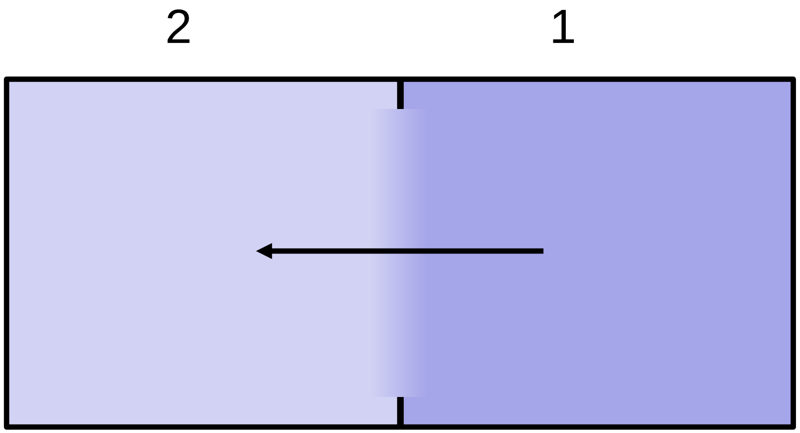
BIF 0442 / 5721 – Fundamentos de TD

Concavidade de S

CONCAVIDADE DE S

- Vamos utilizar o que já foi desenvolvido em “trabalho perdido na difusão”

Generalizar a questão dos volumes



$$n_{1,i} + n_{2,i} = n_T$$

$$V_1 + V_2 = V_T$$

$$C_{1,f} = C_{2,f} = C_f = \frac{n_T}{V_T}$$

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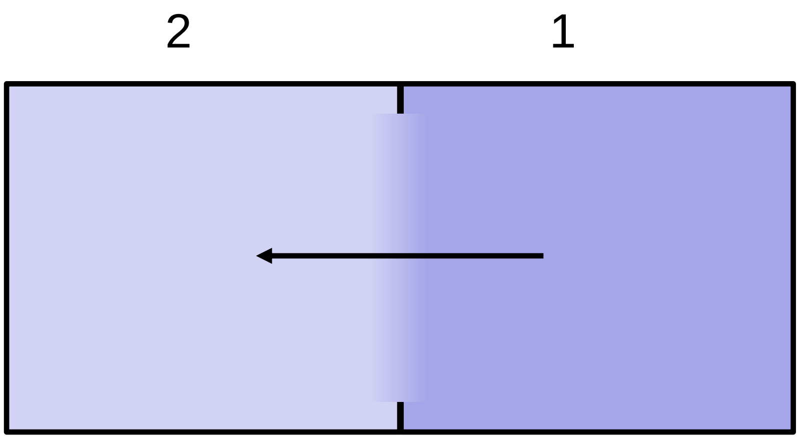

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$$n_{1,i} = \varphi \cdot n_T$$

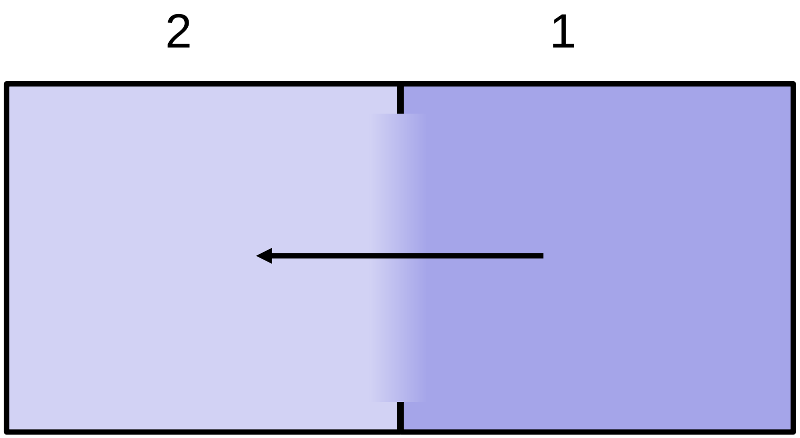
$$V_2 = k \cdot V_1$$

$$k \geq 0$$

$$n_{2,i} = (1 - \varphi) \cdot n_T$$

$$\varphi \in [0\,,1]$$

Generalizar a questão dos volumes



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$$n_{1,i} = \varphi \cdot n_T$$

