.08664 \cdot R_{gas} \cdot T_C}{P_C}$$

$$\alpha = \left(1 + S \cdot (1 - \sqrt{T_R})\right)^2$$

$$S = 0.48 + 1.574 \cdot \omega - 0.176 \cdot \omega^2$$

$$A = \frac{a \cdot P}{(R_{gas} \cdot T)^2}$$

$$B = \frac{b \cdot P}{R_{gas} \cdot T}$$

## Fugacity Coefficient (Z root of the cubic equation)

$$\ln \phi(T, P) = Z - 1 - \frac{A}{B} \cdot \ln\left(\frac{Z+B}{Z}\right) - \ln(Z-B)$$

## RKS parameters for mixtures and mixing rules

$$A_i = \frac{a_i \cdot P}{(R_{gas} \cdot T)^2}$$

$$B_i = \frac{b_i \cdot P}{R_{gas} \cdot T}$$

$$a_{mix} = \left(\sum_i^{NC} x_i \cdot \sqrt{a_i}\right)^2$$

$$b_{mix} = \sum_i^{NC} x_i \cdot b_i$$

$$A_{mix} = \frac{a_{mix} \cdot P}{(R_{gas} \cdot T)^2}$$

$$B_{mix} = \frac{b_{mix} \cdot P}{R_{gas} \cdot T}$$

## Fugacity coefficient for the i-th specie in the $\alpha$ phase with $\bar{x}$ composition

$$\ln \hat{\phi}_i^\alpha(T, P, \bar{x}^\alpha) = \frac{B_i}{B_{mix}} \cdot (Z - 1) + \frac{A_{mix}}{B_{mix}} \cdot \left(\frac{B_i}{B_{mix}} - 2 \cdot \sqrt{\frac{A_i}{A_{mix}}}\right) \cdot \ln\left(\frac{Z + B_{mix}}{Z}\right) - \ln(Z - B_{mix})$$

### Solving procedure for the cubic equation

$$Z^3 + \alpha \cdot Z^2 + \beta \cdot Z + \gamma = 0$$

$$\alpha = -1$$

$$\beta = A - B - B^2$$

$$\gamma = -A \cdot B$$

$$p = \beta - \frac{\alpha^2}{3}$$

$$q = \frac{2\alpha^3}{27} - \frac{\alpha \cdot \beta}{3} + \gamma$$

$$D = \frac{q^2}{4} + \frac{p^3}{27}$$

If  $D > 0$ , only 1 real solution is found.

$$Z = \left(-\frac{q}{2} + \sqrt{D}\right)^{1/3} + \left(-\frac{q}{2} - \sqrt{D}\right)^{1/3} - \frac{\alpha}{3}$$

If  $D = 0$ , 3 real solutions are found, of which 2 are identical.

$$Z_1 = -2 \cdot \left(-\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

$$Z_2 = Z_3 = \left(-\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

If  $D < 0$ , 3 distinct real solutions are found.

$$Z_1 = 2 \cdot r^{1/3} \cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_2 = 2 \cdot r^{1/3} \cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_3 = 2 \cdot r^{1/3} \cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$r = \sqrt{-\frac{p^3}{27}}$$

$$\cos(\theta) = -\frac{q}{2r}$$

## Solution

The equilibrium condition for mass transfer between the vapor phase and the liquid phase is expressed by the equality between the fugacity of each specie in the two phases:

$$\hat{f}_i^V(T, P, \bar{y}) = \hat{f}_i^L(T, P, \bar{x})$$

This equation can be rearranged by taking into account the capability of some equations of state of describing the behavior of both the vapor phase and the liquid phase ( $\phi/\phi$  approach or direct method):

$$P \cdot y_i \cdot \hat{\phi}_i^V(T, P, \bar{y}) = P \cdot x_i \cdot \hat{\phi}_i^L(T, P, \bar{x})$$

Simplifying the value of the pressure, one obtains:

$$y_i \cdot \hat{\phi}_i^V(T, P, \bar{y}) = x_i \cdot \hat{\phi}_i^L(T, P, \bar{x})$$

This equation can be written by introducing the definition of equilibrium constant  $K_i$ :

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^L(T, P, \bar{x})}{\hat{\phi}_i^V(T, P, \bar{y})}$$

The fugacity coefficients of the species of both the vapor and the liquid phases are calculated by application of one equation of state, which is, in this case, the RKS. The solution of the corresponding system can be obtained via several numeric methods, by application of an iterative procedure. The first attempt values are generally assumed as the solutions of simpler cases, such as those obtained under the assumption of ideal gas and ideal mixtures.

