Propiedades diferenciales exactas

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y$$

$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial f}\right)_x}$$

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{dy}{df}\right)_x = -1$$

Ec. fundamentales - Relaciones de Maxwell

$$dU = TdS - Pdv \qquad \left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_v$$

$$dH = TdS + vdP \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial S}\right)_P$$

$$dF = -SdT - Pdv \qquad \left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$dG = -SdT + vdP \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

Definiciones termodinámicas

$$T = \left(\frac{\partial U}{\partial S}\right)_v = \left(\frac{\partial H}{\partial S}\right)_P$$

$$-P = \left(\frac{\partial U}{\partial v}\right)_S = \left(\frac{\partial F}{\partial v}\right)_T$$

$$v = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_v = \left(\frac{\partial G}{\partial T}\right)_P$$

Ec. diferenciales de H, U, S

$$dU = C_v\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv$$

$$dH = C_P\,dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

$$dS = \frac{C_v}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$dS = \frac{C_P}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

Relaciones de C_v y C_P

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_P}{\partial v}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \left(\frac{\partial P}{\partial v}\right)_T$$

$$C_P - C_v = -T\left[\left(\frac{\partial v}{\partial T}\right)_P\right]^2 \left(\frac{\partial P}{\partial v}\right)_T$$

Coeficiente de expansión volumétrica, β

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

Coeficiente de compresibilidad isotérmica, κ

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Coeficiente de Joule-Thompson

$$\mu = \left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]\frac{1}{C_P}$$

Ecuación Clapeyron

$$\left(\frac{dP}{dT}\right)^{\text{sat}} = \frac{\Delta S^{\alpha\beta}}{\Delta v^{\alpha\beta}}$$

Ecuación Clausius-Clapeyron

$$\left(\frac{d\ln P}{dT}\right)^{\text{sat}} = \frac{\Delta H^{lv}}{RT^2}$$

Propiedades de gases ideales

$$dU = C_v\,dT; \qquad dH = C_P\,dT$$

$$dS = C_v\,d\ln T + R\,d\ln v$$

$$dS = C_P\,d\ln T - R\,d\ln P$$

$$C_P - C_v = R; \qquad \mu = 0$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = 0; \qquad \left(\frac{\partial C_v}{\partial v}\right)_T = 0$$

Principio de estados correspondientes (PEC)

$$Z = \frac{Pv}{RT}$$

$$Z = Z^0 + \omega Z^1$$

$$\omega = -\log_{10}\left(P_r^{\text{sat}}\right)_{T_r=0.7} - 1$$

Propiedades residuales

$$M^{\mathrm{R}}(T,P) = M(T,P) - M^{\mathrm{gi}}(T,P)$$

$$H^{\mathrm{R}}(T,P) = \int_0^P \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

$$S^{\mathrm{R}}(T,P) = -\int_0^P \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right]dP$$

$$H^{\mathrm{R}}(T,P) = -T^2 R\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

$$\frac{H^{\mathrm{R}}}{RT_c} = -T_r^2\int_0^{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r}$$

Pitzer/Lee-Kesler

$$\frac{H^{\mathrm{R}}}{RT_c} = \frac{(H^{\mathrm{R}})^0}{RT_c} + \omega\frac{(H^{\mathrm{R}})^1}{RT_c}$$

$$\frac{S^{\mathrm{R}}}{R} = \frac{(S^{\mathrm{R}})^0}{R} + \omega\frac{(S^{\mathrm{R}})^1}{R}$$

Fugacidad, f

- Componente gaseoso

$$f = P\exp\left(\frac{G^R(T,P)}{RT}\right)$$

- Componente líquido

$$f = \phi^{\text{sat}} P^{\text{sat}} \exp\left[\frac{v^{\text{sat}}\left(P - P^{\text{sat}}\right)}{RT}\right]$$