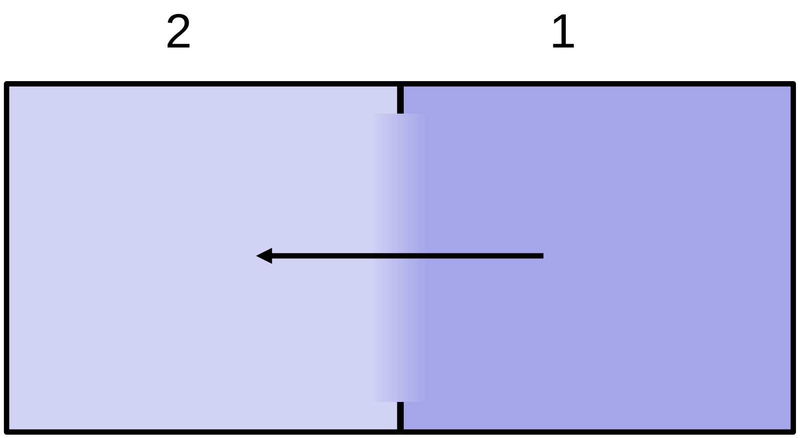
$$n_{2,i} = (1 - \varphi) \cdot n_T$$

$$\varphi \in [0\,,1]$$

$$V_2 = k \cdot V_1 \qquad k \geq 0$$

$$C_f = \frac{n_{1,i}}{V_1 \cdot \varphi \cdot (1 + k)} = C_{1,i} \cdot \frac{1}{\varphi \cdot (1 + k)}$$

Generalizar a questão dos volumes



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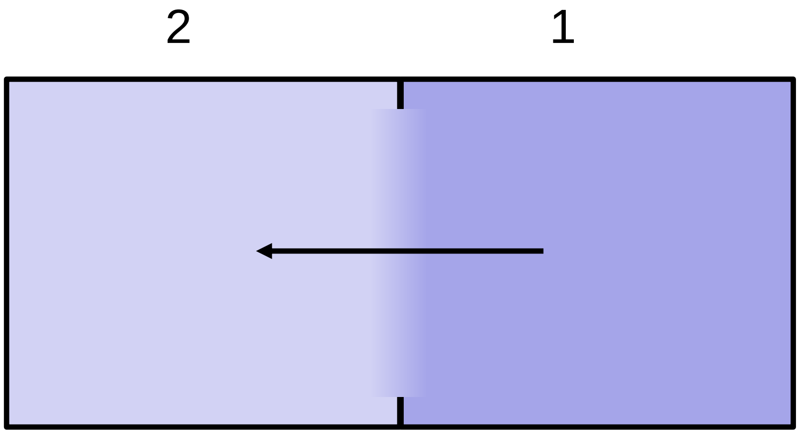
$$n_{1,f} = V_1 \cdot C_f = n_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

$$n_{2,f} = V_2 \cdot C_f = \frac{k \cdot V_1 \cdot n_{1,i}}{V_1 \cdot \varphi \cdot (1+k)} = n_{1,i} \cdot \frac{k}{\varphi \cdot (1+k)}$$

Generalizar a questão dos volumes



$$n_{1,f} = n_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

$$n_{2,f} = n_{1,i} \cdot \frac{k}{\varphi \cdot (1+k)}$$

$$n_{1,i} = \varphi \cdot n_T$$

$$V_2 = k \cdot V_1$$

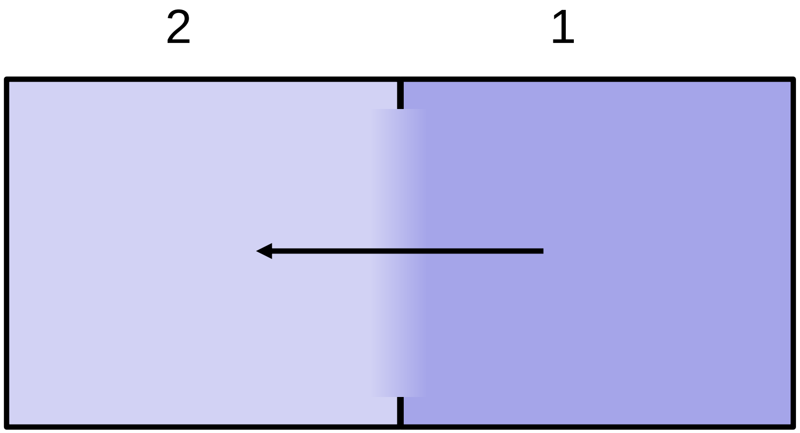
$$n_{2,i} = (1-\varphi) \cdot n_T$$

$$C_f = \frac{n_{1,i}}{V_1 \cdot \varphi \cdot (1+k)} = C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

$$n_{2,i} = n_{1,i} \cdot \frac{(1-\varphi)}{\varphi}$$

$$C_{2,i} = \frac{n_{1,i} \cdot \frac{(1-\varphi)}{\varphi}}{k \cdot V_1} = C_{1,i} \cdot \frac{1-\varphi}{k \cdot \varphi}$$

