# TERMODINAMICA DEL EQUILIBRIO

## CAPÍTULO III. EQUILIBRIO LIQUIDO VAPOR

### Contenido



EQUILIBRIO_31.mcd

## 1. Cálculo de los **Puntos de Rocío y de Burbuja para Mezclas Multicomponentes**

Para el sistema cuaternario: Sistema n-Hexano (1)/ etanol (2)/ metilciclopentano (3)/ benceno (4)

$i := 1..4$ $\quad j := 1..4$ $\quad k := 1..4$

$$\rho := \begin{bmatrix} 0.659 \\ 0.789 \\ 0.754 \\ 0.885 \end{bmatrix} \cdot \frac{g}{cm^3} \qquad PM := \begin{bmatrix} 86.178 \\ 46.069 \\ 84.162 \\ 78.114 \end{bmatrix} \cdot \frac{g}{mol} \qquad V_i := \frac{PM_i}{\rho_i}$$

Constantes de Antoine

$$antA := \begin{bmatrix} 9.2033 \\ 12.2786 \\ 9.1690 \\ 9.2675 \end{bmatrix} \qquad antB := \begin{bmatrix} 2697.55 \\ 3803.98 \\ 2731.00 \\ 2788.51 \end{bmatrix} \qquad antC := \begin{bmatrix} -48.78 \\ -41.68 \\ -47.11 \\ -52.36 \end{bmatrix}$$

Coeficientes Viriales y de Wilson calculados con los procedimientos mostrados previo:

Coeficientes viriales

$$B := \begin{bmatrix} -1360.1 & -657.0 & -1274.2 & -1218.8 \\ -657.0 & -1174.7 & -621.8 & -589.7 \\ -1274.2 & -621.8 & -1191.9 & -1137.9 \\ -1218.8 & -589.7 & -1137.9 & -1086.9 \end{bmatrix} \cdot \frac{cm^3}{mol}$$

$$\delta_{i,j} := 2 \cdot B_{i,j} - B_{i,i} - B_{j,j}$$

Constantes de Wilson

$$a := \begin{bmatrix} 0 & 283.63 & 272.09 & 169.92 \\ 2281.99 & 0 & 2221.47 & 1207.90 \\ -175.70 & 161.53 & 0 & 97.33 \\ 173.93 & 131.47 & 161.44 & 0 \end{bmatrix} \cdot \frac{cal}{mol}$$

### 1.1. **Calculo de la Presión de Burbuja aplicando Raoult**, basado en la Figura 12.12 de SMITH, van Ness & Abbott, 5a. edición, pag. 500.

Condiciones iniciales del sistema: $\quad Tsist := 334.85 \cdot °K \qquad x := \begin{bmatrix} 0.162 \\ 0.068 \\ 0.656 \\ 0.114 \end{bmatrix}$

Calculos iniciales $\quad T := Tsist \qquad \phi'_k := 1 \qquad Psat_i := \exp\left(antA_i - \frac{antB_i}{T + antC_i}\right) \cdot atm$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right]$$

$$P := \sum_k \frac{x_k \cdot \gamma_k}{\phi'_k} \cdot Psat_k \qquad P = 0.9704 \cdot atm \qquad WRITE(P1) := \frac{P}{atm}$$

Iteracion

$$P := READ(P1) \cdot atm \qquad P = 0.976 \cdot atm$$

<-Inicio

$$y_k := \frac{x_k \cdot \gamma_k \cdot Psat_k}{\phi'_k \cdot P}$$

$$\phi'_k := \exp\left[\frac{B_{k,k} \cdot \left(P - Psat_k\right) + \frac{1}{2} \cdot \left[\sum_i \sum_j y_i \cdot y_j \cdot \left(2 \cdot \delta_{i,k} - \delta_{i,j}\right)\right] \cdot P}{R \cdot T}\right]$$

$$Pburb := \sum_k \frac{x_k \cdot \gamma_k}{\phi'_k} \cdot Psat_k$$

$$P = 0.976 \cdot atm$$

$$Pburb = 0.976 \cdot atm$$

$$WRITE(P1) := \frac{Pburb}{atm}$$

<-Final

$$xT := \sum_k x_k \qquad xT = 1 \qquad yT := \sum_k y_k \qquad yT = 0.9942$$

Resultados del calculo BURB P para el sistema n-HEXANO / ETANOL / METILCICLOPENTANO / BENCENO a:

$$Tsist = 334.85 \text{ °K} \qquad Pburb = 0.976 \cdot atm$$

| $x_k$ | $y_k$ | $\frac{Psat_k}{atm}$ | $\phi'_k$ | $\gamma_k$ |
|---|---|---|---|---|
| 0.162 | 0.1417 | 0.7974 | 0.9948 | 1.0708 |
| 0.068 | 0.264 | 0.4982 | 1.0011 | 7.6054 |
| 0.656 | 0.51 | 0.7245 | 0.9918 | 1.0473 |
| 0.114 | 0.0785 | 0.5468 | 0.9855 | 1.2286 |

1.2. **Calculo de la Temperatura de Burbuja aplicando Raoult,** basado en la Figura 12.14 de SMITH, van Ness & Abbott, 5a. edición, pag. 502.

