EQUILIBRIO LÍQUIDO – LÍQUIDO

CONDICIONES DE EQUILIBRIO LÍQUIDO – LÍQUIDO

$$T^{\alpha} = T^{\beta}$$

$$P^{\alpha} = P^{\beta}$$

$$f_1^{\alpha} = f_1^{\beta}$$

$$f_2^{\alpha} = f_2^{\beta}$$

$$\vdots$$

$$f_i^{\alpha} = f_i^{\beta}$$

$$\vdots$$

$$f_C^{\alpha} = f_C^{\beta}$$

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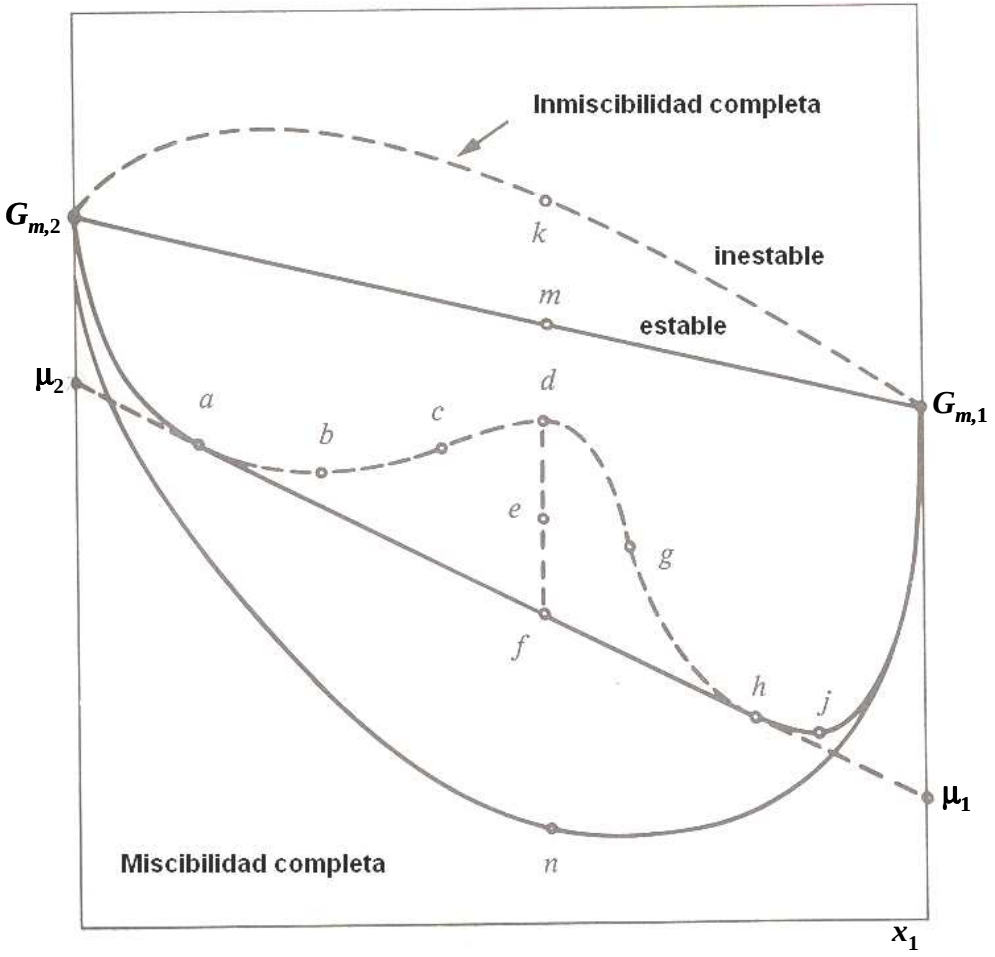
ESTABILIDAD TERMODINÁMICA Y MISCIBILIDAD

