

Mezclas gaseosas ideales

El efecto de p y de la composición están combinados: $p_i = x_i p$

¿Cómo se escribe el potencial químico?

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T, \mathbf{n}} = \left\{ \begin{array}{l} \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} \right]_{T, \mathbf{n}} \stackrel{\text{derivadas cruzadas}}{=} \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial p} \right)_{T, \mathbf{n}} \right]_{T, p, n_{j \neq i}} = V_i \stackrel{\text{gases ideales}}{=} \frac{RT}{p} \\ \left(\frac{\partial \mu_i}{\partial p_i} \right)_{T, \mathbf{n}} \left(\frac{\partial p_i}{\partial p} \right)_{\mathbf{n}} = x_i \left(\frac{\partial \mu_i}{\partial p_i} \right)_{T, \mathbf{n}} \end{array} \right.$$

$\left(\frac{\partial \mu_i}{\partial p_i} \right)_{T, \mathbf{n}} = \frac{RT}{x_i p} = \frac{RT}{p_i}$

integrando, obtengo μ del componente i :
(estado tipo: θ)

$$\mu_i(T, p, x_i) = \mu_i^\theta(T) + RT \ln p_i / p^\theta$$

para mezclas de gases ideales (Euler):

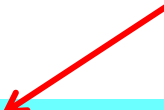
$$G = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^\theta(T) + RT \ln p_i / p^\theta \right)$$

Mezcla de gases reales, fugacidad

se conserva la misma expresión analítica para μ :

(resulta de integrar: $d\mu_i = RT d \ln f_i = V_i dp$)

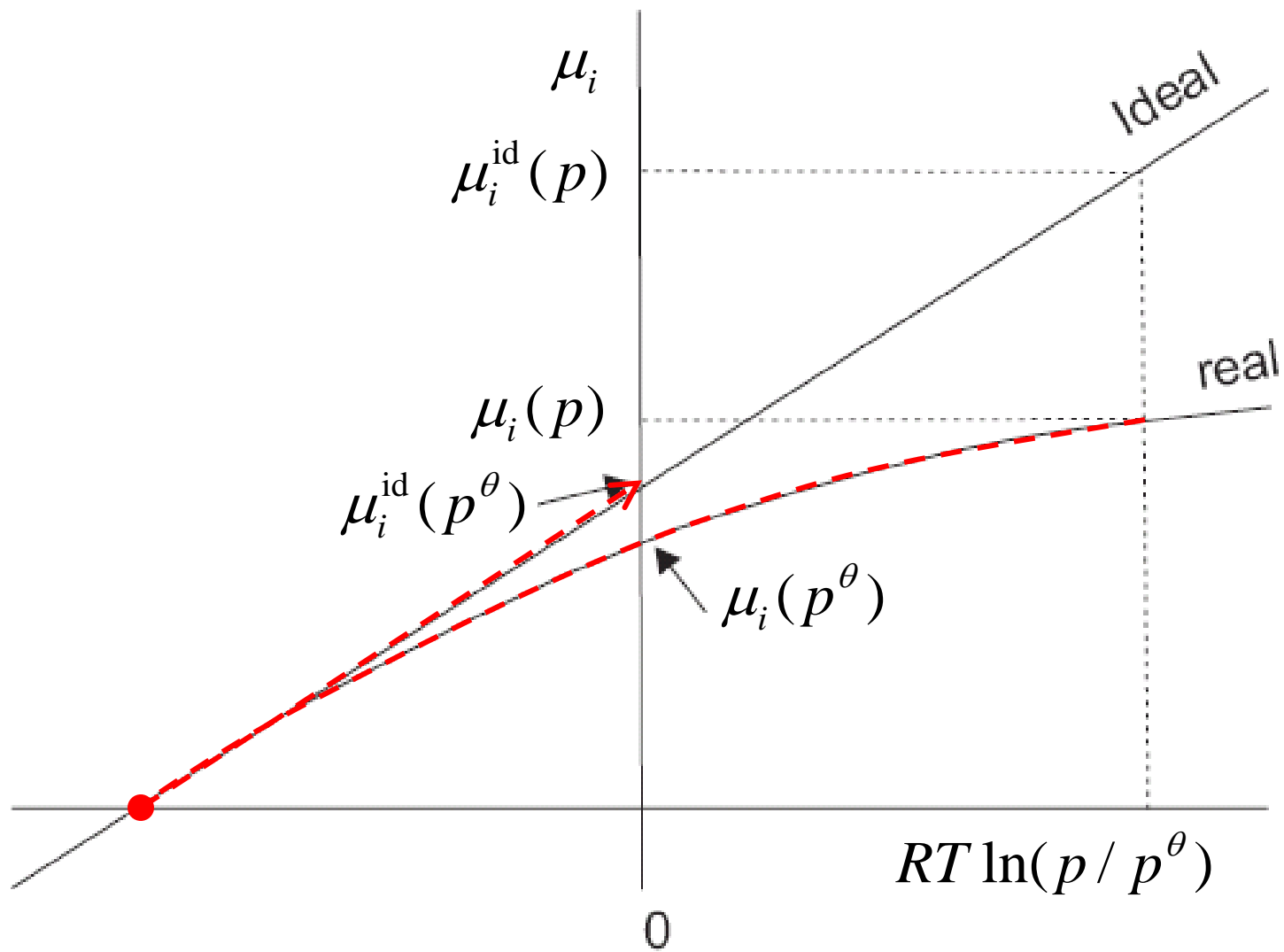
toda la complejidad
(la no-idealidad)


$$\mu_i(T, p, \{x_i\}) = \mu_i^\theta(T) + RT \ln f_i(T, p, \{x_i\}) / p^\theta$$