Generalizar a questão dos volumes



$$n_{1,i} = \varphi \cdot n_T$$

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$$n_{1,f} = n_{1,i} \cdot \frac{1}{\varphi \cdot (1 + k)}$$

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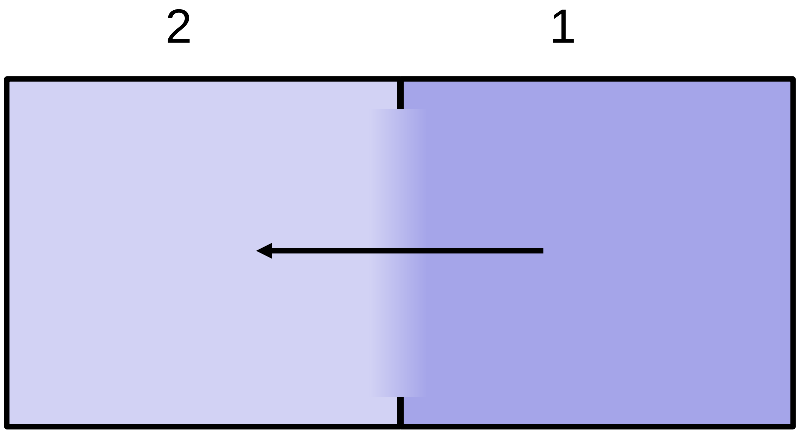
$$n_{2,i} = n_{1,i} \cdot \frac{(1 - \varphi)}{\varphi}$$

$$C_{2,i} = C_{1,i} \cdot \frac{1 - \varphi}{k \cdot \varphi}$$

$$C_f = C_{1,i} \cdot \frac{1}{\varphi \cdot (1 + k)}$$

Generalizar a questão dos volumes



$$n_{1,f} = n_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)} \qquad n_{2,f} = n_{1,i} \cdot \frac{k}{\varphi \cdot (1+k)}$$

$$n_{2,i} = n_{1,i} \cdot \frac{(1-\varphi)}{\varphi}$$

$$C_{2,i} = C_{1,i} \cdot \frac{1-\varphi}{k \cdot \varphi} \qquad C_f = C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

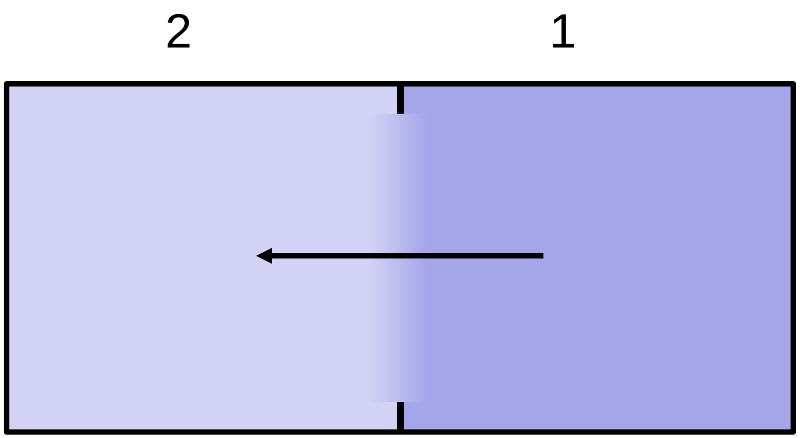
$$\Delta S_T = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = R\left[\left(n_{1,f} - n_{1,i}\right) - n_{1,i} ln\left(\frac{C_{1,f}}{C_{1,i}}\right)\right]$$

$$+ \quad \Delta S_2 = R\left[\left(n_{2,f} - n_{2,i}\right) - n_{2,i} ln\left(\frac{C_{2,f}}{C_{2,i}}\right)\right]$$

$$\Delta S_T = R\left[n_{1,i}\left(\frac{1}{\varphi \cdot (1+k)} - 1 + \frac{k}{\varphi \cdot (1+k)} - \frac{(1-\varphi)}{\varphi}\right) - n_{1,i} ln\left(\frac{C_f}{C_{1,i}}\right) - n_{2,i} ln\left(\frac{C_f}{C_{2,i}}\right)\right]$$

Generalizar a questão dos volumes



$$n_{1,f} = n_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)} \qquad n_{2,f} = n_{1,i} \cdot \frac{k}{\varphi \cdot (1+k)}$$