Condiciones Iniciales del Sistema:

$$Psist := 0.9 \cdot atm \qquad x := \begin{bmatrix} 0.162 \\ 0.068 \\ 0.656 \\ 0.114 \end{bmatrix}$$

Calculo inicial

$$P := Psist \qquad \phi'_k := 1 \qquad Tsat_k := \frac{antB_k}{antA_k - \ln\left(\frac{P}{atm}\right)} - antC_k$$

$$T := \sum_k x_k \cdot Tsat_k \qquad T = 342.5301 \cdot °K \qquad Psat_i := \exp\left(antA_i - \frac{antB_i}{T + antC_i}\right) \cdot atm$$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right]$$

Componente de referencia

$$ref := 1$$

$$Psat_{ref} := \frac{P}{\sum_k \frac{x_k \cdot \gamma_k}{\phi'_k} \cdot \left(\frac{Psat_k}{Psat_{ref}}\right)} \qquad T := \frac{antB_{ref}}{antA_{ref} - \ln\left(\frac{Psat_{ref}}{atm}\right)} - antC_{ref}$$

$$T = 332.0814$$

$$WRITE(T1) := T$$

Iteracion:

$$T := READ(T1) \qquad Psat_i := \exp\left(antA_i - \frac{antB_i}{T + antC_i}\right) \cdot atm$$

<- Inicio

Normalizacion de valores de y

$$y_i := \frac{x_i \cdot \gamma_i \cdot Psat_i}{\phi'_i \cdot P} \qquad y_i := \frac{y_i}{\sum_i y_i}$$

$$\phi'_k := \exp\left[\frac{B_{k,k} \cdot \left(P - Psat_k\right) + \frac{1}{2} \cdot \left[\sum_i \sum_j y_i \cdot y_j \cdot \left(2 \cdot \delta_{i,k} - \delta_{i,j}\right)\right] \cdot P}{R \cdot T}\right]$$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right]$$

$$Psat_i := \frac{P}{\sum_k \frac{x_k \cdot \gamma_k}{\phi'_k} \cdot \left(\frac{Psat_k}{Psat_i}\right)}$$

$$Tburb := \frac{antB_{ref}}{antA_{ref} - \ln\left(\frac{Psat_{ref}}{atm}\right)} - antC_{ref}$$

$T = 332.5744$  $Tburb = 332.5744$

WRITE( T1) := Tburb   <- Final

$xT := \sum_k x_k$  $xT = 1$

$yT := \sum_k y_k$  $yT = 0.9959$

Resultados del calculo BURB T para el sistema n-HEXANO / ETANOL / METILCICLOPENTANO / BENCENO a:

$Psist = 0.9 \cdot atm$  $Tsist = 334.85 \cdot °K$  $Tburb = 332.5744 \cdot °K$

| $x_k$ | $y_k$ | $\frac{Psat_k}{atm}$ | $\phi'_k$ | $\gamma_k$ |
|---|---|---|---|---|
| 0.162 | 0.1444 | 0.7393 | 0.9952 | 1.0713 |
| 0.068 | 0.2562 | 0.4501 | 1.0011 | 7.655 |
| 0.656 | 0.5169 | 0.6718 | 0.9924 | 1.0477 |
| 0.114 | 0.0784 | 0.5047 | 0.9864 | 1.2311 |

**Calculo del Punto de Rocio P aplicando Raou**basado en la Figura 12.13 de SMITH, van Ness & Abbott, 5a. edición, pag. 501.

