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Instituto de Química

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Potencial Químico

Equações fundamentais

$$\left. \begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned} \right\} dn = 0$$

Podemos obter as funções termodinâmicas em qualquer condição de pressão e temperatura e modelar processos de interesse

Sistemas abertos

$$dU = TdS - PdV + \sum_{i=1}^k U_{i,m} dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^k H_{i,m} dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^k A_{i,m} dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^k G_{i,m} dn_i$$

Sistemas abertos

$$U_{i,m} = \left(\frac{\partial U}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} \quad A_{i,m} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j}$$

$$H_{i,m} = \left(\frac{\partial H}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} \quad G_{i,m} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$$

Comparando derivadas totais

$$G = H - TS = U + PV - TS$$

$$U = G - PV + TS$$

$$dU = dG - d(PV) + d(TS)$$

$$dU = dG - PdV - VdP + TdS + SdT$$

Comparando derivadas totais

$$dU = dG - PdV - VdP + TdS + SdT$$

Substituindo a derivada total de U e G:

$$dU = TdS - PdV + \sum_{i=1}^k U_{i,m} dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^k G_{i,m} dn_i$$

$$TdS - PdV + \sum U =$$

$$-SdT + VdP + \sum G - PdV - VdP + TdS + SdT$$

Comparando derivadas totais

$$dU = dG - PdV - VdP + TdS + SdT$$

Substituindo a derivada total de U e G:

$$dU = TdS - PdV + \sum_{i=1}^k U_{i,m} dn_i$$

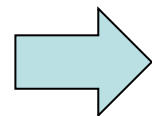
$$dG = -SdT + VdP + \sum_{i=1}^k G_{i,m} dn_i$$

temos:

$$\sum_{i=1}^k U_{i,m} dn_i = \sum_{i=1}^k G_{i,m} dn_i$$

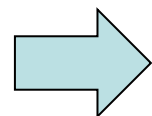
Analogamente

$$G = H - TS$$



$$\sum_{i=1}^k H_{i,m} dn_i = \sum_{i=1}^k G_{i,m} dn_i$$

$$G = A + PV$$



$$\sum_{i=1}^k A_{i,m} dn_i = \sum_{i=1}^k G_{i,m} dn_i$$



$$G = U + PV - TS$$



$$A = U - TS$$

Sistemas abertos

$$dU = TdS - PdV + \sum_{i=1}^k G_{i,m} dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^k G_{i,m} dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^k G_{i,m} dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^k G_{i,m} dn_i$$

Potencial Químico

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^k \mu_i dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

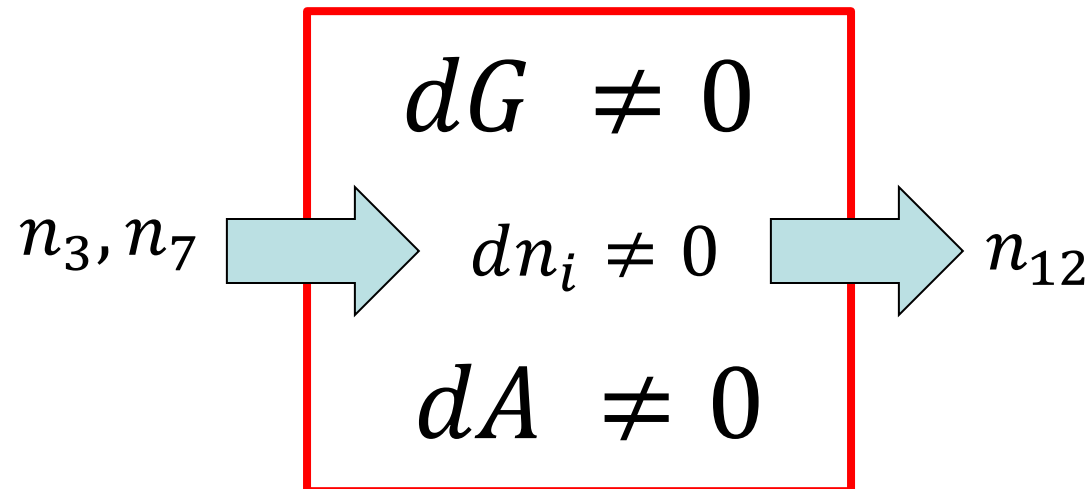
Significado físico do potencial químico

Se V e T constantes:

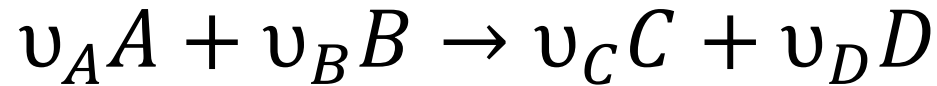
Se P e T constantes:

$$dA = \sum_{i=1}^k \mu_i dn_i \quad dG = \sum_{i=1}^k \mu_i dn_i$$

A mudança da energia livre (A ou G) depende da variação da composição do sistema



Reação química



Se P e T constantes: $dG = \sum_{i=1}^k \mu_i dn_i$

$$dn_A = -d\varepsilon \qquad dn_B = -\frac{\nu_B}{\nu_A} d\varepsilon$$

$$dn_C = \frac{\nu_C}{\nu_A} d\varepsilon \qquad dn_D = \frac{\nu_D}{\nu_A} d\varepsilon$$

$$dG = \frac{d\varepsilon}{\nu_A} (\nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B)$$

$$dG = \frac{d\varepsilon}{\nu_A} \Delta\mu \begin{cases} > 0 \text{ não-espontâneo} \\ = 0 \text{ equilíbrio} \\ < 0 \text{ espontâneo} \end{cases}$$

Dependência de G com pressão

$$dG = -SdT + VdP$$

Se T constante:

$$\int dG = G(T, P) = \int VdP$$

Considerando gás ideal:

$$G(T, P) = \int \frac{RTdP}{P} = RT \int \frac{dP}{P} = \phi(T) + RT \ln P$$

Para n: $G(T, P, n) = n\phi(T) + nRT \ln P$

Potencial químico padrão

$$G(T, P, n) = \underbrace{n\phi(T)} + nRT \ln P$$

$$G(T, P, n) = n\mu^0 + nRT \ln P$$

$$\mu_{ideal} = G_m(T, P, n) = \left(\frac{\partial G(T, P, n)}{\partial n} \right)_{T, P}$$

$$\mu_{ideal}(T) = \mu^0(T) + RT \ln P$$

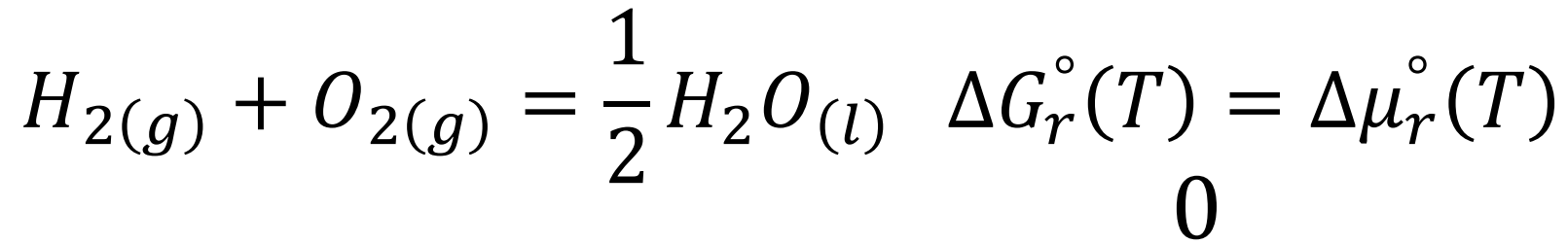
Basta obter os valores para o potencial químico padrão

Potencial químico padrão

Referência para calcular o potencial químico:

Potencial químico padrão: $\mu_i^\circ(T)$

Potencial químico de uma substância i qualquer no estado padrão



$$\Delta \mu_r^\circ(T) = \mu_{H_2O}^\circ(T) - \underbrace{\left(\mu_{H_2}^\circ(T) + \mu_{O_2}^\circ(T) \right)}_0$$

$$\Delta \mu_r^\circ(T) = \mu_{H_2O}^\circ(T) = G_{fH_2O}^\circ(T)$$

Considerando gases ideais

$$dG = \frac{d\xi}{\nu_A} (\nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B)$$