## Ideal gas and ideal mixtures

The Raoult's law is applied. The vapor phase behaves like an ideal gas:

$$\hat{f}_i^V(T, P, \bar{y}) = P_i = P \cdot y_i$$

The liquid phase behaves like an ideal mixture:

$$\hat{f}_i^L(T, P, \bar{x}) = P_i^{SAT}(T) \cdot x_i$$

The Antoine's equation is used to calculate the saturation pressure:

$$\ln P_i^{sat} = A_i - \frac{B_i}{T + C_i}$$

*Saturation temperature of the pure species*

The Antoine's equation is used to estimate the saturation temperature of each of the pure species, given the pressure of the system. The solutions of the bubble point problem and of the dew point problem are comprised in between the saturation temperatures of the two pure components (in case the mixture includes more than two species, in between the lowest saturation temperature and the highest one). From the Antoine's equation, it can be found that:

$$T = -C_i + \frac{B_i}{A_i - \ln P_i^{sat}}$$

At 4.85 bar, the following values are calculated for the saturation temperature:

$$T_{n\text{-hexane}}^{SAT} = 128.79^\circ C$$

$$T_{n\text{-butane}}^{SAT} = 49.40^\circ C$$

*Bubble temperature*

The estimation of the bubble temperature requires the solution of the following equation:

$$\sum_i^{NC} y_i = 1$$

$$\sum_i^{NC} \frac{P_i^{SAT}(T_{Bubble})}{P} \cdot x_i = 1$$

Whose result is:

$$T_{Bubble} = 73.007^\circ C$$

The composition of the corresponding gas phase is:

$$y_{n\text{-hexane}} = 0.119$$

$$y_{n\text{-butane}} = 0.881$$

*Dew temperature*

The estimation of the dew temperature requires the solution of the following equation:

$$\sum_i^{NC} x_i = 1$$

$$\sum_i^{NC} \frac{P}{P_i^{SAT}(T_{Dew})} \cdot y_i = 1$$

Whose result is:

$$T_{Dew} = 105.722^\circ\text{C}$$

The composition of the corresponding liquid phase is:

$$x_{n\text{-hexane}} = 0.853$$

$$x_{n\text{-butane}} = 0.147$$

### **Real Gas and Ideal mixture**

The vapor phase behaves like a real gas:

$$\hat{f}_i^V(T, P, \vec{y}) = P \cdot \hat{\phi}_i^V(T, P, \vec{y}) \cdot y_i$$

Assuming that the mixture is ideal, the fugacity coefficients of each specie in the mixture are equal to those of the pure specie, from which it derives that:

$$\hat{\phi}_i^V(T, P, \vec{y}) = \phi_i^V(T, P) \rightarrow \hat{f}_i^V(T, P, \vec{y}) = P \cdot \phi_i^V(T, P) \cdot y_i$$

In the same way, one obtains for the liquid phase:

$$\hat{\phi}_i^L(T, P, \vec{x}) = \phi_i^L(T, P) \rightarrow \hat{f}_i^L(T, P, \vec{x}) = P \cdot \phi_i^L(T, P) \cdot x_i$$

### Saturation temperature of the pure species

The equation of state is applied to estimate the saturation temperature of the pure species, given that the pressure of the system is known. The equality between the fugacity values in the liquid and in the vapor phase is written by taking into consideration that each phase is pure ( $x_i = y_i = 1$ ):

$$\phi_i^V(T_{SAT}, P) = \phi_i^L(T_{SAT}, P)$$

The resulting equation has only one unknown value, the temperature. In the exercise, the results are:

$$T_{n\text{-hexane}}^{SAT} = 128.28^\circ\text{C}$$

$$T_{n\text{-butane}}^{SAT} = 48.82^\circ\text{C}$$

### Bubble temperature

The estimation of the bubble temperature requires the solution of the following equation, with one unknown value,  $T_{\text{Bubble}}$ :

$$\phi_i^V(T, P) \cdot y_i = \phi_i^L(T, P) \cdot x_i$$
$$\sum_i^{NC} K_i \cdot x_i = 1 \rightarrow \sum_i^{NC} \frac{\phi_i^L(T, P)}{\phi_i^V(T, P)} \cdot x_i = 1$$

