Universidade de São Paulo
Instituto de Química

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Aplicações do equilíbrio termodinâmico

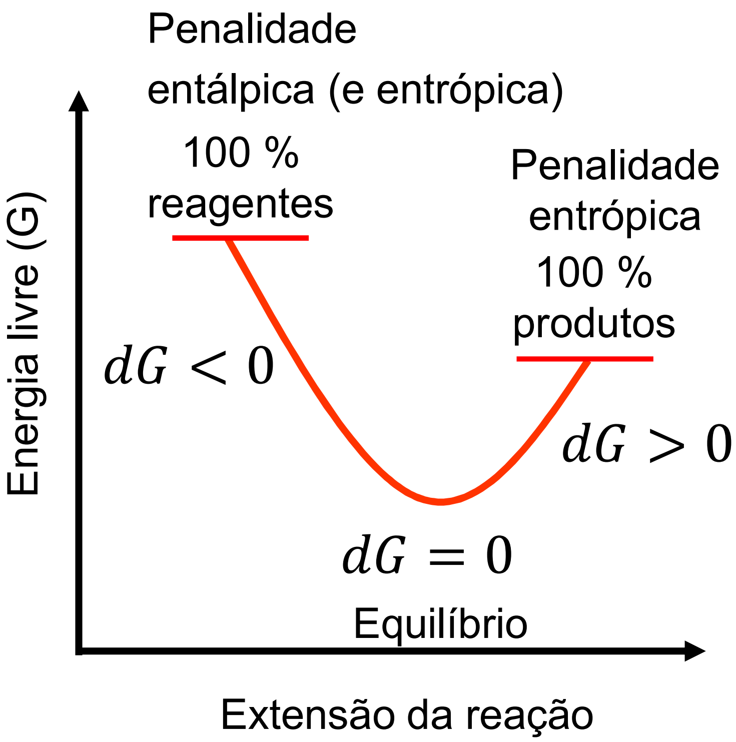
O equilíbrio químico

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

$$dG = \sum_{i=1}^{k} \bar{G}_i dn_i$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$Q = \left(\frac{P_C{}^{\upsilon_C} P_D{}^{\upsilon_D}}{P_A{}^{\upsilon_A} P_B{}^{\upsilon_B}} \right)$$



No equilíbrio:

$$\Delta\mu^0 = -RT \ln K_P \,,$$

$$K_P = \left(\frac{P_C{}^{\upsilon_C} P_D{}^{\upsilon_D}}{P_A{}^{\upsilon_A} P_B{}^{\upsilon_B}} \right)_{eq}$$

Variação de K com a temperatura

$$lnK = -\frac{\Delta G^0}{RT} \Rightarrow \frac{dlnK}{dT} = \frac{\Delta G^0 - T\boxed{\left(\frac{d(\Delta G^0)}{dT}\right)}}{RT^2} \quad \searrow \; -\Delta S^0$$

$$\frac{dlnK}{dT} = \frac{\Delta G^0 + T\Delta S^0}{RT^2} = \frac{\Delta H^0}{RT^2} \Rightarrow \int_{T_1}^{T_2} dlnK = \int_{T_1}^{T_2} \frac{\Delta H^0}{RT^2}\, dT$$

Se $T_1 \cong T_2$,ΔH^0 pode ser considerado constante :

$$ln\frac{K\,(T_2)}{K(T_1)} = \frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Variação de K com a temperatura

$$\int_{T_1}^{T_2} dlnK = \int_{T_1}^{T_2} \frac{\Delta H^0}{RT^2}\, dT$$

E se ΔH^0 não for considerado constante? $\left(\frac{\partial \Delta H^0}{\partial T}\right)_P = \Delta C_P{}^0$

$$\Delta C_P{}^0 = \sum_i \upsilon_i C_{Pi}{}^0 \qquad \Delta C_{Pi}{}^0 = \Delta a + \Delta bT + \Delta cT^2$$