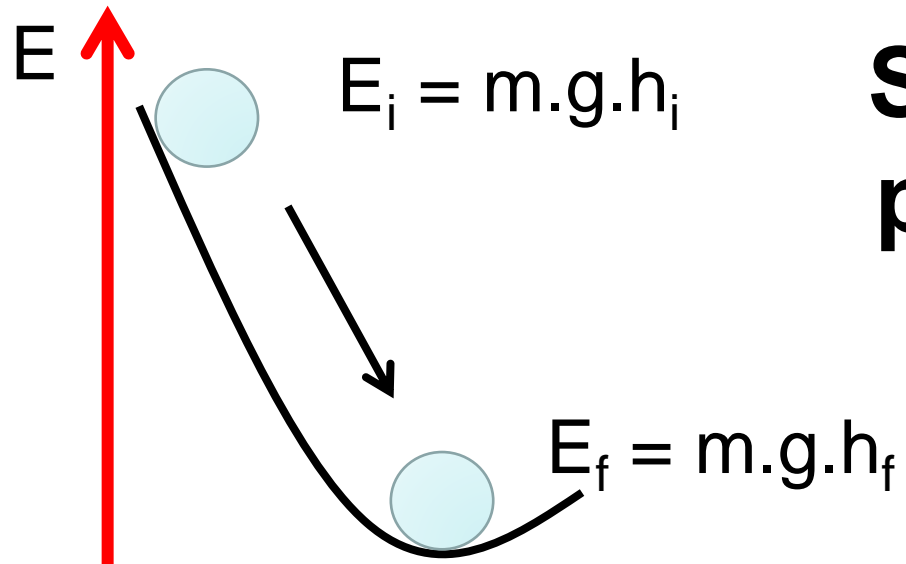
$$\mu_{\text{ideal}} = \mu^0_{\text{ideal}} + RT \ln(P)$$

$$dG = \frac{d\xi}{\nu_A} \Delta\mu^0 + \frac{RT d\xi}{\nu_A} \ln \left(\frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \right)$$

No equilíbrio, $dG = 0$

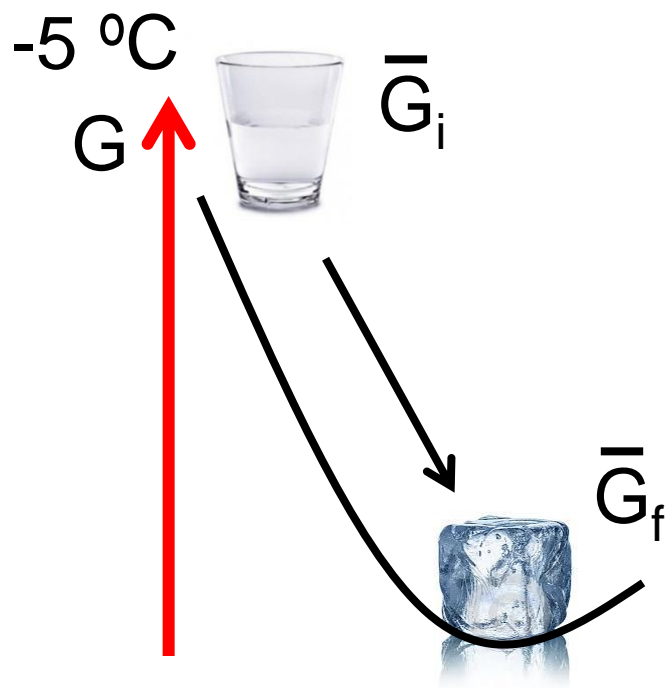
$$\Delta\mu_0 = -RT \ln K_P, K_P = \left(\frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq}$$