Coeficiente de fugacidad, ϕ

$$\ln\phi = \ln\left(\frac{f}{P}\right) = \int_0^P (Z-1)\frac{dP}{P} = \frac{G^{\text{R}}}{RT}$$

Cálculo del Coeficiente de fugacidad

- Propiedades residuales

$$\ln\phi = \frac{H^R}{RT} - \frac{S^R}{R}$$

- Ecuación de El Virial truncada

$$\ln\phi = \frac{P_r}{T_r}\left(B^0 + \omega B^1\right)$$

- Pitzer/Lee-Kesler

$$\phi = (\phi^0)(\phi^1)^\omega$$

Ecuaciones de estado

- Ecuación de El virial

$$Z = \frac{Pv}{RT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \cdots$$

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r}$$

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$\frac{H^{\text{R}}}{RT_c} = P_r\left[B^0 - T_r\frac{dB^0}{dT_r} + \omega\left(B^1 - T_r\frac{dB^1}{dT_r}\right)\right]$$

$$\frac{S^{\text{R}}}{R} = -P_r\left(\frac{dB^0}{dT_r} + \omega\frac{dB^1}{dT_r}\right)$$

$$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}}; \qquad \frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}}$$

- Ecuación Soave-Redlich-Kwong

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

$$a = 0.42748\,\frac{(RT_c)^2}{P_c}\alpha, \quad b = 0.08664\,\frac{RT_c}{P_c}$$

$$\alpha = \left[1 + \left(0.48 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{Tr}\right)\right]^2$$

$$A = 0.42748\left(\frac{P_r}{T_r^2}\right)\alpha, \qquad B = 0.08664\left(\frac{P_r}{T_r}\right)$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$H^R = RT(Z-1) + \frac{T(da/dT) - a}{b}\ln\left(\frac{Z+B}{Z}\right)$$

$$S^R = R\ln(Z-B) + \frac{(da/dT)}{b}\ln\left(\frac{Z+B}{Z}\right)$$

$$\frac{da}{dT} = -0.4278\frac{R^2T_c}{P_c}\frac{\left(1 + \Omega\left(1 - \sqrt{T_r}\right)\right)\Omega}{\sqrt{T_r}}$$

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

- Ecuación Peng-Robinson

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2}$$

$$\alpha = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - \sqrt{Tr}\right)\right]^2$$

$$a = 0.45724\,\frac{(RT_c)^2}{P_c}\alpha$$

$$b = 0.07780\,\frac{RT_c}{P_c}$$

$$A = 0.45724\left(\frac{P_r}{T_r^2}\right)\alpha \qquad B = 0.07780\left(\frac{P_r}{T_r}\right)$$

$$Z^3 + (B-1)Z^2 + (A - 2B - 3B^2)Z - AB + B^2 + B^3 = 0$$

$$H^R = RT(Z-1) + \frac{T(da/dT) - a}{2\sqrt{2}b}\ln\left[\frac{\left(1+\sqrt{2}\right)B + Z}{\left(1-\sqrt{2}\right)B + Z}\right]$$

$$S^R = R\ln(Z-B) + \frac{(da/dT)}{2\sqrt{2}\,b}\ln\left[\frac{\left(1+\sqrt{2}\right)B + Z}{\left(1-\sqrt{2}\right)B + Z}\right]$$

$$\frac{da}{dT} = -\frac{a}{T}\left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\sqrt{\frac{T_r}{\alpha}}$$