(estado tipo: θ - fugacidad f_i en vez de p_i)

¿por qué la constante de integración depende sólo de T , cuando las variables que se mantienen fijas durante la integración son T y n ?

Esquema, dependencia del potencial químico con la composición



Coeficiente de fugacidad

¿cómo se calcula?

$$f_i = p_i \varphi_i$$

para 1 componente era: $RT \ln \varphi^* = RT \ln f / p = \int_{p \rightarrow 0}^p (V^* - RT / p) dp$

$$d\mu_i = RT d \ln f_i$$

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T,n} = V_i$$

$$d \ln f_i = \frac{V_i}{RT} dp$$

$$d \ln \frac{f_i}{p} = \left(\frac{V_i}{RT} - \frac{1}{p} \right) dp$$

resto (d ln p)

$$\ln \frac{f_i}{p} - \ln \left(\frac{p_i}{p} \right)_{p \rightarrow 0} = \int_{p \rightarrow 0}^p \left(\frac{V_i}{RT} - \frac{1}{p} \right) dp$$

$$\ln \Phi_i \equiv \ln \frac{f_i}{p_i} = \int_{p \rightarrow 0}^p \left(\frac{V_i}{RT} - \frac{1}{p} \right) dp$$

$p_i/p = x_i = \text{cte}$

$$RT \ln \varphi_i = RT \ln f_i / p_i = \int_{p \rightarrow 0}^p (V_i - RT / p) dp$$

Modelo del virial para mezcla de gases reales

$$\frac{p\bar{V}}{RT} = Z = 1 + \frac{\bar{B}_{\text{mix}}(T)}{\bar{V}} + \frac{\bar{C}_{\text{mix}}(T)}{\bar{V}^2} + \dots \approx 1 + \frac{\bar{B}_{\text{mix}}(T)}{\bar{V}}$$

$$\bar{B}_{\text{mix}} = x_1^2 \bar{B}_{11} + 2x_1 x_2 \bar{B}_{12} + x_2^2 \bar{B}_{22} = x_1 \bar{B}_{11} + x_1 x_2 \Delta_{12} + x_2 \bar{B}_{22}$$

$$\Delta_{12} = 2\bar{B}_{12} - \bar{B}_{11} - \bar{B}_{22}$$

$$dG = \bar{V} dp$$

$$dG(p, T, \mathbf{n}) = \sum_i n_i \left(\frac{RT}{p} + \bar{B}_{\text{mix}} \right) dp$$

integrando

$$G(p, T, \mathbf{n}) - G(p \rightarrow 0, T, \mathbf{n}) = \sum_i n_i \left[RT \ln \left(\frac{p}{p \rightarrow 0} \right) + \bar{B}_{\text{mix}} p \right]$$

(gases ideales)

Reemplazando la expresión de B_{mix} :

$$G(p, T, \mathbf{n}) = n_1 \mu_1^\theta + n_2 \mu_2^\theta + (n_1 + n_2) RT \ln p / p^\theta + \\ + n_1 RT \ln x_1 + n_2 RT \ln x_2 + p \left(n_1 \bar{B}_{11} + n_2 \bar{B}_{22} + \frac{n_1 n_2}{n_1 + n_2} \Delta_{12} \right)$$

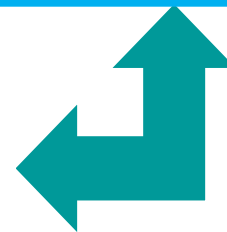
Ahora podemos calcular los potenciales químicos y evaluar φ :

mezcla 1,2

$$\mu_1 \equiv (\partial G / \partial n_1)_{p, T, n_2} = \mu_1^\theta + RT \ln p_1 / p^\theta + p(B_{11} + x_2^2 \Delta_{12})$$

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$$\mu_1 \equiv G / n_1 = \mu_1^\theta + RT \ln p / p^\theta + pB_{11}$$