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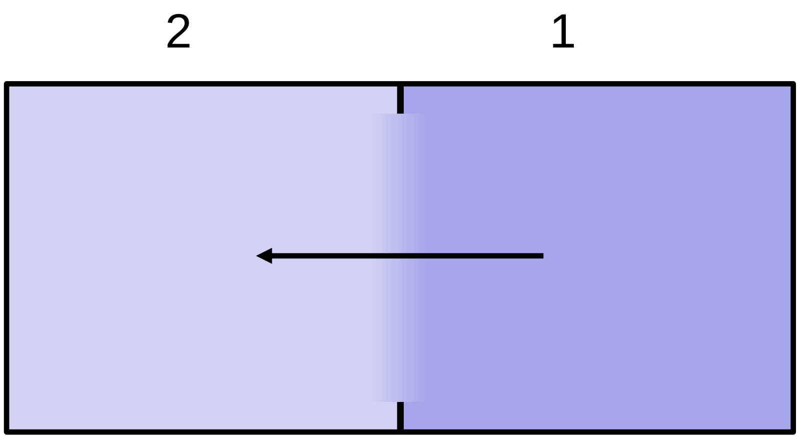
$$C_{2,i} = C_{1,i} \cdot \frac{1-\varphi}{k \cdot \varphi} \qquad C_f = C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

$$\Delta S_T = \Delta S_1 + \Delta S_2$$

0

$$\Delta S_T = R\left[n_{1,i}\left(\frac{1}{\varphi \cdot (1+k)} - 1 + \frac{k}{\varphi \cdot (1+k)} - \frac{(1-\varphi)}{\varphi}\right) - n_{1,i} ln\left(\frac{C_f}{C_{1,i}}\right) - n_{2,i} ln\left(\frac{C_f}{C_{2,i}}\right)\right]$$

Generalizar a questão dos volumes



$$n_{1,f} = n_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

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$$n_{2,i} = n_{1,i} \cdot \frac{(1-\varphi)}{\varphi}$$

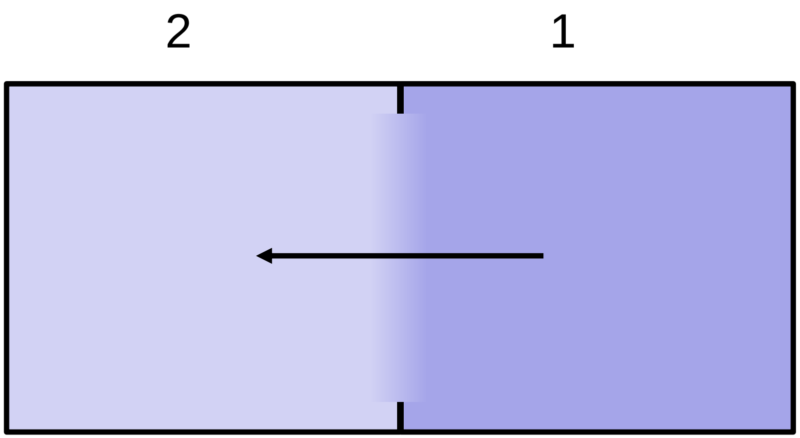
$$C_{2,i} = C_{1,i} \cdot \frac{1-\varphi}{k \cdot \varphi}$$

$$C_f = C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}$$

$$\Delta S_T = R\left[-n_{1,i} ln\left(\frac{C_f}{C_{1,i}}\right) - n_{2,i} ln\left(\frac{C_f}{C_{2,i}}\right)\right]$$

$$\Delta S_T = n_{1,i} R\left[ln\left(\frac{C_{1,i}}{C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}}\right) + \frac{(1-\varphi)}{\varphi} ln\left(\frac{C_{1,i} \cdot \frac{1-\varphi}{k \cdot \varphi}}{C_{1,i} \cdot \frac{1}{\varphi \cdot (1+k)}}\right)\right]$$

Generalizar a questão dos volumes



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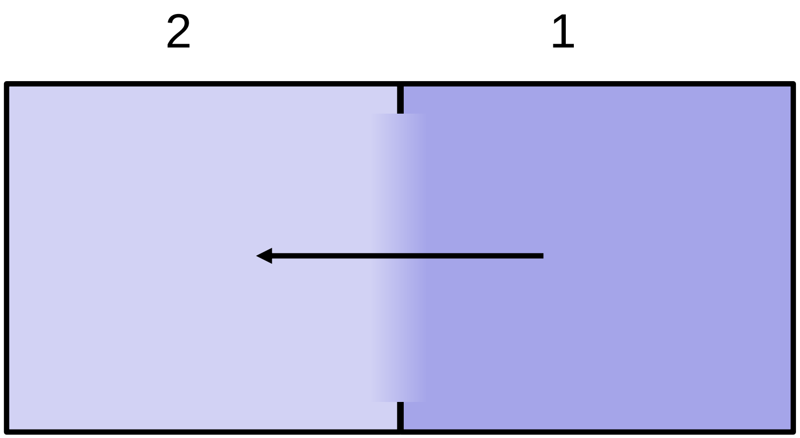
$$\Delta S_T = \frac{n_{1,i}}{\varphi} R \left[\varphi ln(\varphi \cdot (1+k)) + (1-\varphi) ln\left(\frac{(1-\varphi) \cdot (1+k)}{k} \right) \right]$$

