①

Processos

Reversíveis

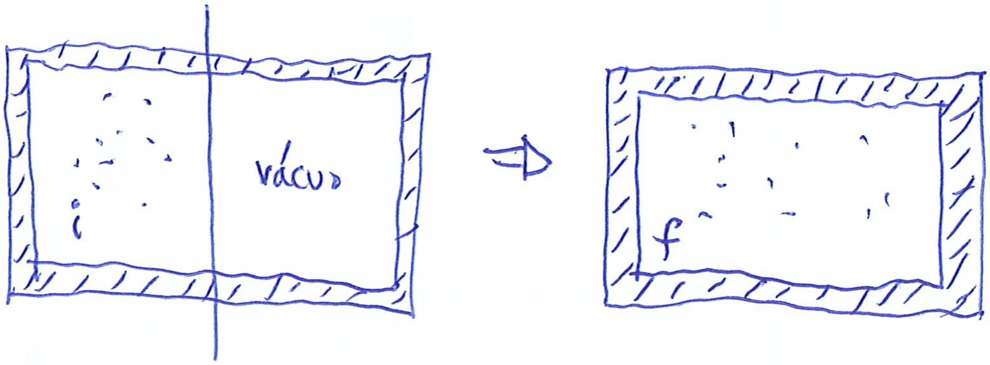
$ds = \frac{dQ}{T}$

Irreversíveis

$\times$

Mas é possível calcular a entropia em processos irreversíveis pois ela só depende dos estados inicial e final.

Ex1 expansão livre: calcule a variação da entropia



$i \to f \left\{ \Delta Q = \Delta U + W \right.$ $W_{if} = 0$ pois não há transferência de momento (e força) nem pressão $p\,dV$

$\Delta Q = 0$ sistema isolado (tr. adiabática)

$\therefore \Delta U_{if} = U_f - U_i = 0 \to U_i = U_f \to T_i = T_f$

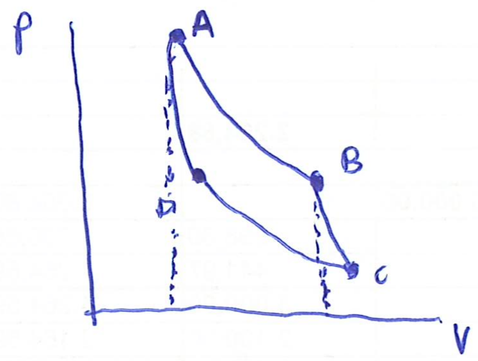
Processo reversível equivalente: transf. isotérmica reversível

$$\begin{cases} dS = \frac{dQ}{T} \to S_f - S_i = \int_{V_i}^{V_f} \frac{dQ}{T} = \frac{1}{T}\Delta Q \\ \Delta Q = \Delta W \quad W_{if} = \int_{V_i}^{V_f} p\,dV = nRT \ln \frac{V_f}{V_i} \end{cases}$$

$\therefore S_f - S_i = \frac{1}{\cancel{T}} nR\cancel{T} \ln \frac{V_f}{V_i} \to \boxed{\Delta S = nR \ln \frac{V_f}{V_i} > 0}$

Entropia aumenta!

Ex 2 ciclo de Carnot : variação da entropia é zero!



AD e BC adiabáticas $dS = \frac{dQ}{T} = 0$

AB : $Q = \cancel{\Delta U}^{0} + W = W$

$$\Delta S_{AB} = nR \ln\left(\frac{V_B}{V_A}\right)$$

$$\Delta S_{CD} = nR \ln\left(\frac{V_D}{V_C}\right)$$

$$\Delta S_{total} = \Delta S_{AB} + \Delta S_{CD} = nR\left[\ln\left(\frac{V_B}{V_A}\right) + \ln\left(\frac{V_D}{V_C}\right)\right]$$

$$= nR \ln\left[\frac{V_B}{V_A}\frac{V_D}{V_C}\right]$$

Tr. adiabáticas $\left\{ TV^{\gamma-1} = cte \right. \rightarrow$ $T_A V_A^{\gamma-1} = T_D V_D^{\gamma-1}$ $\quad \frac{1}{\gamma-1} = \alpha$