Condiciones iniciales del sistema: $Tsist := 334.85 °K$ $y := \begin{bmatrix} 0.162 \\ 0.068 \\ 0.656 \\ 0.114 \end{bmatrix}$

Calculo inicial $T := Tsist$ $\phi'_k := 1$ $\gamma_k := 1$

$$Psat_i := \exp\left(antA_i - \frac{antB_i}{T + antC_i}\right) \cdot atm \qquad P := \frac{1}{\sum_k \frac{y_k \cdot \phi'_k}{\gamma_k \cdot Psat_k}} \qquad x_k := \frac{y_k \cdot \phi'_k \cdot P}{\gamma_k \cdot Psat_k}$$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right] \qquad WRITEPRN(FUGX) := \gamma$$

$$P := \frac{1}{\sum_k \frac{y_k \cdot \phi'_k}{\gamma_k \cdot Psat_k}} \qquad P = 0.8194 \cdot atm \qquad WRITE(P1) := \frac{P}{atm}$$

Iteracion Exterio

$P := READ(P1) \cdot atm$ $P = 0.7918 \cdot atm$ <- Inicio

$$\phi'_k := \exp\left[\frac{B_{k,k} \cdot \left(P - Psat_k\right) + \frac{1}{2} \cdot \left[\sum_i \sum_j y_i \cdot y_j \cdot \left(2 \cdot \delta_{i,k} - \delta_{i,j}\right)\right] \cdot P}{R \cdot T}\right]$$

Iteración Interior

<- Inicio

$\gamma := READPRN(FUGX)$

$$x_k := \frac{y_k \cdot \phi'_k \cdot P}{\gamma_k \cdot Psat_k} \qquad x_k := \frac{x_k}{\sum_{k=1}^{4} x_k} \qquad x = \begin{bmatrix} 0.1568 \\ 0.0064 \\ 0.7091 \\ 0.1277 \end{bmatrix} \qquad \gamma = \begin{bmatrix} 1.026 \\ 17.16 \\ 1.008 \\ 1.28 \end{bmatrix}$$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) \ldots + -\left[\sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right]\right] \qquad \gamma = \begin{bmatrix} 1.0258 \\ 17.16 \\ 1.0083 \\ 1.2802 \end{bmatrix}$$

WRITEPRN(FUGX) := γ <- Final Iteración Interio

$P = 0.8194\,atm$

$$Procio := \frac{1}{\sum_k \frac{y_k \cdot \phi'_k}{\gamma_k \cdot Psat_k}}$$

$Procio = 0.7946\,atm$

$WRITE(P1) := \frac{Procio}{atm}$ <- Final Iteración Exteric

$xT := \sum_k x_k$ $xT = 0.9992$ $yT := \sum_k y_k$ $yT = 1$

Resultados del calculo ROCIO P para el sistema n-HEXANO / ETANOL / METILCICLOPENTANO / BENCENO:

$Tsist = 334.85\,°K$ $Psist = 0.9\,atm$ $Procio = 0.7946\,atm$

| $x_k$ | $y_k$ | $\frac{Psat_k}{atm}$ | $\phi'_k$ | $\gamma_k$ |
|---|---|---|---|---|
| 0.151 | 0.162 | 0.7974 | 0.9993 | 1.0356 |
| 0.0193 | 0.068 | 0.4982 | 1.0158 | 13.4583 |
| 0.6895 | 0.656 | 0.7245 | 0.996 | 1.0162 |
| 0.1395 | 0.114 | 0.5468 | 0.9894 | 1.2523 |

**Calculo del Punto de Rocio T,** basado en la Figura 12.12 de SMITH, van Ness & Abbott, 5a. edición, pag. 505.

Condiciones Iniciales $\quad Psist := 0.9 \cdot atm \quad y := \begin{bmatrix} 0.139 \\ 0.279 \\ 0.500 \\ 0.082 \end{bmatrix}$

Calculo inicial $\quad P := Psist$

$\phi'_k := 1 \qquad \gamma_k := 1 \qquad Tsat_k := \dfrac{antB_k}{antA_k - \ln\left(\dfrac{P}{atm}\right)} - antC_k$

$T := \sum_k y_k \cdot Tsat_k \qquad T = 343.8684 \cdot {}^\circ K$ <--

$Psat_k := \exp\left(antA_k - \dfrac{antB_k}{T + antC_k}\right) \cdot atm$

Seleccion de un compuesto de referencia $\quad ref := 1$

$Psat_{ref} := P \cdot \left(\sum_k \dfrac{y_k \cdot \phi'_k}{\gamma_k} \cdot \dfrac{Psat_{ref}}{Psat_k}\right) \qquad T := \dfrac{antB_{ref}}{antA_{ref} - \ln\left(\dfrac{Psat_{ref}}{atm}\right)} - antC_{ref} \qquad Psat_{ref} = 1.09 \cdot atm \quad T = 344.6581$