When the pressure is assigned, the bubble point equation is implicit in the temperature. It is therefore necessary to use a numerical method (for instance, the bisection method) to solve for the temperature. A reasonable first attempt value is the bubble point estimated in the ideal case ( $T_{\text{Bubble}} = 73.007^\circ\text{C}$ ). Starting from this value, the RKS parameters are estimated:

$$a = \frac{0.42748 \cdot \alpha \cdot (R_{\text{gas}} \cdot T_C)^2}{P_C}$$

$$b = \frac{0.08664 \cdot R_{\text{gas}} \cdot T_C}{P_C}$$

$$\alpha = \left(1 + S \cdot (1 - \sqrt{T_R})\right)^2$$

$$S = 0.48 + 1.574 \cdot \omega - 0.176 \cdot \omega^2$$

$$A = \frac{a \cdot P}{(R_{\text{gas}} \cdot T)^2}$$

$$B = \frac{b \cdot P}{R_{\text{gas}} \cdot T}$$

The results are:

$$A_{n\text{-hexane}} = 0.1995 \quad B_{n\text{-hexane}} = 0.0204$$

$$A_{n\text{-butane}} = 0.0955 \quad B_{n\text{-butane}} = 0.0136$$

Once the A and B parameters are estimated, the parameters of the cubic equations associated to the equilibrium of each of the species are calculated:

$$Z^3 + \alpha \cdot Z^2 + \beta \cdot Z + \gamma = 0$$

$$\alpha = -1$$

$$\beta = A - B - B^2$$

$$\gamma = -A \cdot B$$

Specie	$\alpha$	$\beta$	$\gamma$
n-C <sub>6</sub> H <sub>14</sub>	-1	0.1787	-4.06E-03
n-C <sub>4</sub> H <sub>10</sub>	-1	0.0817	-1.30E-03

The cubic equation is rigorously solved after the estimation of the following parameters:

$$p = \beta - \frac{\alpha^2}{3}$$

$$q = \frac{2\alpha^3}{27} - \frac{\alpha \cdot \beta}{3} + \gamma$$

$$D = \frac{q^2}{4} + \frac{p^3}{27}$$

The D parameter is the discriminant of the solving roots: if  $D > 0$ , only one real root exists.

$$Z = \left( -\frac{q}{2} + \sqrt{D} \right)^{1/3} + \left( -\frac{q}{2} - \sqrt{D} \right)^{1/3} - \frac{\alpha}{3}$$

If D is equal to 0, 3 real solutions exist, two of which are identical.



$$Z_1 = -2 \cdot \left(-\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

$$Z_2 = Z_3 = \left(-\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

If  $D < 0$ , 3 distinct real roots are found.

$$Z_1 = 2 \cdot r^{1/3} \cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_2 = 2 \cdot r^{1/3} \cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$Z_3 = 2 \cdot r^{1/3} \cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

$$r = \sqrt{-\frac{p^3}{27}}$$

$$\cos(\theta) = -\frac{q}{2r}$$

In the present case (bubble point, real gas, ideal mixture), the results are:

Specie	p	q	D	r	cos θ	θ	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>
n-C <sub>6</sub> H <sub>14</sub>	-0.1547	-0.0186	-5.07E-05	0.0117	0.7936	0.6541	0.7767	0.0266	0.1967
n-C <sub>4</sub> H <sub>10</sub>	-0.2516	-0.0481	-1.08E-05	0.0243	0.9908	0.1358	0.9119	0.0213	0.0667

Since  $D < 0$ , the lowest root ( $Z_2$ ) corresponds to the compressibility factor of the liquid phase, the highest root ( $Z_1$ ) corresponds to the compressibility factor of the vapor phase, while the intermediate root has no practical physical meaning. Once the compressibility factors are estimated, the fugacity coefficients are calculated via the following equation:

$$\ln \phi(T, P) = Z - 1 - \frac{A}{B} \cdot \ln\left(\frac{Z+B}{Z}\right) - \ln(Z-B)$$