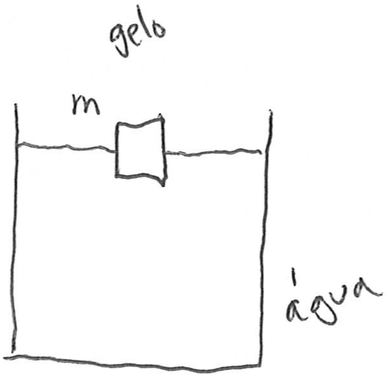
$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}$

$$\left.\begin{array}{l} \frac{V_D}{V_A} = \left(\frac{T_A}{T_D}\right)^{\alpha} \\ \frac{V_B}{V_C} = \left(\frac{T_C}{T_B}\right)^{\alpha} \end{array}\right\} \quad \Delta S = nR \ln\left(\frac{T_A}{T_D}\right)^{\alpha}\left(\frac{T_C}{T_B}\right)^{\alpha}$$

$$= nR \ln\left[\frac{T_A T_C}{T_D T_B}\right]^{\alpha}$$

$$\boxed{\Delta S = nR\alpha \ln\left(\underbrace{\frac{T_A T_C}{T_D T_B}}_{1}\right) = 0 !}$$

Ex 3



L, m

Variação de entropia do gelo na sua fusão? ③

(reversível)

(isotérmico)

$$dS = \frac{dQ}{T} \Rightarrow \Delta S = \int \frac{dQ}{T} = \frac{1}{T}\Delta Q \qquad \Delta Q = mL$$

$$\begin{cases} m = 0{,}235 \text{ kg} \\ L = 333 \ \frac{\text{kJ}}{\text{kg}} \end{cases} \qquad \Delta S = \frac{\Delta Q}{T} = \frac{mL}{T} = \frac{0{,}235 \times 333}{273} = 0{,}287 \ \frac{\text{kJ}}{\text{K}}$$

$$\boxed{\Delta S = 287 \ \frac{\text{J}}{\text{K}}}$$

Ex 4 Gelo aquecido vai de zero a cem °C. ΔS?

$$dS = \frac{1}{T} dQ = \frac{1}{T} mc\, dT \Rightarrow \Delta S = mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln\left(\frac{T_f}{T_i}\right)$$

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⑭ 1 kg

$$\underbrace{-15° \rightarrow 0°C}_{1} \underbrace{\rightarrow 0°C}_{\substack{\text{água} \\ 2}} \underbrace{\rightarrow 100°C}_{3} \underbrace{\rightarrow 100°C}_{\substack{\text{vapor} \\ 4}}$$

$$1 \left\{ \Delta S = mc \ln\left(\frac{T_f}{T_i}\right) = 1(\text{kg}) \times 0{,}5\left(\frac{\text{cal}}{\text{g °C}}\right) \ln \frac{273}{(273-15)} = 0{,}5 \times 4{,}18 \times 1000 \ln \underbrace{\frac{27}{25}}_{0{,}056} \right.$$

$$0{,}5\left(\frac{\text{cal}}{\text{g °C}}\right) = \frac{0{,}5 \times 4{,}18}{10^{-3}} \left(\frac{\text{J}}{\text{kg °C}}\right) \qquad \ldots = 118 \left(\frac{\text{J}}{\text{K}}\right)$$

$$\boxed{\Delta S = 118 \ \frac{\text{J}}{\text{K}}}$$

$L = 79{,}6 \ \frac{cal}{g}$

2 $\left\{ \Delta S = \frac{mL}{T} = 1000\,(g) \times 79{,}6 \left(\frac{\overset{4{,}18J}{\overset{\shortparallel}{cal}}}{g}\right) \times \frac{1}{273\,(K)} \right.$

$$\boxed{\Delta S = 1218 J}$$

3 $\left\{ \Delta S = mc \ln \frac{T_f}{T_i} = 1000\, g \times 1 \left(\frac{\overset{4{,}18J}{\overset{\shortparallel}{cal}}}{g°C}\right) \times \overset{0.31}{\overset{\shortparallel}{\ln\left(\frac{373}{273}\right)}} \right.$

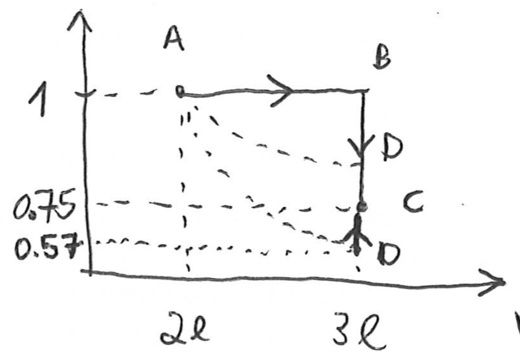
$$\boxed{\Delta S = 1304 \ J}$$

4 $\left\{ \Delta S = \frac{mL}{T} = \frac{1000 \times 539{,}6 \times 4{,}18}{373} \boxed{= 6047 J} \right.$

15

$\gamma = 1.4$

$V = 2\ell$



CNPT ($0°C$, 1atm)

$\left\{ \begin{array}{l} 1\,mol \ — \ 22{,}4\,\ell \\ n \ — \ 2\ell \end{array} \right.$

$n = \frac{2}{22{,}4} = 0{,}09$

$pV = nRT$

AB $\left\{ dS = \frac{dQ}{T} \right.$?