⇩

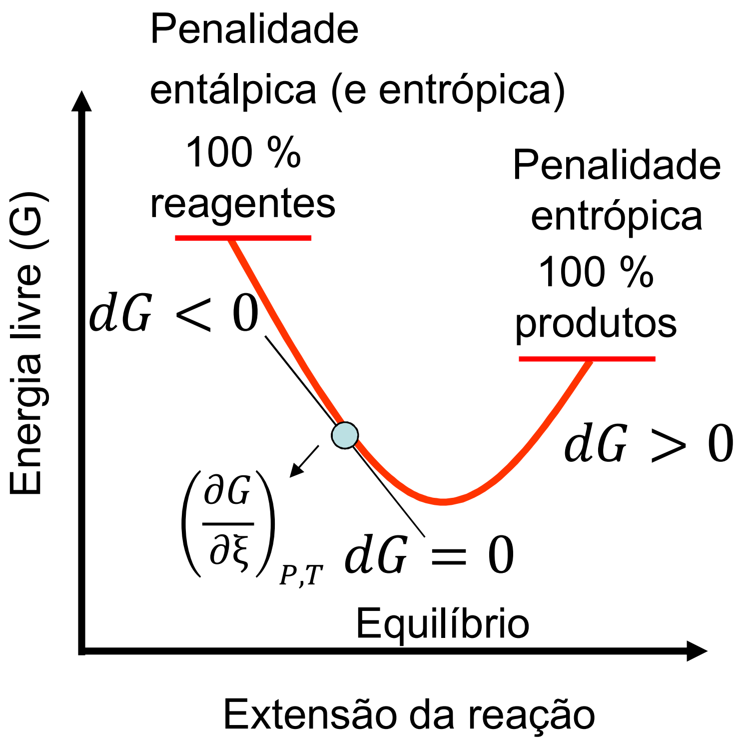
$$\Delta H^0 = \Delta aT + \frac{1}{2}\Delta bT^2 + \frac{1}{3}\Delta cT^3 + \Delta'$$

⇩

$$lnK = -\frac{\Delta'}{RT} + \frac{\Delta a}{R} lnT + \frac{\Delta b}{2R} T + \frac{\Delta c}{6R} T^2 + \Delta''$$

O equilíbrio químico

$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$ $\Delta H_0 = -25\ \text{kJ mol}^{-1}$ $\Delta G = \Delta G^0 + RT \ln Q$



No equilíbrio:

$$K_P = \left(\frac{x_C}{x_A x_B}\right)\frac{1}{P}_T$$

$$ln\frac{K\,(T_2)}{K(T_1)} = \frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Downarrow$$

$$K_P(T) = C\ e^{\frac{-\Delta H_0}{RT}}$$

O equilíbrio químico

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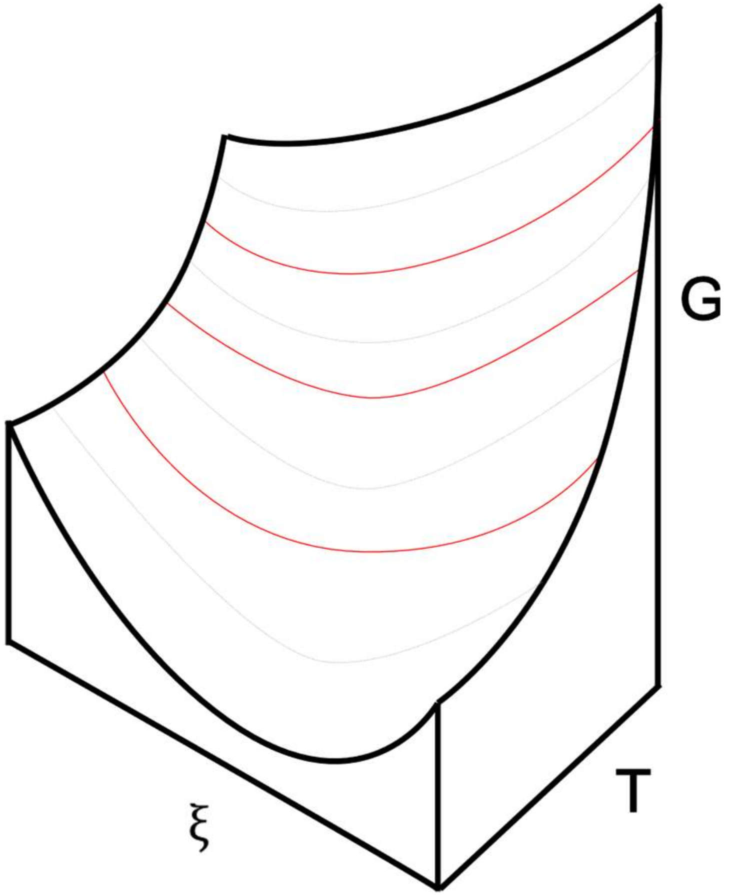