$$\ln\phi = Z - 1 - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right)$$

Ecuación de Rackett

$$v^{\text{sat}} = v_c Z_c^{(1-T_r)^{0.2857}}$$

Resolvente de Cardano

$$z^3 + az^2 + bz + c = 0$$

- Se calcula los parámetros Q y R

$$Q = \frac{a^2 - 3b}{9}; \quad R = \frac{2a^3 - 9ab + 27c}{54}$$

- Si $R^2 < Q^3$

$$z_1 = -2\sqrt{Q}\cos\left(\frac{\theta}{3}\right) - \frac{a}{3}$$

$$z_2 = -2\sqrt{Q}\cos\left(\frac{\theta + 2\pi}{3}\right) - \frac{a}{3}$$

$$z_3 = -2\sqrt{Q}\cos\left(\frac{\theta - 2\pi}{3}\right) - \frac{a}{3}$$

$$\theta \equiv \arccos\left(\frac{R}{\sqrt{Q^3}}\right)$$

- Si $R^2 > Q^3$

$$A = -\text{sign}(R)\left(|R| + \sqrt{R^2 - Q^3}\right)^{1/3}$$

$$B = \begin{cases} Q/A & \text{Si } A \neq 0 \\ 0 & \text{Si } A = 0 \end{cases}$$

$$z_1 = (A + B) - \frac{a}{3}$$

Sistema multicomponente Para cualquier propiedad termodinámica $nM = f(T, P, n)$:

$$d\,(nM) = \left(\frac{\partial\,(nM)}{\partial T}\right)_{P,n} dT + \left(\frac{\partial\,(nM)}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{\mathcal{C}} \overline{M}_i dn_i$$

Potencial químico

$$\mu_i = \left(\frac{\partial\,(nG)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Propiedad molar parcial

$$\overline{M}_i = \left(\frac{\partial (nM)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Teorema de Euler

$$M = \sum_i x_i \overline{M}_i$$

Ecuación Gibbs-Duhem

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\overline{M}_i = 0$$

Evaluación de prop. molar parcial

- Si $nM = f(T, P, n_1, \cdots, n_{\mathcal{C}})$

$$\overline{M}_i = \left(\frac{\partial (nM)}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

- Si $M = f(T, P, x_1, x_{i-1}, x_{i+1}, \cdots, x_{\mathcal{C}})$

$$\overline{M}_i = M - \sum_{\substack{j\neq i\\ j=1}} x_j \left(\frac{\partial M}{\partial x_j}\right)_{\substack{T,P,x_l\\ l\neq i,\, l\neq j}}$$

Relaciones entre prop. molar parcial

$$d\overline{U}_i = T d\overline{S}_i - P d\overline{v}_i$$
$$d\overline{H}_i = T d\overline{S}_i + \overline{v}_i dP$$
$$d\overline{F}_i = -\overline{S}_i dT - P d\overline{v}_i$$
$$d\overline{G}_i = -\overline{S}_i dT + \overline{v}_i dP$$

Propiedad de cambio de mezclado, ΔM_m

$$\Delta M_m = M - \sum x_i M_i$$

Mezclador adiabático

$$\frac{H_a - H_c}{H_c - H_b} = \frac{x_{1,a} - x_{1,c}}{x_{1,c} - x_{1,b}} = \frac{n_b}{n_a}$$

Mezclas de gases ideales

$$\overline{M}_i^{\text{gi}}(T, P) = M_i^{\text{gi}}(T, p_i)$$
$$\overline{U}_i^{\text{gi}}(T, y_i) = U_i^{\text{gi}}(T)$$
$$\overline{H}_i^{\text{gi}}(T, y_i) = H_i^{\text{gi}}(T)$$
$$\overline{v}_i^{\text{gi}}(T, P, y_i) = v_i^{\text{gi}}(T, P)$$
$$\overline{S}_i^{\text{gi}}(T, P, y_i) = S_i^{\text{gi}}(T, P) - R\ln y_i$$
$$\overline{G}_i^{\text{gi}}(T, P, y_i) = G_i^{\text{gi}}(T, P) + RT\ln y_i$$

Reglas de mezclado

- Ecuación de El virial (truncada)

$$Z = 1 + \frac{B\,P_c}{R\,T_c}\frac{P_r}{T_r}$$

$$B = \sum_i \sum_j y_i y_j B_{ij}$$

con B_{ii} y B_{jj} son los compuestos puros

$$\frac{B_{ii}P_{ci}}{RT_{ci}} = B^0 + \omega_i B^1 \begin{cases} B^0 = 0.083 - \dfrac{0.422}{T_r^{1.6}} \\ B^1 = 0.139 - \dfrac{0.172}{T_r^{4.2}} \end{cases}$$