BC $\left\{ Q = \Delta U + \cancel{W}^{\,0} = nC_V \Delta T \right.$

$P_A V_A^{\gamma} = P_D V_D^{\gamma}$

$1\ 2^{\gamma} = P_D\ 3^{\gamma}$

$P_D = \left(\frac{2}{3}\right)^{\gamma} = 0{,}567 \text{ atm}$

$T_C = \frac{0{,}75 \times 3}{0{,}09 \times 8{,}31} \times 101325$

(Tudo bem, mas muito demorado)

AD $\left\{ \text{adiábatica} \quad \Delta S = 0 \right.$

DC $\left\{ \begin{array}{l} P_C V_C = nRT_C \\ P_D V_D = nRT_D \end{array} \right. \div \rightarrow \frac{P_C}{P_D} = \frac{T_C}{T_D} \rightarrow T_D = \frac{P_D}{P_C} T_C = \frac{0{,}57}{0{,}75} T_C$

15 continuação

$$S = S(p,V) \qquad \begin{cases} S_f = n C_v \ln p_f V_f^{\gamma} + S_0 \\ S_i = n C_v \ln p_i V_i^{\gamma} + C_0 \end{cases}$$

$\gamma = 1{,}4$

$C_v = \dfrac{R}{\gamma - 1}$

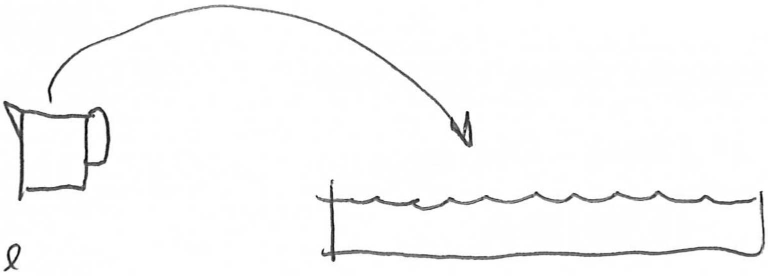
$n = 0{,}09$

$$\Delta S = S_f - S_1 = n C_v \ln p_f V_f^{\gamma} - n c_v \ln p_i V_i^{\gamma}$$

$$\Delta S = n C_v \ln \frac{p_f V_f^{\gamma}}{p_i V_i^{\gamma}}$$

$$\Delta S = 0{,}09 \times \frac{8{,}31}{1{,}4-1} \underbrace{\ln \left(\frac{0{,}75 \;\; 3^{1{,}4}}{1 \;\; 2^{1{,}4}} \right)}_{[illegible] \; 0.29} = [illegible]\;\frac{}{K} = 0.55 \; \frac{J}{K}$$

(19)



$T = 293\ K$

$$\begin{cases} V = 1\,\ell \\ T_i = 373\ K \\ T_f = 293 \end{cases} \qquad \begin{cases} \rho = \dfrac{g}{cm^3} = \dfrac{1000\,g}{1000\,cm^3} \\ \quad = \dfrac{1\,kg}{\ell} \end{cases}$$

a)

$$dS = \frac{dQ}{T} \Rightarrow \Delta S = \int_{T_i'}^{T_f} mc\,\frac{dT}{T} = mc\,\ln\frac{T_f}{T_i} = 1000\,(g) \times 1\left(\frac{cal}{g\,K}\right) \ln\frac{T_f}{T_i}$$

$$\boxed{\Delta S =} \; 1000\,\ln\underbrace{\frac{293}{373}}_{-0{,}241} = \boxed{-241\ \frac{cal}{K}}$$

b) calor que a piscina recebe

$Q_c = Q_r$

$mc(T_1 - T_f) = Mc(T_f - T_2)$

$mc\,T_1 - mcT_f = McT_f - McT_2$

$T_f\,(Mc + mc) = mcT_1 + McT_2$

$\therefore \; T_f\,Mc = McT_2$

$T_f \cong T_2$

$$\boxed{\Delta S = \frac{\Delta Q}{T}} = 1000\,(g) \times 1\left(\frac{cal}{g\,K}\right) \times \frac{373 - 293}{293} = \boxed{273\ \frac{cal}{K}}$$

$$\boxed{\Delta S =} \; 273 - 241 = \boxed{32\ \frac{cal}{K}}$$

a entropia do "universo" aumentou