$Psat_k := \exp\left(antA_k - \dfrac{antB_k}{T + antC_k}\right) \cdot atm \qquad \phi'_k := \exp\left[\dfrac{B_{k,k} \cdot (P - Psat_k) + \dfrac{1}{2} \cdot \left[\sum_i \sum_j y_i \cdot y_j \cdot (2 \cdot \delta_{i,k} - \delta_{i,j})\right] \cdot P}{R \cdot T}\right]$

$x_k := \dfrac{y_k \cdot \phi'_k \cdot P}{\gamma_k \cdot Psat_k} \qquad \lambda_{i,j} := \dfrac{V_j}{V_i} \cdot \exp\left(\dfrac{-a_{i,j}}{R \cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \dfrac{x_k \cdot \lambda_{k,i}}{\sum_j (x_j \cdot \lambda_{k,j})}\right]$

$Psat_{ref} := P \cdot \left(\sum_k \dfrac{y_k \cdot \phi'_k}{\gamma_k} \cdot \dfrac{Psat_{ref}}{Psat_k}\right)$

WRITEPRN(FUGX) := γ

$T := \dfrac{antB_{ref}}{antA_{ref} - \ln\left(\dfrac{Psat_{ref}}{atm}\right)} - antC_{ref}$

T = 344.6581

T = 330.7836

WRITE(T1) := T

Iteracion Exterior
<- Inicio

$T := READ(T1)$  $T = 332.2511$

$$Psat_i := \exp\left(antA_i - \frac{antB_i}{T + antC_i}\right) \cdot atm$$

$$\phi'_k := \exp\left[\frac{B_{k,k}\cdot(P - Psat_k) + \frac{1}{2}\cdot\left[\sum_i\sum_j y_i\cdot y_j\cdot(2\delta_{i,k} - \delta_{i,j})\right]\cdot P}{R\cdot T}\right]$$

Iteración Interior
<- Inicio

$\gamma := READPRN(FUGX)$

$$x_k := \frac{y_k\cdot\phi'_k\cdot P}{\gamma_k\cdot Psat_k} \qquad x_k := \frac{x_k}{\sum_{k=1}^{4} x_k} \qquad \gamma = \begin{bmatrix} 1.106 \\ 5.56 \\ 1.077 \\ 1.213 \end{bmatrix}$$

$$\Lambda_{i,j} := \frac{V_j}{V_i}\cdot\exp\left(\frac{-a_{i,j}}{R\cdot T}\right) \qquad \gamma_i := \exp\left[1 - \ln\left(\sum_j x_j\cdot\Lambda_{i,j}\right) - \sum_k \frac{x_k\cdot\Lambda_{k,i}}{\sum_j (x_j\cdot\Lambda_{k,j})}\right] \qquad \gamma = \begin{bmatrix} 1.1064 \\ 5.5603 \\ 1.0771 \\ 1.2133 \end{bmatrix}$$

Iteración Interior

$WRITEPRN(FUGX) := \gamma$  $T = 332.2511$  <- Final

$$Psat_{ref} := P\cdot\left(\sum_k \frac{y_k\cdot\phi'_k}{\gamma_k}\cdot\frac{Psat_{ref}}{Psat_k}\right) \qquad Trocio := \frac{antB_{ref}}{antA_{ref} - \ln\left(\frac{Psat_{ref}}{atm}\right)} - antC_{ref} \qquad Trocio = 332.2511$$

Iteración Exterior
<- Final

$WRITE(T1) := Trocio$

$xT := \sum_k x_k$  $xT = 1$  $yT := \sum_k y_k$  $yT = 1$

Resultados del calculo ROCIO T para el sistema n-HEXANO / ETANOL / METILCICLO PENTANO / BENCENO:

$Trocio = 332.2511°K$  $Psist = 0.9\cdot atm$  $Tsist = 334.85°K$

| $x_k$ | $y_k$ | $\frac{Psat_k}{atm}$ | $\phi'_k$ | $\gamma_k$ |
|---|---|---|---|---|
| 0.1539 | 0.139 | 0.7314 | 0.9954 | 1.1064 |
| 0.1018 | 0.279 | 0.4436 | 0.9998 | 5.5603 |
| 0.624 | 0.5 | 0.6645 | 0.9925 | 1.0771 |
| 0.1203 | 0.082 | 0.4989 | 0.9866 | 1.2133 |

2. Calculo de **Destilacion FLASH** para una mezcla multicomponente, utilizando el procedimiento de la Figra 12.18 de Smith,van Ness & Abbott, 5a. edición, pag. 522.