No equilíbrio:

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$$ln \frac{K\,(T_2)}{K(T_1)} = \frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$K_P(T) = C\, e^{\frac{-\Delta H^0}{RT}}$$

O equilíbrio químico

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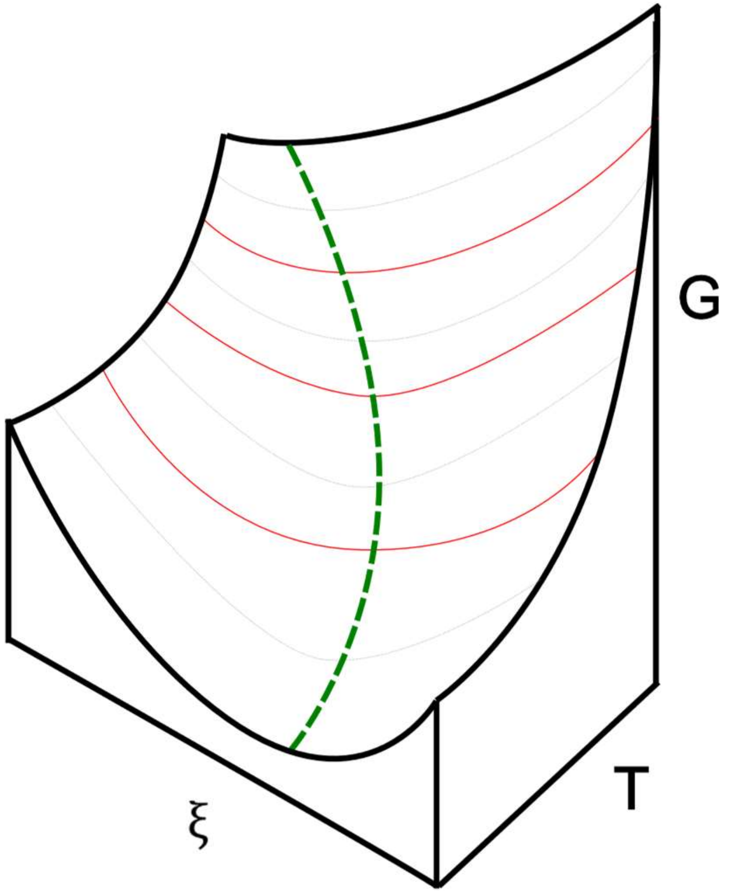
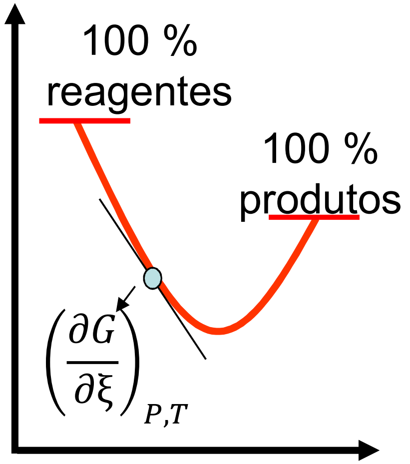


O critério para encontrar equilíbrio:



$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T}$$

Depende de:

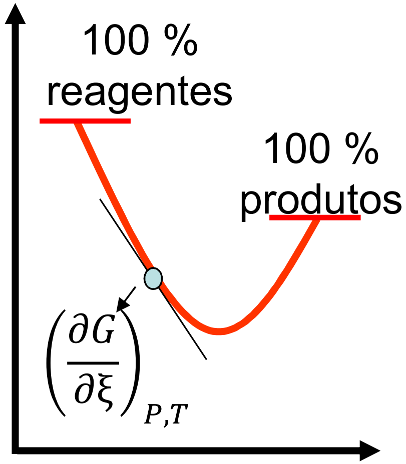
- Temperatura
- Pressão
- Extensão da reação

A derivada total:

$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = X\,dP + Y\,dT + Z\,\mathrm{d}\xi$$

Le Chatelier pela termoquímica

$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = X\,dP + Y\,dT + Z\,\mathrm{d}\xi$$



$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \left(\frac{\partial}{\partial \mathrm{P}}\left(\frac{\partial G}{\partial \xi}\right)_{P,T}\right)_{T,\xi} dP + \left(\frac{\partial}{\partial \mathrm{T}}\left(\frac{\partial G}{\partial \xi}\right)_{P,T}\right)_{P,\xi} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \mathrm{d}\xi$$