Con respecto a B_{ij};

$$\frac{B_{ij}P_{cij}}{RT_{cij}} = B^0 + \omega_{ij}B^1 \quad \text{con} \quad T_r = \frac{T}{T_{cij}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij}), \quad P_{cij} = \frac{Z_{cij}\,R\,T_{cij}}{v_{cij}}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

$$v_{cij} = \left(\frac{v_{ci}^{1/3} + v_{cj}^{1/3}}{2}\right)^3$$

- Ecuaciones Peng-Robinson.

$$Z_{\text{mix}}^3 + pZ_{\text{mix}}^2 + qZ_{\text{mix}} + r = 0$$
$$p = B_{\text{mix}} - 1$$
$$q = A_{\text{mix}} - 2B_{\text{mix}} - 3B_{\text{mix}}^2$$
$$r = -A_{\text{mix}}B_{\text{mix}} + B_{\text{mix}}^2 + B_{\text{mix}}^3$$
$$A_{\text{mix}} = \sum_i \sum_j x_i\, x_j A_{ij}$$
$$A_{ij} = (1 - k_{ij})\sqrt{A_i\, A_j}$$
$$B_{\text{mix}} = \sum_i x_i B_i$$
$$\Omega_{\text{mix}} = -\frac{1}{2}\sum_{i=1}^{k}\sum_{j=1}^{k} x_i\, x_j\, A_{ij}\,(\Gamma_i + \Gamma_j) - A_{\text{mix}}$$
$$\Gamma_i = \left(0.37464 + 1.54226\,\omega_i - 0.26992\,\omega_i^2\right)\sqrt{\frac{T_{r_i}}{\alpha_i}}$$
$$\Theta_{\text{mix}} = \Omega_{\text{mix}} + A_{\text{mix}}$$
$$\frac{H^R(T, P)}{RT} = Z_{\text{mix}} - 1 + \cdots$$
$$\cdots + \frac{\Omega_{\text{mix}}}{\sqrt{8}B_{\text{mix}}}\ \ln\left[\frac{Z_{\text{mix}} + \left(1 + \sqrt{2}\right)\ B_{\text{mix}}}{Z_{\text{mix}} + \left(1 - \sqrt{2}\right)\ B_{\text{mix}}}\right]$$
$$\frac{S^R(T, P)}{R} = \ln\left(Z_{\text{mix}} - B_{\text{mix}}\right) + \cdots$$
$$\cdots + \frac{\Theta_{\text{mix}}}{\sqrt{8}B_{\text{mix}}}\ \ln\left[\frac{Z_{\text{mix}} + \left(1 + \sqrt{2}\right)\ B_{\text{mix}}}{Z_{\text{mix}} + \left(1 - \sqrt{2}\right)\ B_{\text{mix}}}\right]$$

- Principio de los estados correspondientes.

$$Z = \frac{PV}{RT} = Z\left(T_r, P_r, \omega\right)$$
$$T_{psr} = \frac{T}{T_{psc}} \qquad P_{psr} = \frac{P}{P_{psc}}$$
$$T_{psc} = \sum_i y_i T_{c,i} \qquad P_{psc} = \sum_i y_i P_{c,i}$$

Coeficiente de fugacidad parcial, $\hat{\phi}_i$

$$\hat{\phi}_i = \left(\frac{\hat{f}_i}{\hat{f}_i^{\text{gi}}}\right) = \left(\frac{\hat{f}_i}{y_i\,P}\right)$$
$$\lim_{P\to 0} \hat{f}_i = y_i P; \quad \lim_{P\to 0} \hat{\phi}_i = 1$$
$$\ln\left(\frac{\hat{f}_i}{\hat{f}_i^{\text{gi}}}\right) = \frac{\overline{G}_i^R}{RT} = \frac{1}{RT}\int_0^P \overline{v}_i^R\,dP$$