Generalizar a questão dos volumes



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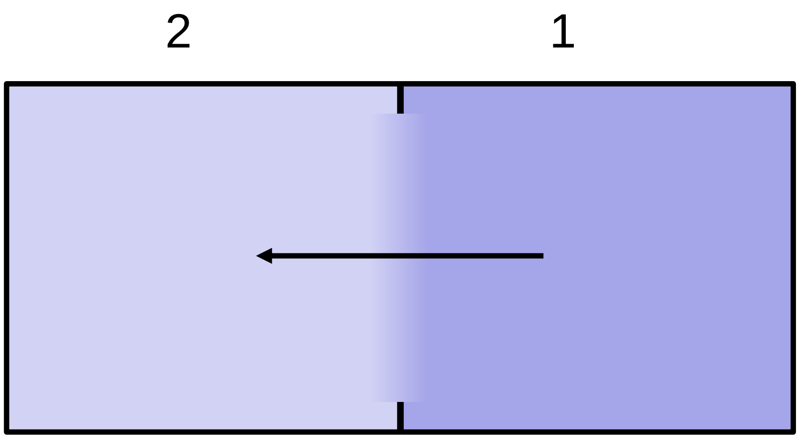
$$\Delta S_T = n_T R \left[\varphi ln(\varphi \cdot (1+k)) + (1-\varphi) ln\left(\frac{(1-\varphi)\cdot(1+k)}{k} \right) \right]$$

$$\Delta S_T = n_T R \left[\varphi ln(k \cdot \varphi) + ln\left(\frac{1+k}{k} \right) + (1-\varphi) ln(1-\varphi) \right]$$

Generalizar a questão dos volumes



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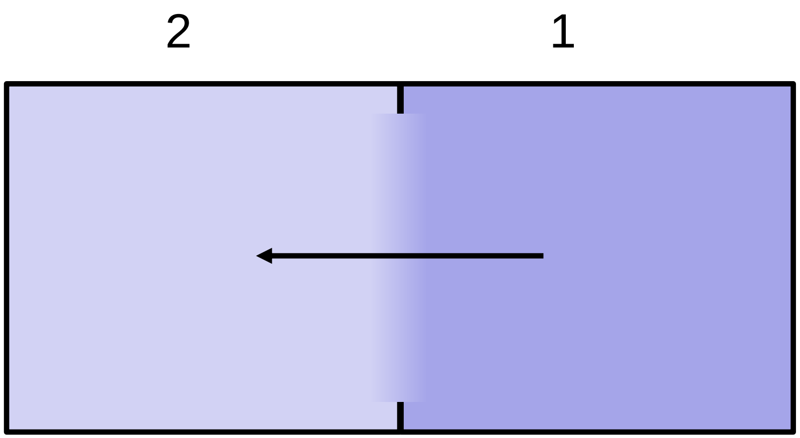
$$\Delta S_T = n_T R \left[\varphi ln \left(\frac{k \cdot \varphi}{1-\varphi} \right) + ln \left(\frac{(1+k) \cdot (1-\varphi)}{k} \right) \right]$$

Generalizar a questão dos volumes

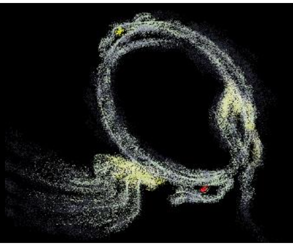


$$\Delta S_T = n_T R \left[\varphi ln \left(\frac{k \cdot \varphi}{1 - \varphi} \right) + ln \left(\frac{(1 + k) \cdot (1 - \varphi)}{k} \right) \right]$$

$$\Delta S_T = n_T R \left[\varphi \cdot ln \left(\frac{\varphi}{1 - \varphi} \right) + ln(2 \cdot (1 - \varphi)) \right]$$

caso já visto, com
k = 1

Concavidade de S – condição inicial



$$\Delta S_T = n_T R\left[\varphi ln\left(\frac{k\cdot\varphi}{1-\varphi}\right) + ln\left(\frac{(1+k)\cdot(1-\varphi)}{k}\right)\right]$$