$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \left(\frac{\partial \Delta G}{\partial \mathrm{P}}\right)_{T,\xi} dP + \left(\frac{\partial \Delta G}{\partial \mathrm{T}}\right)_{P,\xi} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \mathrm{d}\xi$$

$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta V dP - \Delta S dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \mathrm{d}\xi$$

Le Chatelier pela termoquímica

$$d\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta V dP \; - \Delta S dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \mathrm{d}\xi$$

No equilíbrio: $\Delta S = \Delta H / T$ e $\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = 0$

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \mathrm{d}\xi = - \Delta V dP + \frac{\Delta H}{T} dT$$

Derivando em T com P constante:

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \left(\frac{\partial \xi}{\partial T}\right)_{P} = \frac{\Delta H}{T} \left(\frac{\partial T}{\partial T}\right)_{P}$$

Derivando em P com T constante:

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} \left(\frac{\partial \xi}{\partial P}\right)_{T} = - \Delta V \left(\frac{\partial P}{\partial P}\right)_{T}$$

Le Chatelier pela termoquímica

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}\left(\frac{\partial \xi}{\partial P}\right)_T = -\,\Delta V\left(\frac{\partial P}{\partial P}\right)_T$$

$$\left(\frac{\partial \xi}{\partial P}\right)_T = -\frac{\Delta V}{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}}$$

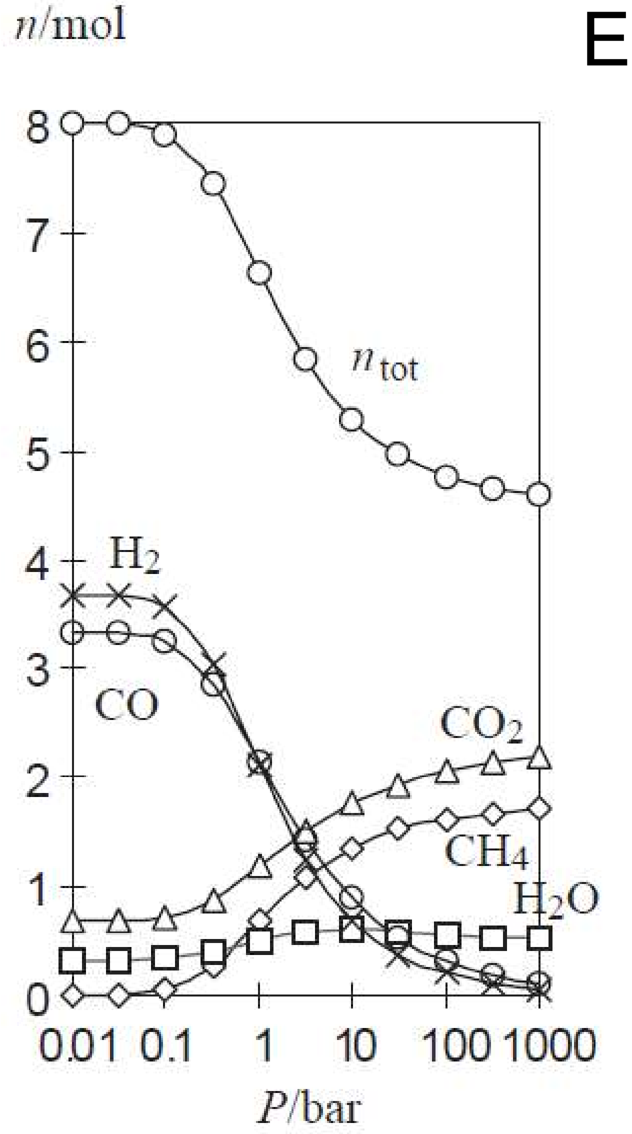
$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta H}{T}\left(\frac{\partial T}{\partial T}\right)_P$$

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta H}{T\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T}}$$

Como $\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{P,T} > 0$ $\quad \left(\frac{\partial \xi}{\partial P}\right)_T \propto -\Delta V, \quad \left(\frac{\partial \xi}{\partial T}\right)_P \propto \frac{\Delta H}{T}$

$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$ $\quad \Delta H_0 = -\ 25\ \mathrm{kJ\ mol^{-1}}$