$$G_m = G^*_{m,1}\, x_1 + G^*_{m,2}\, x_2$$

$$G_m = G^*_{m,1}\, x_1 + G^*_{m,2}\, x_2 + \Delta G_m$$

$$\left(\frac{\partial^2 G_m}{\partial x_1^2}\right)_{T,P} < 0$$

$$\left(\frac{\partial^2 \Delta G_m}{\partial x_1^2}\right)_{T,P} < 0$$



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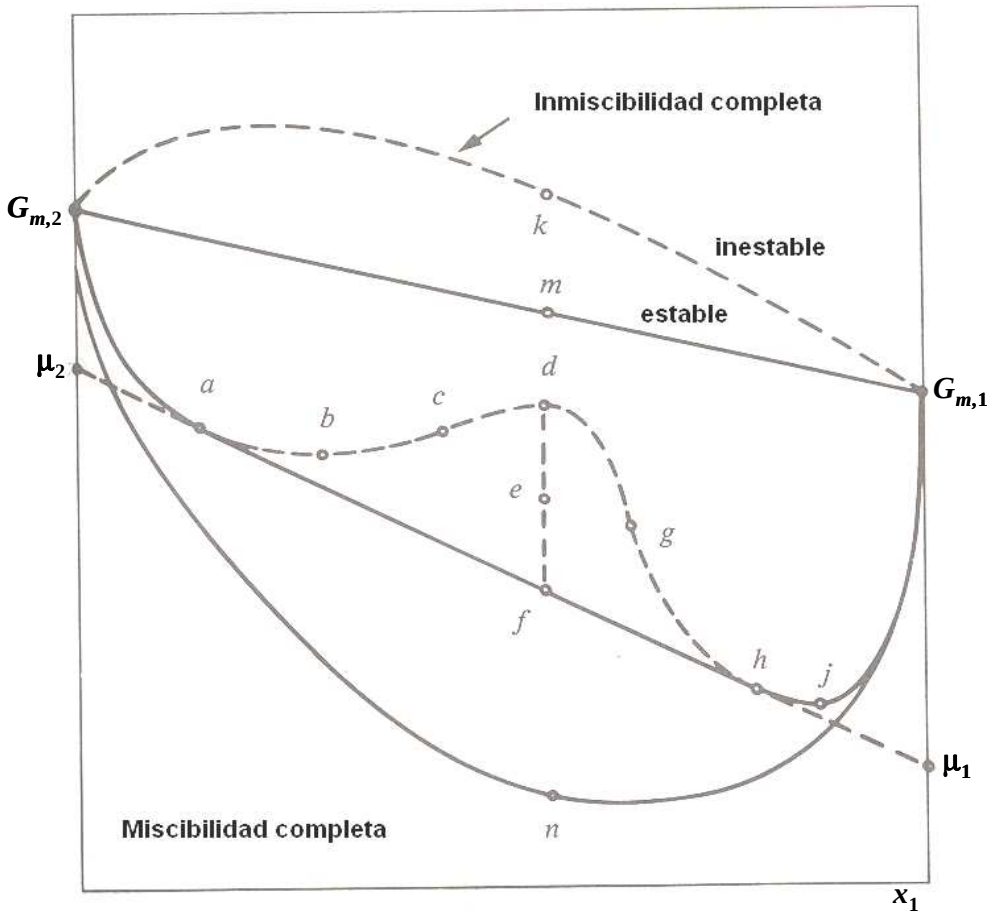
ESTABILIDAD TERMODINÁMICA Y MISCIBILIDAD

$$\mu_1 \equiv \overline{G_1} = G_m + (1 - x_1)\left(\frac{\partial G_m}{\partial x_1}\right)_{T,P}$$

$$\mu_2 \equiv \overline{G_2} = G_m - x_1\left(\frac{d G_m}{d x_1}\right)_{T,\ P}$$

$$\left(\frac{dG_m}{dx_1}\right)_{T,P} = \frac{\mu_1 - G_m}{1 - x_1} = \frac{G_m - \mu_2}{x_1 - 0}$$