Cálculo de coeficiente de fugacidad parcial

- Ecuación El Virial (truncada)

$$\ln\hat{\phi}_k = \frac{P}{RT}\left[B_{kk} + \frac{1}{2}\sum_i\sum_j y_i y_j (2\delta_{ik} - \delta_{ij})\right]$$
$$\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}, \quad \delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj}$$
$$\delta_{ii} = 0, \delta_{kk} = 0, \quad \delta_{ki} = \delta_{ik}$$

- EDE Peng-Robinson

$$\ln\hat{\phi}_i = \frac{B_i}{B_{\text{mix}}}(Z_{\text{mix}} - 1) - \ln(Z_{\text{mix}} - B_{\text{mix}}) - \cdots$$
$$\cdots - \frac{C_i}{2\sqrt{2}}\ln\left[\frac{Z_{\text{mix}} + \left(\sqrt{2}+1\right)B_{\text{mix}}}{Z_{\text{mix}} - \left(\sqrt{2}-1\right)B_{\text{mix}}}\right]$$
$$C_i = \frac{A_{\text{mix}}}{B_{\text{mix}}}\left(\frac{2}{A_{\text{mix}}}\sum_{j=1} y_j A_{ij} - \frac{B_i}{B_{\text{mix}}}\right)$$

Soluciones líquidas ideales

- Generales

$$G^{\text{id}} = \sum x_i \overline{G}_i^{\text{id}} = \sum\nolimits_i x_i G_i + RT\sum\nolimits_i x_i \ln x_i$$
$$S^{\text{id}} = \sum x_i \overline{S}_i^{\text{id}} = \sum\nolimits_i x_i S_i - R\sum\nolimits_i x_i \ln x_i$$
$$V^{\text{id}} = \sum x_i \overline{V}_i^{\text{id}} = \sum x_i V_i$$
$$H^{\text{id}} = \sum x_i \overline{H}_i^{\text{id}} = \sum x_i H_i$$

- Ley de Lewis-Randall

$$\hat{f}_i^{\text{id}} = f_i x_i$$

- Ley de Henry

$$\hat{f}_i^{\text{id}} = \mathcal{H}_i\,x_i = x_i\,f_i^{\infty}$$

Soluciones líquidas no ideales

- Coeficiente de actividad, γ_i

$$\gamma_i = \frac{\hat{f}_i}{f_i x_i}(\text{Lewis/Randall})$$
$$\ln\gamma_i = \frac{\overline{G}_i^{\text{E}}}{RT}$$

- Propiedad de Exceso

$$M^{\text{E}} \equiv M - M^{\text{id}}$$
$$d\left(\frac{nG^{\text{E}}}{RT}\right) = \frac{(nV)^{\text{E}}}{RT}dP - \frac{(nH)^{\text{E}}}{RT^2}dT + \sum_{i=1}^{\mathcal{C}} \ln\gamma_i dn_i$$
$$\left(\frac{\partial\ln\gamma_i}{\partial P}\right)_{T,\vec{x}} = \frac{\overline{v}_i^{\text{E}}}{RT}$$
$$\left(\frac{\partial\ln\gamma_i}{\partial T}\right)_{P,\vec{x}} = -\frac{\overline{H}_i^{\text{E}}}{RT^2}$$
$$\sum_{i=1}^{\mathcal{C}} x_i d\ln\gamma_i = 0$$
$$\frac{G^{\text{E}}}{RT} = \sum_{i=1}^{n} x_i \ln\gamma_i$$
$$v^{\text{E}} = v - v^{\text{id}} = \sum x_i\overline{v}_i - \sum x_i v_i = \Delta v_{\text{m}}$$
$$H^{\text{E}} = H - H^{\text{id}} = \sum x_i\overline{H}_i - \sum x_i H_i = \Delta H_{\text{m}}$$