Equilíbrios simultâneos



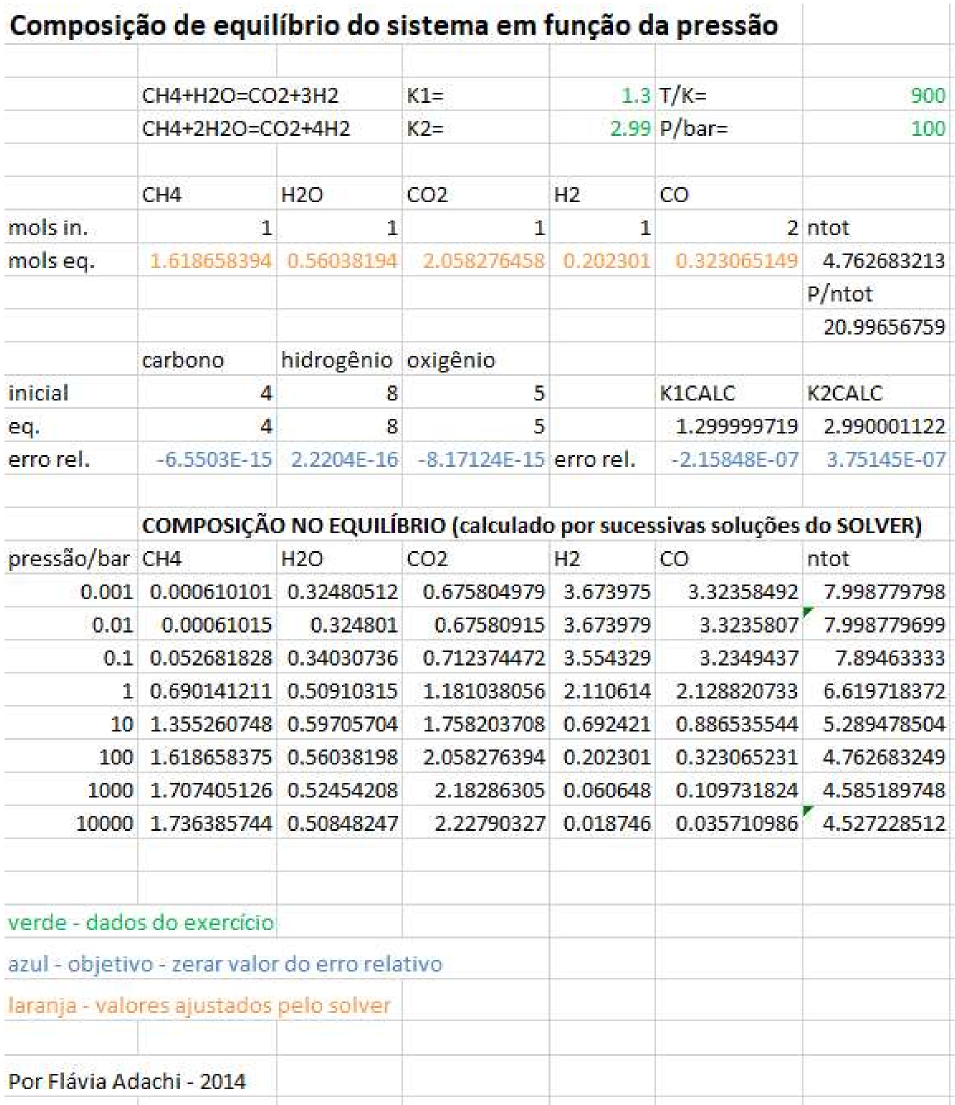
$$(1)\quad CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

$$(2)\quad CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

Ver seção 6.5 Levine

Discussão na aula ao vivo do dia 06 de maio

Equilíbrios simultâneos



Composição de equilíbrio do sistema em função da pressão

	CH4+H2O=CO2+3H2		K1=	1.3	T/K=	900
	CH4+2H2O=CO2+4H2		K2=	2.99	P/bar=	100
	CH4	H2O	CO2	H2	CO	
mols in.	1	1	1	1	2	ntot
mols eq.	1.618658394	0.56038194	2.058276458	0.202301	0.323065149	4.762683213
						P/ntot
						20.99656759
	carbono	hidrogênio	oxigênio			
inicial	4	8	5		K1CALC	K2CALC
eq.	4	8	5		1.299999719	2.990001122
erro rel.	-6.5503E-15	2.2204E-16	-8.17124E-15	erro rel.	-2.15848E-07	3.75145E-07