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MEZCLAS BINARIAS

$$\left(\frac{\partial^2 G_m}{\partial\, x_i^2}\right)_{T,P} < 0 \qquad i = 1,2$$

$$\left(\frac{\partial^2 \Delta G_m}{\partial\, x_i^2}\right)_{T,P} < 0 \qquad i = 1,2$$

$$G_m^E \equiv G_m - G_m^{id}$$

$$G_m^E = G_m - \sum_{i=1}^{C} x_i\, G_{m,1}^* - R\,T \sum_{i=1}^{C} x_i \ln x_i$$

$$\Delta G_m = G_m - \sum_{i=1}^{C} x_i\, G_{m,1}^* = G_m^E + R\,T \sum_{i=1}^{C} x_i \ln x_i$$

$$\frac{\Delta G_m}{R\,T} = \frac{G_m^E}{R\,T} + \sum_{i=1}^{C} x_i \ln x_i$$

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MEZCLAS BINARIAS

$\frac{G_m^E}{R\,T}$	$\left(\frac{\partial^2 \Delta G_m}{\partial x_1^2}\right)_{T,P}$
Simétrica	$-2A+\frac{1}{x_1 x_2}$
Margules	$2\,(-2+3x_1)\,A_{12}+2\,(1-3x_1)\,A_{21}+\frac{1}{x_1 x_2}$
van Laar	$\frac{-2\,A_{12}^2\;A_{21}^2}{(A_{12}\,x_1+A_{21}\,x_2)^3}+\frac{1}{x_1 x_2}$
Wilson	$\frac{1}{x_1}\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}\;x_2}\right]^2+\frac{1}{x_2}\left[\frac{\Lambda_{21}}{\Lambda_{21}\;x_1+x_2}\right]^2+\frac{1}{x_1 x_2}$
NRTL	$-2\left[\frac{\tau_{21}\,G_{21}}{x_1+x_2\,G_{21}}+\frac{\tau_{12}\,G_{12}}{x_1\,G_{12}+x_2}\right]-(1-2\,x_1)\left[\frac{\tau_{21}\,G_{21}\,(1-G_{21})}{(x_1+x_2\,G_{21})^2}+\frac{\tau_{12}\,G_{12}\,(1+G_{12})}{(x_1\,G_{12}+x_2)^2}\right]$ $+2\,x_1\,x_2\left[\frac{\tau_{21}\,G_{21}\,(1-G_{21})^2}{(x_1+x_2\,G_{21})^3}+\frac{\tau_{12}\,G_{12}\,(1+G_{12})^2}{(x_1\,G_{12}+x_2)^3}\right]+\frac{1}{x_1\,x_2}$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS BINARIAS

$$f_i^{\alpha} = f_i^{\beta} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\alpha}\, \gamma_i^{\alpha} (f_i^{0})^{\alpha} = x_i^{\beta}\, \gamma_i^{\beta} (f_i^{0})^{\beta} \qquad (i = 1, 2, \ldots, C)$$

$$x_1^{\alpha}\, \gamma_1^{\alpha} = x_1^{\beta}\, \gamma_1^{\beta}$$
$$(1 - x_1^{\alpha})\, \gamma_2^{\alpha} = (1 - x_1^{\beta})\, \gamma_2^{\beta}$$

$$\gamma_i^{\alpha} = \gamma_i\,(T, x_1^{\alpha}) \qquad i = 1, 2$$
$$\gamma_i^{\beta} = \gamma_i\,(T, x_1^{\beta}) \qquad i = 1, 2$$

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MEZCLAS BINARIAS

$$x_1^{\alpha}\,\gamma_1^{\alpha} = x_1^{\beta}\,\gamma_1^{\beta}$$
$$(1-x_1^{\alpha})\,\gamma_2^{\alpha} = (1-x_1^{\beta})\,\gamma_2^{\beta}$$

$$f \equiv \ln\left(\frac{\gamma_1^{\alpha}}{\gamma_1^{\beta}}\right) + \ln\left(\frac{x_1^{\alpha}}{x_1^{\beta}}\right) = 0$$
$$g \equiv \ln\left(\frac{\gamma_2^{\alpha}}{\gamma_2^{\beta}}\right) + \ln\left(\frac{1-x_1^{\alpha}}{1-x_1^{\beta}}\right) = 0$$