Test de consistencia termodinámica

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0$$
$$\frac{d\ln\gamma_2}{dx_1} = -\frac{x_1}{x_2}\frac{d\ln\gamma_1}{dx_1}$$
$$\lim_{x_1\to 0}\left(\ln\frac{\gamma_1}{\gamma_2}\right) = \gamma_1^{\infty} \Rightarrow \lim_{x_1\to 0}\frac{G^{\text{E}}}{x_1 x_2 RT} = \gamma_1^{\infty}$$
$$\lim_{x_1\to 1}\left(\ln\frac{\gamma_1}{\gamma_2}\right) = \gamma_2^{\infty} \Rightarrow \lim_{x_1\to 1}\frac{G^{\text{E}}}{x_1 x_2 RT} = \gamma_2^{\infty}$$

Modelos de coeficientes de actividad

- Margules de 2 constantes

$$\frac{G^{\text{E}}}{RT} = x_1 x_2\left[A + B\left(x_1 - x_2\right)\right]$$
$$\ln\gamma_1 = x_2^2\left(A + 3B - 4Bx_2\right)$$
$$\ln\gamma_2 = x_1^2\left(A - 3B + 4Bx_1\right)$$
$$\ln\gamma_1^{\infty} = A - B$$
$$\ln\gamma_2^{\infty} = A + B$$

- Modelo de van Laar

$$\frac{G^{\text{E}}}{x_1 x_2 RT} = \frac{AB}{Ax_1 + Bx_2}$$
$$\ln\gamma_1 = A\left(1 + \frac{Ax_1}{Bx_2}\right)^{-2}$$
$$\ln\gamma_2 = B\left(1 + \frac{Bx_2}{Ax_1}\right)^{-2}$$
$$x_1 = 0 \qquad \ln\gamma_1^{\infty} = A$$
$$x_1 = 1 \qquad \ln\gamma_2^{\infty} = B$$

- Modelo de Wilson

$$\frac{G^{\mathrm{E}}}{RT} = -x_1 \ln\left(x_1 + \Lambda_{12} x_2\right) - x_2 \ln\left(\Lambda_{21} x_1 + x_2\right)$$
$$\ln\gamma_1 = -\ln\left(x_1 + \Lambda_{12} x_2\right) + \beta x_2$$
$$\ln\gamma_2 = -\ln\left(x_2 + \Lambda_{21} x_1\right) - \beta x_1$$
$$\beta \equiv \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2}\right)$$
$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{a_{12}}{RT}\right)$$
$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{a_{21}}{RT}\right)$$
$$\ln\gamma_1^{\infty} = -\ln\Lambda_{12} + (1 - \Lambda_{21})$$
$$\ln\gamma_2^{\infty} = -\ln\Lambda_{21} + (1 - \Lambda_{12})$$

- Modelo de NRTL

$$\frac{G^{\mathrm{E}}}{RT} = x_1 x_2\left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right]$$
$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12} G_{12}}{\left(x_2 + x_1 G_{12}\right)^2}\right]$$
$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21} G_{21}}{\left(x_1 + x_2 G_{21}\right)^2}\right]$$
$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$
$$G_{12} = \exp\left(-\alpha\,\tau_{12}\right) \qquad G_{21} = \exp\left(-\alpha\,\tau_{21}\right)$$
$$\ln\gamma_1^{\infty} = \tau_{21} + \tau_{12}\exp\left(-\alpha\,\tau_{12}\right)$$
$$\ln\gamma_2^{\infty} = \tau_{12} + \tau_{21}\exp\left(-\alpha\,\tau_{21}\right)$$