φ é a condição inicial do sistema

$\varphi \in [0\,,1]$

Concavidade de S – condição de equilíbrio

$$S_{eq} = S(\varphi) + \Delta S(\varphi)$$

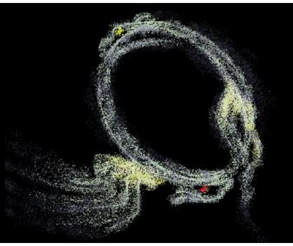
CONCAVIDADE DE S – CONDIÇÃO DE EQUILÍBRIO

$$S_{eq} = S(\varphi) + \Delta S(\varphi)$$

como dS ≥ 0, então

$$S_{eq} = S_{max} \vdash \Delta S = 0$$

Concavidade de S – condição de equilíbrio



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$$S(\varphi) = S_{eq} - \Delta S(\varphi)$$

Concavidade de S – condição de equilíbrio

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como dS ≥ 0, então

$$S_{eq} = S_{max} \vdash \Delta S = 0$$

$$S_{eq} = S(\varphi^*)$$

$$S(\varphi) = S_{eq} - \Delta S(\varphi)$$

$$\frac{dS}{d\varphi} = \frac{dS_{eq}}{d\varphi} - \frac{d\Delta S}{d\varphi}$$

Concavidade de S – condição de equilíbrio

0 pois S_{eq} não depende da condição inicial

$$\frac{dS}{d\varphi} = \frac{dS_{eq}}{d\varphi} - \frac{d\Delta S}{d\varphi}$$

Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

Para S ser ponto de máximo:

Concavidade de S – condição de equilíbrio

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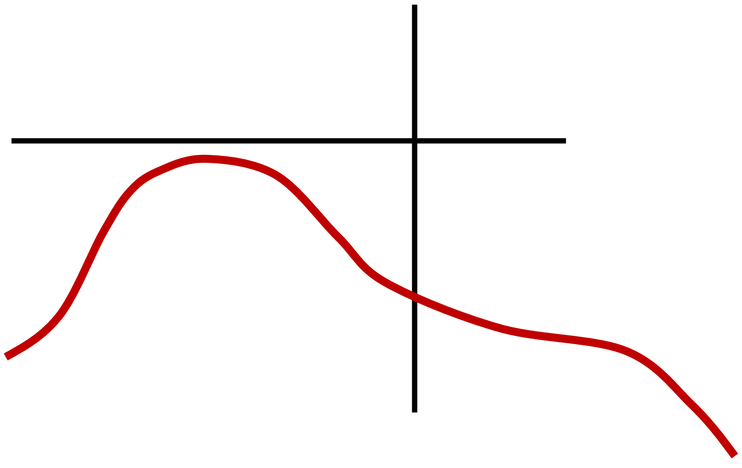

Concavidade de S – condição de equilíbrio

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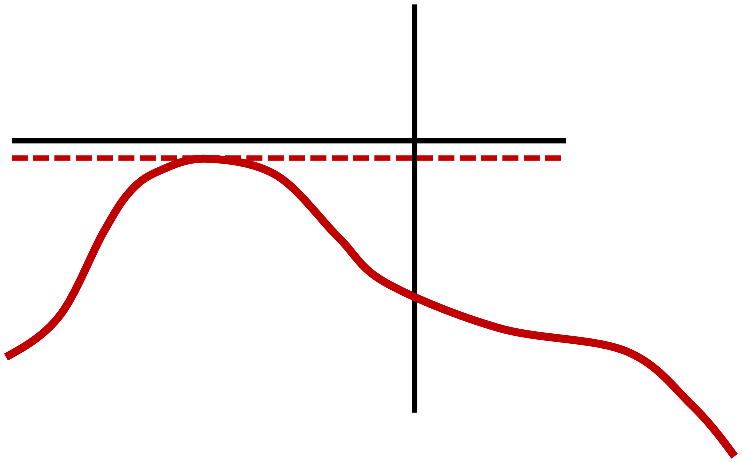
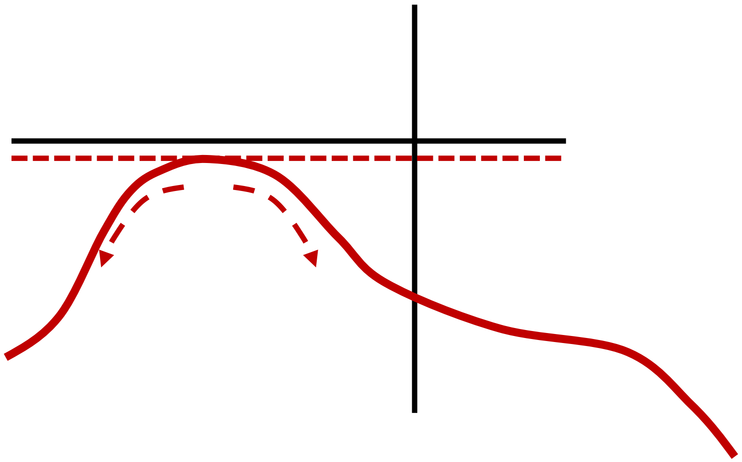
Para S ser ponto de máximo: $\left\{ \frac{dS}{d\varphi} = 0 \right.$



Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

Para S ser ponto de máximo:
$$\begin{cases} \dfrac{dS}{d\varphi} = 0 \\ \dfrac{d^2S}{d\varphi^2} < 0 \end{cases}$$



Concavidade de S – condição de equilíbrio

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Para S ser ponto de máximo:

$$\begin{cases} \dfrac{dS}{d\varphi} = 0 \\[2ex] \dfrac{d^2S}{d\varphi^2} < 0 \end{cases}$$

$$\Delta S_T = n_T R\left[\varphi ln\left(\frac{k\cdot\varphi}{1-\varphi}\right) + ln\left(\frac{(1+k)\cdot(1-\varphi)}{k}\right)\right]$$

Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = 0 \qquad \frac{d^2S}{d\varphi^2} < 0$$

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$\Delta S = n_T R\left[\varphi ln\left(\frac{k \cdot \varphi}{1-\varphi}\right) + ln\left(\frac{(1+k)\cdot(1-\varphi)}{k}\right)\right]$$

$$\Delta S = n_T R[\varphi \ln(k) + \varphi \ln(\varphi) - \varphi \ln(1-\varphi) + \ln(1+k) + \ln(1-\varphi) - \ln(k)\,]$$

Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = 0 \qquad \frac{d^2S}{d\varphi^2} < 0$$

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$$\Delta S = n_T R[\varphi\ln(k) + \varphi\ln(\varphi) - \varphi\ln(1-\varphi) + \ln(1+k) + \ln(1-\varphi) - \ln(k)\,]$$

$$\frac{d\Delta S}{d\varphi} = n_T R\left[\ln(k) + \ln(\varphi) + 1 - \ln(1-\varphi) + \frac{\varphi}{1-\varphi} - \frac{1}{1-\varphi}\right]$$

CONCAVIDADE DE S – CONDIÇÃO DE EQUILÍBRIO

$$\frac{dS}{d\varphi} = 0 \qquad \frac{d^2S}{d\varphi^2} < 0$$

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

-1

$$\frac{d\Delta S}{d\varphi} = n_T R \left[\ln(k) + \ln(\varphi) + 1 - \ln(1-\varphi) + \frac{\varphi}{1-\varphi} - \frac{1}{1-\varphi} \right]$$

Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = 0 \qquad \frac{d^2S}{d\varphi^2} < 0$$

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$\frac{d\Delta S}{d\varphi} = n_T R[\ln(k) + \ln(\varphi) - \ln(1-\varphi)]$$

Concavidade de S – condição de equilíbrio

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$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$-\frac{d\Delta S}{d\varphi} = n_T R \left[ln \frac{1-\varphi}{k\varphi} \right]$$

Concavidade de S – condição de equilíbrio

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$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$-\frac{d\Delta S}{d\varphi} = n_T R \left[ln \frac{1-\varphi}{k\varphi} \right] = 0$$

Concavidade de S – condição de equilíbrio

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$$\left[ln \frac{1-\varphi}{k\varphi} \right] = 0$$

Concavidade de S – condição de equilíbrio

$$\frac{dS}{d\varphi} = 0 \qquad \frac{d^2S}{d\varphi^2} < 0$$

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$\frac{1-\varphi}{k\varphi} = 1$$

Concavidade de S – condição de equilíbrio

$$\frac{d^2S}{d\varphi^2} < 0$$

$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$\frac{dS}{d\varphi} = 0 \longrightarrow \boxed{\varphi = \frac{1}{1+k}}$$