Specie	ln Φ <sub>SAT</sub> <sup>V</sup>	ln Φ <sub>SAT</sub> <sup>L</sup>	Φ <sub>SAT</sub> <sup>V</sup>	Φ <sub>SAT</sub> <sup>L</sup>
n-C <sub>6</sub> H <sub>14</sub>	-0.1975	-1.4628	0.8208	0.2316
n-C <sub>4</sub> H <sub>10</sub>	-0.0848	0.4185	0.9187	1.5197

A correct solution is not obtained when these values are substituted in the bubble point equation. It is therefore necessary to assume a new value for the bubble temperature and then repeat the numeric procedure up to the convergency. The bubble temperature and the composition of the vapor mixture are:

$$T_{Bubble} = 74.633^{\circ}C$$

$$y_{n-hexane} = 0.1475$$

$$y_{n-butane} = 0.8525$$

#### Dew temperature

The estimation of the dew temperature requires the solution of the following equation, with one unknown value,  $T_{Dew}$ :

$$\phi_i^V(T, P) \cdot y_i = \phi_i^L(T, P) \cdot x_i$$

$$\sum_i^{NC} \frac{y_i}{K_i} = 1 \rightarrow \sum_i^{NC} \frac{\phi_i^V(T, P)}{\phi_i^L(T, P)} \cdot y_i = 1$$

When the pressure is assigned, the dew point equation is implicit in the temperature. It is therefore necessary to use a numerical method to solve for the temperature. A reasonable first attempt value is the bubble point estimated in the ideal case ( $T_{Dew} = 105.722^{\circ}C$ ). Starting from this value, the RKS parameters are estimated:

$$A_{n-hexane} = 0.1564 \quad B_{n-hexane} = 0.0186$$

$$A_{n-butane} = 0.0750 \quad B_{n-butane} = 0.0124$$

The parameters of the associated cubic equations are:

Specie	$\alpha$	B	$\gamma$
n-C <sub>6</sub> H <sub>14</sub>	-1	0.1375	-2.91E-03
n-C <sub>4</sub> H <sub>10</sub>	-1	0.0624	-9.31E-04

The solving parameters are:

Specie	p	q	D	r	cos $\theta$	$\theta$	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>
n-C <sub>6</sub> H <sub>14</sub>	-0.1959	-0.0312	-3.55E-05	0.0167	0.9340	0.3653	0.8406	0.0259	0.1335
n-C <sub>4</sub> H <sub>10</sub>	-0.2710	-0.0542	-2.02E-06	0.0271	0.9986	0.0524	0.9343	0.0238	0.0419

As in the previous case, the value of the discriminant D is negative and therefore three distinct real solutions are present. Once the correct values of the roots are assigned to the compressibility coefficients of the liquid and the vapor phases, the following first attempt values are calculated for the fugacity coefficients:

Specie	$\ln \Phi_{SAT}^V$	$\ln \Phi_{SAT}^L$	$\Phi_{SAT}^V$	$\Phi_{SAT}^L$
n-C <sub>6</sub> H <sub>14</sub>	-0.1474	-0.6039	0.8629	0.5467
n-C <sub>4</sub> H <sub>10</sub>	-0.0641	0.9656	0.9380	2.6263

A correct solution is not obtained when this values are substituted in the bubble point equation. It is therefore necessary to assume a new value for the bubble temperature and then repeat the numeric procedure up to the convergency. The dew temperature and the composition of the liquid mixture are:

$$T_{Dew} = 104.129^\circ C$$

$$x_{n-hexane} = 0.8175$$

$$x_{n-butane} = 0.1825$$

### Real Gas and Real mixture

This is the most complex case, since the fugacity coefficients depend on the composition of the corresponding phase.

$$\hat{f}_i^V(T, P, \bar{y}) = P \cdot \hat{\phi}_i^V(T, P, \bar{y}) \cdot y_i$$

$$\hat{f}_i^L(T, P, \bar{x}) = P \cdot \hat{\phi}_i^L(T, P, \bar{x}) \cdot x_i$$

From these relations, it follows that:

$$\hat{\phi}_i^L(T, P, \bar{x}) \cdot x_i = \hat{\phi}_i^V(T, P, \bar{y}) \cdot y_i$$