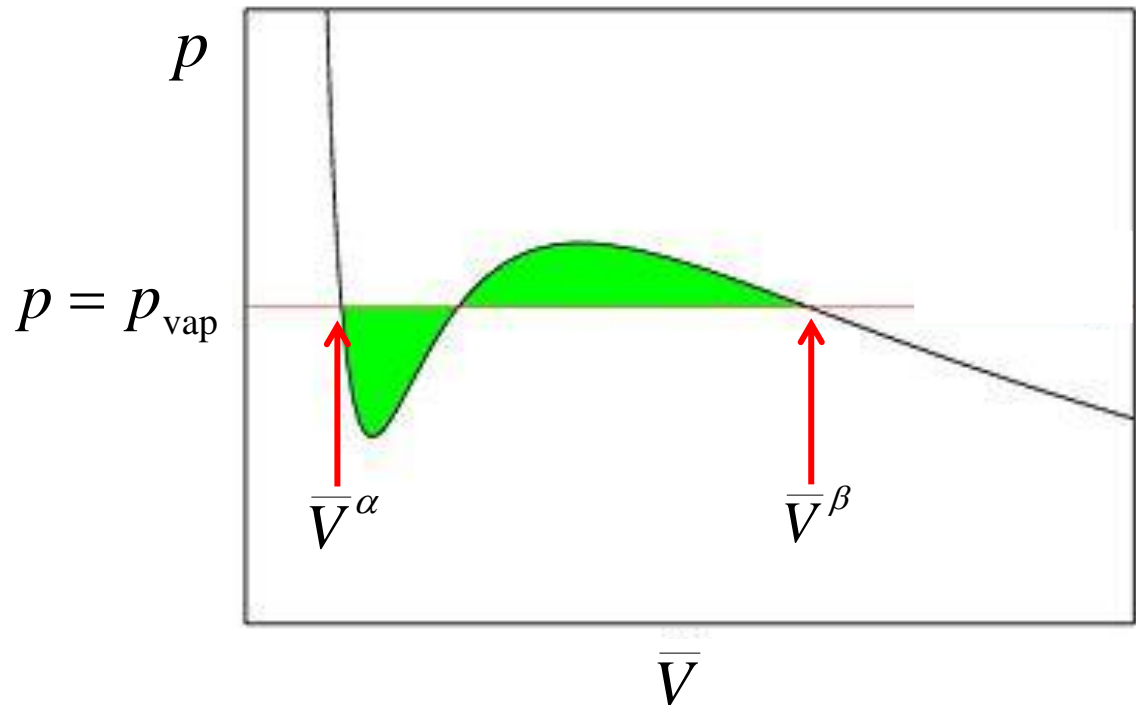
¿qué pasa si la mezcla posee $\Delta_{12}=0$?

Modelo de van der Waals para mezcla de gases reales

$$\left(p + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \quad \left\{ \begin{array}{l} a = \sum_{i,j=1,2} x_i x_j a_{ij} \quad a_{ij} = \sqrt{a_i a_j} \\ b = \sum_{i=1,2} x_i b_i \end{array} \right.$$

$$\mu^\beta - \mu^\alpha = \int_\alpha^\beta \bar{V} dp = 0$$

$$p_{\text{vap}}(\bar{V}^\beta - \bar{V}^\alpha) = \int_\alpha^\beta p d\bar{V}$$



¿Cómo calcular ϕ_{vdW} ?

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T, \{nj\}} = -\left(\frac{\partial p}{\partial n_i}\right)_{T, V, \{nj \neq i\}}$$

$$d\mu_i = RT d \ln f_i = -(\partial p / \partial n_i)_{T, V, nj \neq ni} dV$$

$$RT \ln \phi_i = RT \ln Z + \int_V^{V \rightarrow \infty} \left[(\partial p / \partial n_i)_{T, V, nj \neq ni} + RT / V \right] dV$$

$$RT \ln \phi_1 = \frac{b_1}{V - b} - \ln \left(Z - \frac{pb}{RT} \right) - \frac{2(x_1 a_{11} + x_2 a_{12})}{RTV}$$

Propiedades de mezcla en gases

$$\Delta_{\text{mix}} X = X(p, T, \{x_i\}) - \sum_i n_i X_i^*$$

$$\begin{aligned} \Delta_{\text{mix}} G &= n_1 [\mu_1^\ominus(T) + RT \ln \frac{f_1}{p^\ominus}] + n_2 [\mu_2^\ominus(T) + RT \ln \frac{f_2}{p^\ominus}] \\ &\quad - n_1 [\mu_1^\ominus(T) + RT \ln \frac{f_1^*}{p^\ominus}] - n_2 [\mu_2^\ominus(T) + RT \ln \frac{f_2^*}{p^\ominus}] \end{aligned}$$

$$\Delta_{\text{mix}} G = n_1 RT \ln \frac{f_1}{f_1^*} + n_2 RT \ln \frac{f_2}{f_2^*}$$

$$p_i = x_i p$$

$$f_i = \Phi_i p_i$$

$$\Delta_{\text{mix}} G = \underbrace{n_1 RT \ln \frac{\Phi_1}{\Phi_1^*} + n_2 RT \ln \frac{\Phi_2}{\Phi_2^*}}_{G^{\text{ex}}} + \underbrace{n_1 RT \ln x_1 + n_2 RT \ln x_2}_{\Delta_{\text{mix}} G^{\text{id}}}$$