$$f + h\,f'_{x^{\alpha}} + k\,f'_{x^{\beta}} = 0$$

$$g + h\,g'_{x^{\alpha}} + k\,g'_{x^{\beta}} = 0$$

$$f'_{x^{\alpha}} = \frac{\partial f}{\partial x_1^{\alpha}} = \frac{\partial \ln \gamma_1^{\alpha}}{\partial x_1^{\alpha}} + \frac{1}{x_1^{\alpha}}$$

$$f'_{x^{\beta}} = \frac{\partial f}{\partial x_1^{\beta}} = -\frac{\partial \ln \gamma_1^{\beta}}{\partial x_1^{\beta}} - \frac{1}{x_1^{\beta}}$$

$$g'_{x^{\alpha}} = \frac{\partial g}{\partial x_1^{\alpha}} = \frac{\partial \ln \gamma_2^{\alpha}}{\partial x_1^{\alpha}} - \frac{1}{1-x_1^{\alpha}}$$

$$g'_{x^{\beta}} = \frac{\partial g}{\partial x_1^{\beta}} = -\frac{\partial \ln \gamma_2^{\beta}}{\partial x_1^{\beta}} + \frac{1}{1-x_1^{\beta}}$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas

$$x_i^{\beta} = \left(\frac{\gamma_i^{\alpha}}{\gamma_i^{\beta}} \right) x_i^{\alpha} = K_i \; x_i^{\alpha} \qquad \left(i = 1, 2, \ldots, C \right)$$

$$z_i = \theta \; x_i^{\alpha} + (1-\theta) \; x_i^{\beta} = x_i^{\alpha} \left[\theta + (1-\theta) \; K_i \right] \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\alpha} = \frac{z_i}{\theta + (1-\theta) \, K_i} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\beta} = K_i \; x_i^{\alpha} = \frac{K_i \; z_i}{\theta + (1-\theta) \, K_i} \qquad (i = 1, 2, \ldots, \ldots C)$$

$$\sum_{i=1}^{C} x_i^{\beta} - \sum_{i=1}^{C} x_i^{\alpha} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i - 1 \right)}{\theta + (1-\theta) \, K_i} = 0$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas

1.- Leer P, T, z_i

2.- Suponer x_i^{α}, θ

3.- Calcular x_i^{β}

4.- Calcular γ_i^{α}, γ_i^{β}

5.- Calcular K_i

6.- Calcular θ

7.- Calcular x_i^{α}, x_i^{β}

8.- Comparar con los valores supuestos: NO, ir a 4.

SI, fin

$$x_i^{\beta} = \frac{z_i - \theta\, x_i^{\alpha}}{1-\theta} \qquad (i = 1, 2, \ldots, C)$$

$$\sum_{i=1}^{C} x_i^{\beta} - \sum_{i=1}^{C} x_i^{\alpha} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i - 1\right)}{\theta + \left(1-\theta\right) K_i} = 0$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Tres fases líquidas

$$z_i = \theta_1\, x_i^{\alpha} + \theta_2\, x_i^{\beta} + \left(1 - \theta_1 - \theta_2\right) x_i^{\delta} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\alpha}\, \gamma_i^{\alpha} = x_i^{\beta}\, \gamma_i^{\beta} = x_i^{\delta}\, \gamma_i^{\delta} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\alpha} = \frac{\gamma_i^{\delta}}{\gamma_i^{\alpha}}\, x_i^{\delta} = K_i'\, x_i^{\delta} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\beta} = \frac{\gamma_i^{\delta}}{\gamma_i^{\beta}}\, x_i^{\delta} = K_i''\, x_i^{\delta} \qquad (i = 1, 2, \ldots, C)$$

$$x_i^{\delta} = \frac{z_i}{1 + \left(K_i' - 1\right)\theta_1 + \left(K_i'' - 1\right)\theta_2} \qquad (i = 1, 2, \ldots, C)$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Tres fases líquidas

$$f \equiv \sum_{i=1}^{C} x_i^{\alpha} - \sum_{i=1}^{C} x_i^{\delta} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i' - 1\right)}{1 + \left(K_i' - 1\right)\theta_1 + \left(K_i'' - 1\right)\theta_2} = 0$$

$$g \equiv \sum_{i=1}^{C} x_i^{\beta} - \sum_{i=1}^{C} x_i^{\delta} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i'' - 1\right)}{1 + \left(K_i' - 1\right)\theta_1 + \left(K_i'' - 1\right)\theta_2} = 0$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Tres fases líquidas