#### Bubble temperature

In this case (a mixture of two components), the problem asks for the determination of three unknowns, the bubble temperature and the composition of the vapor phase. The constraint on the molar fraction can be used to simplify the calculations:

$$\sum_i^{NC} y_i = 1$$

In this way, the solution can be rearranged for the determination of only 2 unknown values. Other two equations are then required. The final solution is obtained via an iterative procedure, which involves the equilibrium equation for one of the two species (n-hexane) and the bubble point equation:

$$y_{n\text{-hexane}} \cdot \hat{\phi}_{n\text{-hexane}}^V(T, P, \bar{y}) = x_{n\text{-hexane}} \cdot \hat{\phi}_{n\text{-hexane}}^L(T, P, \bar{x})$$

$$y_{n\text{-butane}} = 1 - y_{n\text{-hexane}}$$

$$\sum_i^{NC} K_i \cdot x_i = 1 \rightarrow \sum_i^{NC} \frac{\hat{\phi}_i^L(T, P, \bar{x})}{\hat{\phi}_i^V(T, P, \bar{y})} \cdot x_i = 1$$

The following procedure can be applied to solve the problem:

- The values of P and x are assigned.
- The first attempt values are assigned respectively to  $T_{\text{Bubble}}$  and to the molar fractions of the vapor phase, y. It is convenient to use the values estimated in the case of real gas and ideal mixtures.
- The fugacity coefficients of the liquid phase are calculated by solving the cubic equation for the liquid mixture, knowing the values of T, P and x. In case three distinct and positive real roots are found, the lowest root is assigned to the compressibility factor of the liquid phase. With this value, the fugacity coefficients  $\hat{\phi}_i^L(T, P, \bar{x})$  are calculated.
- The fugacity coefficients of the vapor phase are calculated by solving the cubic equation for the vapor mixture, knowing the values of T, P and y. In case three distinct and positive real roots are found, the highest root is assigned to the compressibility factor of the vapor phase. With this value, the fugacity coefficients  $\hat{\phi}_i^V(T, P, \bar{y})$  are calculated.
- The equilibrium equation is solved for the y composition
- The bubble point equation is solved for the  $T_{\text{Bubble}}$  value.
- The procedure is repeated up to the variables converge to stable values.

To solve the cubic roots associated to each of the phases, mixing rules are required, which allow for the estimation of the  $A_{\text{mix}}$  and  $B_{\text{mix}}$  parameters of each mixture. These parameters are calculated starting from the A and B parameters of the pure species and from the composition of the associated phase:

$$A_i = \frac{a_i \cdot P}{(R_{gas} \cdot T)^2}$$

$$B_i = \frac{b_i \cdot P}{R_{gas} \cdot T}$$

$$a_{mix} = \left( \sum_i^{NC} x_i \cdot \sqrt{a_i} \right)^2$$

$$b_{mix} = \sum_i^{NC} x_i \cdot b_i$$

$$A_{mix} = \frac{a_{mix} \cdot P}{(R_{gas} \cdot T)^2}$$

$$B_{mix} = \frac{b_{mix} \cdot P}{R_{gas} \cdot T}$$

Once  $A_{mix}$  and  $B_{mix}$  are calculated, it is possible to calculate the parameters for the cubic equation associated to the phase:

$$Z^3 + \alpha \cdot Z^2 + \beta \cdot Z + \gamma = 0$$

$$\alpha = -1$$

$$\beta = A_{mix} - B_{mix} - B_{mix}^2$$

$$\gamma = -A_{mix} \cdot B_{mix}$$

The cubic equation is solved in the same way followed in the previous cases. Once the correct root is assigned to the compressibility coefficient of the phase, the fugacity coefficients of the species are calculated. The following equation is applied, wherein  $\alpha$  is the generic phase (either liquid or vapor) and  $x$  its composition:

$$\ln \hat{\phi}_i^\alpha(T, P, \vec{x}^\alpha) = \frac{B_i}{B_{mix}} \cdot (Z - 1) + \frac{A_{mix}}{B_{mix}} \cdot \left( \frac{B_i}{B_{mix}} - 2 \cdot \sqrt{\frac{A_i}{A_{mix}}} \right) \cdot \ln \left( \frac{Z + B_{mix}}{Z} \right) - \ln(Z - B_{mix})$$