$$\Delta G = \Delta G_0 + RT \ln Q$$



**Sistema evolui
para o mínimo
de energia**

$$E_i > E_f$$



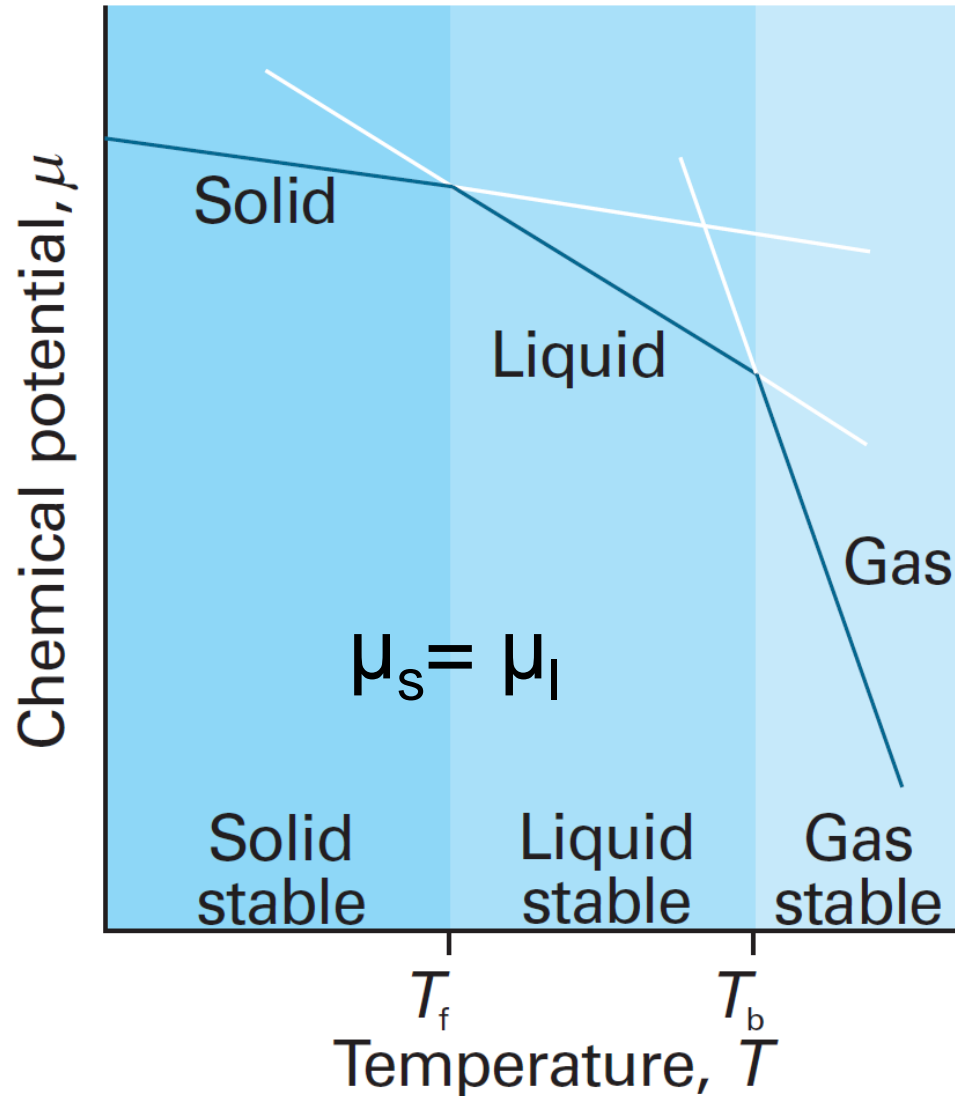
Seja ele físico
ou químico ...

$$\mu_j = \overline{G}_j$$

$$\mu_i > \mu_f$$

Equilíbrio de fases

$$dG = -SdT + VdP + \sum_{i=1}^k G_{i,m} dn_i$$



$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S \quad \left(\frac{\partial \mu}{\partial T}\right)_{P, n_i} = -Sm$$

Derivada total do potencial químico

$$d\mu = \left(\frac{d\mu}{dT}\right)_p dT + \left(\frac{d\mu}{dP}\right)_T dP \Rightarrow d\mu = -\bar{S}dT + \bar{V}dP$$