1.- Leer P, T, z_i

2.- Suponer x_i^{α}, x_i^{β}, θ_1, θ_2

3.- Calcular x_i^{δ}

4.- Calcular γ_i^{α}, γ_i^{β}, γ_i^{δ}

5.- Calcular K_i', K_i''

6.- Calcular θ_1, θ_2

7.- Calcular x_i^{α}, x_i^{β}, x_i^{δ}

8.- Comparar con los valores supuestos: NO, ir a 4.

SI, fin

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas y una vapor

$$z_i = \theta_1\, y_i + (1-\theta_1)\,\theta_2\, x_i^{\alpha} + (1-\theta_1)(1-\theta_2)\, x_i^{\beta} \qquad (i = 1, 2, \ldots, C)$$

$$P\,\phi_i^V\, y_i = x_i^{\alpha}\,\gamma_i^{\alpha}\, P_i^s\,\phi_i^s\,(FP)_i$$

$$P\,\phi_i^V\, y_i = x_i^{\beta}\,\gamma_i^{\beta}\, P_i^s\,\phi_i^s\,(FP)_i \qquad (i = 1, 2, \ldots, C)$$

$$y_i = \frac{\gamma_i^{\alpha}\, P_i^s\,\phi_i^s (FP)_i}{P\,\phi_i^V}\, x_i^{\alpha} = K_i'\, x_i^{\alpha} \qquad (i = 1, 2, \ldots, C)$$

$$y_i = \frac{\gamma_i^{\beta}\, P_i^s\,\phi_i^s (FP)_i}{P\,\phi_i^V}\, x_i^{\beta} = K_i''\, x_i^{\beta} \qquad (i = 1, 2, \ldots, C)$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas y una vapor

$$x_i^{\alpha} = \frac{z_i}{K_i' \theta_1 + (1-\theta_1)\left[\theta_2 + (1-\theta_2)\left(\frac{K_i'}{K_i''}\right)\right]}$$

$$x_i^{\beta} = \frac{z_i \left(\frac{K_i'}{K_i''}\right)}{K_i' \theta_1 + (1-\theta_1)\left[\theta_2 + (1-\theta_2)\left(\frac{K_i'}{K_i''}\right)\right]}$$

$$y_i = \frac{z_i K_i'}{K_i' \theta_1 + (1-\theta_1)\left[\theta_2 + (1-\theta_2)\left(\frac{K_i'}{K_i''}\right)\right]}$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas y una vapor

$$f \equiv \sum_{i=1}^{C} y_i - \sum_{i=1}^{C} x_i^{\alpha} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i' - 1\right)}{K_i' \theta_1 + (1-\theta_1)\left[\theta_2 + (1-\theta_2)\left(\frac{K_i'}{K_i''}\right)\right]} = 0$$

$$g \equiv \sum_{i=1}^{C} y_i - \sum_{i=1}^{C} x_i^{\beta} = 0; \qquad \sum_{i=1}^{C} \frac{z_i \left(K_i'' - 1\right)}{K_i'' \theta_1 + (1-\theta_1)\left[\theta_2\left(\frac{K_i''}{K_i'}\right) + 1 - \theta_2\right]} = 0$$

EQUILIBRIO LÍQUIDO – LÍQUIDO

MEZCLAS MULTICOMPONENTES

Dos fases líquidas y una vapor

1.- Leer P, T, z_i

2.- Suponer x_i^{α}, x_i^{β}, θ_1, θ_2

3.- Calcular y_i

4.- Calcular γ_i^{α}, γ_i^{β}, ϕ_i^{s} ,ϕ_i^{V}

5.- Calcular K_i', K_i''

6.- Calcular θ_1, θ_2

7.- Calcular x_i^{α}, x_i^{β}, y_i

8.- Comparar con los valores supuestos: NO, ir a 4.

SI, fin