CONCAVIDADE DE S – CONDIÇÃO DE EQUILÍBRIO

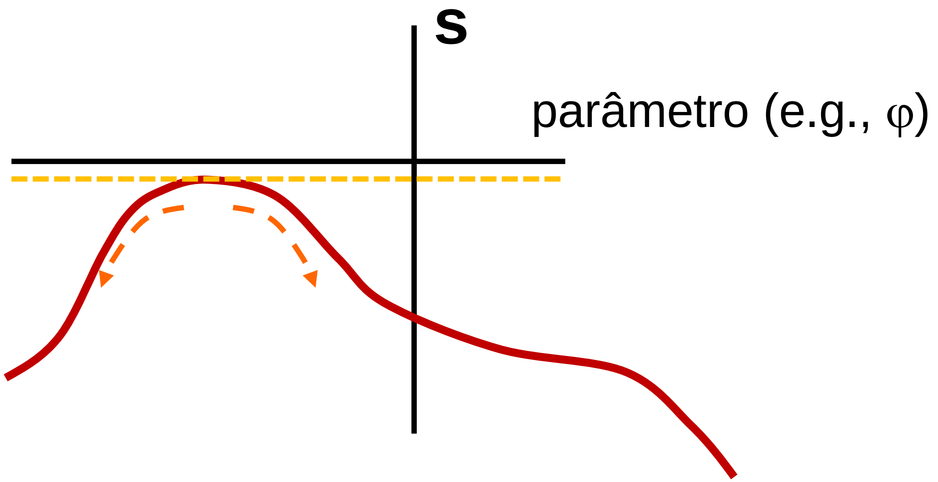
$$\frac{dS}{d\varphi} = -\frac{d\Delta S}{d\varphi}$$

$$\frac{dS}{d\varphi} = 0 \longrightarrow \boxed{\varphi^* = \frac{1}{1+k}}$$

$$\frac{d^2S}{d\varphi^2} < 0 \qquad \boxed{\frac{d\left(-\frac{d\Delta S}{d\varphi}\right)}{d\varphi} = n_T R\left[-\frac{1}{1-\varphi^*} - \frac{1}{\varphi^*}\right] < 0}$$

Concavidade de S

LOGO, A CONDIÇÃO DE EQUILÍBRIO TERMODINÂMICO CORRESPONDE AO PONTO DE MÁXIMO DA ENTROPIA



$$\frac{dS}{d\varphi} = 0 \longrightarrow \boxed{\varphi^* = \frac{1}{1+k}}$$

$$\boxed{\frac{d\left(-\frac{d\Delta S}{d\varphi}\right)}{d\varphi} = n_T R \left[-\frac{1}{1-\varphi^*} - \frac{1}{\varphi^*} \right] < 0}$$

Checar a concavidade de S para K

Concavidade de S – condição inicial

$$\Delta S_T = n_T R \left[\varphi ln\left(\frac{k \cdot \varphi}{1-\varphi}\right) + ln\left(\frac{(1+k)\cdot(1-\varphi)}{k}\right)\right]$$

φ é a condição final do sistema que resulta em igualdade de concentrações

$\varphi \in [0\,,1]$

k $\in [0\,,\infty[$

Checar a concavidade de S para k

Passos:

1. Obter $d\Delta S/dk$
2. Checar a condição para $d\Delta S/dk = 0$ (i.e., k^*)
3. Obter a 2ª derivada de ΔS em relação a k^*
4. Checar se é negativa

EM BRANCO, DE PROÓSITO RSRSRS

resolvam !

EM BRANCO, DE PROÓSITO RSRSRS

Os seguintes resultados devem ser obtidos

$$\frac{dS}{dk} = -\frac{d\Delta S}{dk} = \frac{1-\varphi-\varphi\cdot k}{k\cdot(1+k)} = 0$$

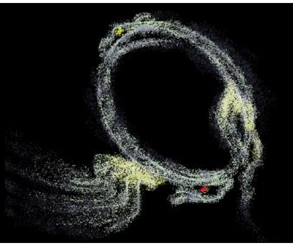
$$k = \frac{1}{1+\varphi}$$

$$\varphi = \frac{1}{1+k}$$

$$\frac{d^2S}{dk^2} = -\frac{1}{\lfloor k\cdot(1+k)\rfloor^2}\cdot\left[2\cdot\frac{1-\varphi}{1+\varphi} + (1-\varphi) - \frac{\varphi}{(1+\varphi)^2}\right]$$

Assim ...

Portanto, $S_{EQ}(k^*)$ é ponto de máximo



$$\frac{dS}{dk} = -\frac{d\Delta S}{dk} = \frac{1 - \varphi - \varphi \cdot k}{k \cdot (1 + k)} = 0$$

$$k^* = \frac{1}{1 + \varphi}$$

$$\varphi = \frac{1}{1 + k}$$

$$\frac{d^2S}{dk^2} = -\frac{1}{\lfloor k \cdot (1 + k) \rfloor^2} \cdot \left[(1 - \varphi) \cdot \frac{2 + \varphi}{(1 + \varphi)^2} \right] < 0$$