COMPOSIÇÃO NO EQUILÍBRIO (calculado por sucessivas soluções do SOLVER)

pressão/bar	CH4	H2O	CO2	H2	CO	ntot
0.001	0.000610101	0.32480512	0.675804979	3.673975	3.32358492	7.998779798
0.01	0.00061015	0.324801	0.67580915	3.673979	3.3235807	7.998779699
0.1	0.052681828	0.34030736	0.712374472	3.554329	3.2349437	7.89463333
1	0.690141211	0.50910315	1.181038056	2.110614	2.128820733	6.619718372
10	1.355260748	0.59705704	1.758203708	0.692421	0.886535544	5.289478504
100	1.618658375	0.56038198	2.058276394	0.202301	0.323065231	4.762683249
1000	1.707405126	0.52454208	2.18286305	0.060648	0.109731824	4.585189748
10000	1.736385744	0.50848247	2.22790327	0.018746	0.035710986	4.527228512

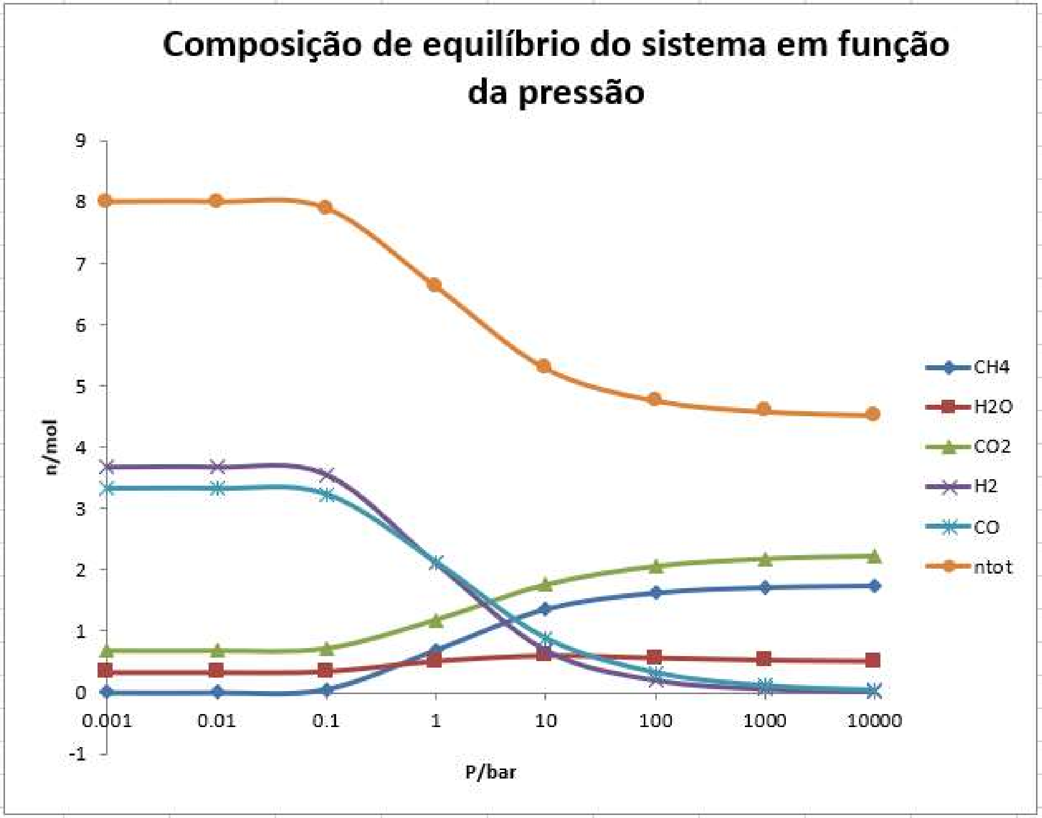
verde - dados do exercício

azul - objetivo - zerar valor do erro relativo

laranja - valores ajustados pelo solver

Por Flávia Adachi - 2014

Habilitar o SOLVER em Arquivo, Opções, Suplementos, selecionar suplementos excel na caixa dropdown e clicar em Ir. Selecionar SOLVER nas opções. Solver deve aparecer no final da faixa superior em "Dados"



Desafio: criar uma série de gráficos como esse para outros 10 valores de temperatura usando os valores de K fornecidos e corrigindo com base nas funções termodinâmicas adequadas e construir uma superfícies de resposta que forneça n em função de P e T!