Para el sistema cuaternario: Sistema n-Hexano (1)/ etanol (2)/ metilciclopentano (3)/ benceno (4)

Condiciones de entrada $Tsist := 334.85 \cdot {}^{\circ}K$ $Psist = 0.9 \cdot atm$ $z := \begin{bmatrix} 0.162 \\ 0.068 \\ 0.656 \\ 0.114 \end{bmatrix}$

1. se calcula la Presión de Recío según el procedimiento mostrado anteriormente.

$$Procio = 0.7946 \cdot atm$$

2. Se calcula la Presión de Burbuja según el procedimiento mostrado anteriormente.

$$Pburb = 0.9757 \cdot atm$$

3. Se compara la presión del sistema con los puntos de burbuja y de rocío:

$$Procio = 0.7946 \cdot atm \quad < \quad Psist = 0.9 \cdot atm \quad < \quad Pburb = 0.9757 \cdot atm$$

4. Se estiman los coeficientes de Actividad, de Fugacidad:

$T := Tsist$ $P := Psist$

$$\lambda_{i,j} := \frac{V_j}{V_i} \cdot \exp\left(\frac{-a_{i,j}}{R \cdot T}\right) \qquad Psat_k := \exp\left(antA_k - \frac{antB_k}{T + antC_k}\right) \cdot atm$$

$$\gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j \left(x_j \cdot \lambda_{k,j}\right)}\right]$$

$$\phi'_k := \exp\left[\frac{B_{k,k} \cdot \left(P - Psat_k\right) + \frac{1}{2} \cdot \left[\sum_i \sum_j y_i \cdot y_j \cdot \left(2 \cdot \delta_{i,k} - \delta_{i,j}\right)\right] \cdot P}{R \cdot T}\right]$$

$$K_i := \frac{\gamma_i \cdot Psat_i}{\phi'_k \cdot P} \qquad WRITEPRN(K1) := K$$

$F := 1$ $V := 0.0$

$K := READPRN(K1)$ Given $\sum_i \frac{z_i \cdot K_i}{1 + V \cdot (K_i - 1)} = 1$ Iteración <- Inicio

$V := Find(V)$ $V = 0.2458$

$L := F - V$ $L = 0.7542$

$x_i := \frac{z_i}{1 + V \cdot (K_i - 1)}$ $x = \begin{bmatrix} 0.1652 \\ 0.0286 \\ 0.6854 \\ 0.1209 \end{bmatrix}$ $\gamma_i := \exp\left[1 - \ln\left(\sum_j x_j \cdot \lambda_{i,j}\right) - \sum_k \frac{x_k \cdot \lambda_{k,i}}{\sum_j (x_j \cdot \lambda_{k,j})}\right]$

$y_i := K_i \cdot x_i$ $y = \begin{bmatrix} 0.1523 \\ 0.189 \\ 0.5658 \\ 0.0929 \end{bmatrix}$ $\phi'_k := \exp\left[\frac{B_{k,k} \cdot (P - Psat_k) + \frac{1}{2}\left[\sum_i \sum_j y_i \cdot y_j \cdot (2 \cdot \delta_{i,k} - \delta_{i,j})\right] \cdot P}{R \cdot T}\right]$

$K = \begin{bmatrix} 0.9221 \\ 6.614 \\ 0.8255 \\ 0.769 \end{bmatrix}$ $K_i := \frac{\gamma_i \cdot Psat_i}{\phi'_i \cdot P}$ $K = \begin{bmatrix} 0.9221 \\ 6.6139 \\ 0.8255 \\ 0.769 \end{bmatrix}$

$WRITEPRN(K1) := K$ <- Final Iteración

$xT := \sum_k x_k$ $xT = 1$ $yT := \sum_k y_k$ $yT = 1$

Resultados del calculo FLASH para el sisteman-Hexano (1)/ etanol (2)/ metilciclopentano (3)/ benceno (4)

$Tsist = 334.85 \cdot °K$ $Psist = 0.9 \cdot atm$ $Pburb = 0.9757 \cdot atm$ $Procio = 0.7946 \cdot atm$

| $z_k$ | $x_k$ | $\gamma_k$ | $y_k$ | $\phi'_k$ |
|---|---|---|---|---|
| 0.162 | 0.1652 | 1.0375 | 0.1523 | 0.9969 |
| 0.068 | 0.0286 | 12.0352 | 0.189 | 1.0073 |
| 0.656 | 0.6854 | 1.0189 | 0.5658 | 0.9937 |
| 0.114 | 0.1209 | 1.2495 | 0.0929 | 0.9872 |

$F = 1$ $V = 0.2458$ $L = 0.7542$

Ing. Federico G. Salazar