Extensión a multicomponentes

Modelo	$\ln\gamma_i$	parámetros requeridos
Wilson	$1 - \ln\left[\sum_{j=1}^{n}\Lambda_{ij}\,x_j\right] - \sum_{k=1}^{n}\left[\frac{\Lambda_{ki}\,x_k}{\sum_{j=1}^{n}\Lambda_{kj}\,x_j}\right]$	$\Lambda_{ij} = \frac{V_j}{V_i}\exp\left(\frac{-a_{ij}}{RT}\right)$
NRTL	$\frac{\sum_{j=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k} + \sum_{j=1}^{n}\left[\frac{G_{ij}\,x_j}{\sum_{k=1}^{n}G_{kj}\,x_k}\right]\left[\tau_{ij} - \frac{\sum_{m=1}^{n}\tau_{mj}G_{mj}\,x_m}{\sum_{k=1}^{n}G_{kj}\,x_k}\right]$	$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$ $G_{ji} = \exp\left(-\alpha\tau_{ij}\right)$

Criterio de Equilibrio fásico

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \cdots = \hat{f}_i^{\pi} \quad (i = 1, 2, \cdots N)$$
$$T^{\alpha} = T^{\beta} = T_i^{(j)} = \cdots = T^{\pi}$$
$$P^{\alpha} = P^{\beta} = P_i^{(j)} = \cdots = P^{\pi}$$

Parámetros básicos de ELV

- Factor de vaporización

$$\psi = \frac{V}{F}$$

- Constante de reparto.

$$K_i = \frac{y_i}{x_i}$$

- Volatilidad relativa

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2}$$

Ecuación general de equilibrio

$$y_i\,\hat{\phi}_i\,P = x_i\,\gamma_i\,\phi_i^{\mathrm{sat}} P_i^{\mathrm{sat}}\exp\left[\frac{V_i^{\mathrm{sat}}(P - P_i^{\mathrm{sat}})}{RT}\right]$$

Cálculo de evaporación instantánea

Método de Rachford-Rice (Caso general)

$$y_i = \frac{z_i\,K_i}{1+\psi(K_i-1)}$$

$$x_i = \frac{z_i}{1+\psi(K_i-1)}$$

$$\sum_i \frac{z_i\,(K_i-1)}{1+\psi(K_i-1)} = 0$$

$$\psi\,H_V + (1-\psi)\,H_L - H_F - q = 0$$

Método de Newton-Raphson

Aplicación a ELV conociendo T, P, z_i

- Una ecuación

$$f(\psi) = \sum_{i=1}^{k} \frac{z_i\,(K_i-1)}{\psi\,(K_i-1)+1} = 0$$

$$\psi_n = \psi_{n-1} + \frac{f(\psi_{n-1})}{f'(\psi_{n-1})} \quad n>0$$

$$\psi_n = \psi_{n-1} + \frac{\sum_{i=1}^{k} \dfrac{z_i\,(K_i-1)}{\psi_{n-1}\,(K_i-1)+1}}{\sum_{i=1}^{k} \dfrac{z_i\,(K_i-1)^2}{\left[1+\psi_{n-1}\,(K_i-1)\right]^2}} \quad n>0$$

- Sistema de ecuaciones.
  Suponiendo sistema de dos ecuaciones

$$f_1(x,y) = 0$$

$$f_2(x,y) = 0$$

$$\underbrace{\begin{bmatrix} \dfrac{\partial f_1}{\partial x} & \dfrac{\partial f_1}{\partial y} \\ \dfrac{\partial f_2}{\partial x} & \dfrac{\partial f_2}{\partial y} \end{bmatrix}}_{\mathbf{J}} \cdot \underbrace{\begin{bmatrix} \Delta_1 \\ \Delta_2 \end{bmatrix}}_{\mathbf{Y}} = -\underbrace{\begin{bmatrix} f_1 \\ f_2 \end{bmatrix}}_{\mathbf{F}}$$