Once the numerical procedure has reached the convergence, the final values for the bubble point problem are:

$$T_{Bubble} = 74.382^\circ C$$

$$y_{n-hexane} = 0.1446$$

$$y_{n-butane} = 0.8554$$

### Dew Point temperature

The dew point problem asks for the determination of three unknowns, the dew temperature and the composition of the liquid phase (the mixture has two components). The constraint on the molar fraction can be used to simplify the system:

$$\sum_i^{NC} x_i = 1$$

In this way, the solution can be rearranged for the determination of only 2 unknown values. Other two equations are then required. The final solution is obtained via an iterative procedure, which involves the equilibrium equation for one of the two species (n-hexane) and the dew point equation:

$$y_{n\text{-hexane}} \cdot \hat{\phi}_{n\text{-hexane}}^V(T, P, \vec{y}) = x_{n\text{-hexane}} \cdot \hat{\phi}_{n\text{-hexane}}^L(T, P, \vec{x})$$
$$x_{n\text{-butane}} = 1 - x_{n\text{-hexane}}$$
$$\sum_i^{NC} \frac{y_i}{K_i} = 1 \rightarrow \sum_i^{NC} \frac{\hat{\phi}_i^V(T, P, \vec{y})}{\hat{\phi}_i^L(T, P, \vec{x})} \cdot y_i = 1$$

The following procedure can be applied to solve the problem:

- The values of P and y are assigned.
- The first attempt values are assigned respectively to  $T_{\text{Dew}}$  and to the molar fractions of the liquid phase, x. It is convenient to use the values estimated in the case of real gas and ideal mixtures.
- The fugacity coefficients of the vapor phase are calculated by solving the cubic equation for the vapor mixture, knowing the values of T, P and y. In case three distinct and positive real roots are found, the highest root is assigned to the compressibility factor of the vapor phase. With this value, the fugacity coefficients  $\hat{\phi}_i^V(T, P, \vec{y})$  are calculated.
- The fugacity coefficients of the liquid phase are calculated by solving the cubic equation for the liquid mixture, knowing the values of T, P and x. In case three distinct and positive real roots are found, the lowest root is assigned to the compressibility factor of the vapor phase. With this value, the fugacity coefficients  $\hat{\phi}_i^L(T, P, \vec{x})$  are calculated.
- The equilibrium equation is solved for the x composition
- The bubble point equation is solved for the  $T_{\text{Dew}}$  value.
- The procedure is repeated up to the variables converge to stable values.

The numerical procedure is solved in the same way followed in the previous case. Once the numerical procedure has reached the convergency, the final values for the dew point problem are:

$$T_{Dew} = 104.085^{\circ}C$$

$$x_{n-hexane} = 0.8222$$

$$x_{n-butane} = 0.1778$$

### Summary

The final values for the three cases are:

#### Ideal Gas and Ideal Mixtures

Specie	T <sub>SAT</sub> [°C]	Y <sub>Bubble</sub>	X <sub>Dew</sub>
n-C <sub>6</sub> H <sub>14</sub>	128.79	0.119	0.853
n-C <sub>4</sub> H <sub>10</sub>	49.40	0.881	0.147

$$T_{Bubble} = 73.007^{\circ}C$$

$$T_{Dew} = 105.722^{\circ}C$$

#### Real Gas and Ideal Mixtures

Specie	T <sub>SAT</sub> [°C]	Bubble Point			Dew Point		
		Φ <sup>V</sup>	Φ <sup>L</sup>	y	Φ <sup>V</sup>	Φ <sup>L</sup>	X
n-C <sub>6</sub> H <sub>14</sub>	128.28	0.8232	0.2429	0.1475	0.8612	0.5267	0.8175
n-C <sub>4</sub> H <sub>10</sub>	48.82	0.9198	1.5681	0.8525	0.9372	2.5676	0.1825

$$T_{Bubble} = 74.633^{\circ}C$$

$$T_{Dew} = 104.129^{\circ}C$$

#### Real Gas and Real Mixtures

Specie	Bubble Point			Dew Point		
	Φ <sup>V</sup>	Φ <sup>L</sup>	y	Φ <sup>V</sup>	Φ <sup>L</sup>	x
n-C <sub>6</sub> H <sub>14</sub>	0.8403	0.2423	0.1446	0.8659	0.5265	0.8222
n-C <sub>4</sub> H <sub>10</sub>	0.9201	1.5741	0.8554	0.9417	2.6487	0.1778

$$T_{Bubble} = 74.382^{\circ}C$$

$$T_{Dew} = 104.085^{\circ}C$$