$$\mathbf{Y} = -\mathbf{J}^{-1}\cdot\mathbf{F}$$

$$\Delta_1 = x^{(k)} - x^{(k-1)}$$

$$\Delta_2 = y^{(k)} - y^{(k-1)}$$

Relaciones para estimar valores semillas

$$T = \sum x_i T_i^{\text{sat}}$$

$$P = \sum x_i P_i^{\text{sat}}$$

$$K_i = \frac{P_i^{\text{sat}}}{P}$$

Coordenada de reacción, ξ

$$d\xi = \frac{dn_i}{\nu_i}$$

$$\xi = \frac{1}{\nu_i}(n_i - n_{i_0}) \equiv n_i = n_{i_0} + \nu_i\,\xi$$

ν_i: Coeficiente estequiométrico

Para UNA reacción gaseosa

$$n = n_0 + \xi\nu$$

$$y_i = \frac{n_i}{n} = \frac{n_{i_0} + \nu_i\,\xi}{n_0 + \nu\,\xi}$$

$$X_i = \frac{-\nu_i\,\xi}{n_{i_0}} \quad \text{con} \quad 0 \leqslant \alpha \leqslant 1$$

X_i: conversión fraccional.

Reacciones simultáneas

$$\nu_j = \sum_i \nu_{i,j}$$

$$n = n_0 + \sum_j \nu_j\,\xi_j$$

$$y_i = \frac{n_{i_0} + \sum_j \nu_{i,j}\,\xi_j}{n_0 + \sum_j \nu_j\,\xi_j} \quad (i = 1, 2, \cdots N)$$

Actividad, a

$$a_i = \frac{\hat{f}_i}{f_i^0}$$

Criterio de equilibrio

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i\,\nu_i\,d\xi = 0$$

$$\left[\frac{d(nG)}{d\xi}\right]_{T,P} = \sum_i^{\mathcal{C}} \mu_i\,\nu_i = 0$$

Constante de equilibrio químico, K

$$\Delta G^\circ(T_o) = \sum_i^{\mathcal{C}} \nu_i \Delta G^\circ_{f,i}(T_o)$$

$$K = \prod_i \left(\frac{\hat{f}_i}{f_i^\circ}\right)^{\nu_i} = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

Efecto de T. Ecuación de van't Hoff

$$\frac{\Delta H_r^\circ(T)}{RT^2} = \frac{d\ln K(T)}{dT}$$

$$\Delta H_r^\circ(T^\circ) = \sum_i^{\mathcal{C}} \nu_i \Delta H^\circ_{f,i}(T^\circ)$$

$$\Delta H_r^\circ(T) = \Delta H_r^\circ(T^\circ) + \int_{T^\circ}^{T} \Delta C_p^\circ(t)\,dt$$

$$\Delta C_p^\circ = \sum \nu_i C^\circ_{p_i}$$

Cálculo de ΔG_r° a cualquier T

$$\Delta H_r^\circ(T) = \Delta H_r^\circ(T_0) + \int_{T_0}^{T} \Delta C_p^\circ\,dT$$

$$\Delta S_r^\circ(T) = \Delta S_r^\circ(T_0) + \int_{T_0}^{T} \Delta C_p^\circ\,\frac{dT}{T}$$

$$\Delta G_r^\circ(T) = \Delta H_r^\circ(T) - T\,\Delta S_r^\circ(T)$$

Efecto de composición sobre K

Fase gaseosa

$$K = \prod_i (y_i\,\hat{\phi}_i)^{\nu_i}\left(\frac{P}{P^\circ}\right)^{\nu}$$

Fase líquida

$$K = \prod_i (\gamma_i\,x_i)^{\nu_i} \exp\left[\frac{(P - P^\circ)}{RT}\sum_i (V_i\nu_i)\right]$$

Balance de energía en sistema reactivo

$$\dot{Q} = \sum_i n_i^e \int_{T^e}^{T_0} Cp_i^\circ\,dT + \sum_i n_i^s \int_{T_0}^{T^s} Cp_i^\circ\,dT + \cdots$$

$$\cdots + \sum_j^{\mathcal{N}} \xi_j\,\Delta H_j^\circ(T_0)$$