Cap. 10, Vol. 2 - Moyses Nussenzveig
Segunda Lei da Termodinâmica

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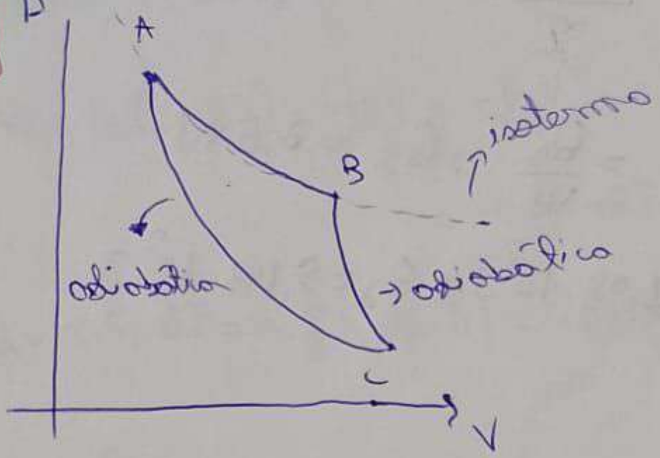
Física / Bacharelado - UFC

01



$\Delta U_{AB} = 0$ (isotérmica)

$\to Q_{AB} = W_{AB} > 0$

$Q_{BC} = Q_{CA} = 0$ (adiabáticos)

$\hookrightarrow Q_{Tot} = Q_{AB}$

$\Delta U_{Tot} = 0 \to W_{Tot} = Q_{Tot}$

Ou seja, todo o calor Q_{Tot} que entra no sistema é convertido em trabalho, W_{Tot}, o que viola a segunda lei

02 $T_1 = 500 + 273 = 773\ K$

$T_2 = 20 + 273 = 293\ K$

Eficiência ideal (de Carnot): $\eta_c = 1 - \frac{293}{773} = 0{,}62$

Eficiência obtida: $\eta_\theta = 0{,}4$

Fração: $\frac{\eta_\theta}{\eta_c} = \frac{0{,}4}{0{,}62} = 64{,}4\%$

03 a) Ideal: $\frac{T_1}{T_2} = \frac{Q_1}{Q_2} \Rightarrow Q_1 = Q_2 \cdot \frac{T_1}{T_2}$

$W = Q_1 - Q_2 = Q_2 \cdot \frac{T_1}{T_2} - Q_2 \Rightarrow W = Q_2 \left(\frac{T_1 - T_2}{T_2}\right)$

$K = \frac{Q_2}{W} \to Q_2 = KW$

$\Big\}\ W = KW \left(\frac{T_1 - T_2}{T_2}\right)$

$$K = \frac{T_2}{T_1 - T_2}$$

b) Carnot: $\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$ $\left|\begin{array}{l} \frac{T_2}{T_1} = 1 - \eta \to T_2 = (1-\eta) T_1 \\ T_1 - T_2 = \eta T_1 \end{array}\right.$

$$K = \frac{T_2}{T_1 - T_2} = \frac{(1-\eta) T_1}{\eta T_1} \to K = \frac{1-\eta}{\eta}$$

c) $K' = 0{,}4 . K = 0{,}4 . \frac{260}{300-260} = 2{,}6 = \frac{Q_2}{W} \to Q_2 = 2{,}6 W$

Mas: $W = P . \Delta T = 220 . 15 . 60 = 1{,}98 . 10^5 J \to Q_2 = 5{,}148 . 10^5 J$

$Q_2 = \frac{5{,}148 . 10^5}{4{,}184} = 1{,}23 . 10^5 cal$

$\to m = \frac{1{,}23 . 10^5}{80} = 1538 g$

04 a) $P_A . V_A = nRT_A \to 10^5 . 20 . 10^{-3} = 1 . 8{,}314 . T_A \to T_A = 240{,}56 K$

$P_B . V_B = nRT_B \to 2 . 10^5 . 20 . 10^{-3} = 1 . 8{,}314 . T_B \to T_B = 481{,}12 K$

$P_C . V_C = nRT_C \to 2 . 10^5 . 30 . 10^{-3} = 1 . 8{,}314 . T_C \to T_C = 721{,}67 K$

$P_D . V_D = nRT_D \to 1 . 10^5 . 30 . 10^{-3} = 1 . 8{,}314 . T_D \to T_D = 360{,}84 K$

b) $Q_{AB} = n . C_V \Delta T = 1 . \frac{5}{2} . 8{,}314 . (481{,}12 - 240{,}56) = 5 kJ$

$Q_{BC} = n . C_p . \Delta T = 1 \frac{7}{2} . 8{,}314 . (721{,}67 - 481{,}12) = 7 kJ$

$Q_{CD} = n . C_V \Delta T = 1 . \frac{5}{2} . 8{,}314 (360{,}84 - 721{,}67) = -7{,}5 kJ$

$Q_{DA} = n . C_p . \Delta T = 1 . \frac{7}{2} . 8{,}314 . (240{,}56 - 360{,}84) = -3{,}5 kJ$

$\to Q_1 = 5 + 7 = 12 kJ$

$Q_2 = 7{,}5 + 3{,}5 = 11 kJ$ $\to \eta_R = \frac{W}{Q_1} = \frac{1}{12} = 8{,}33\%$

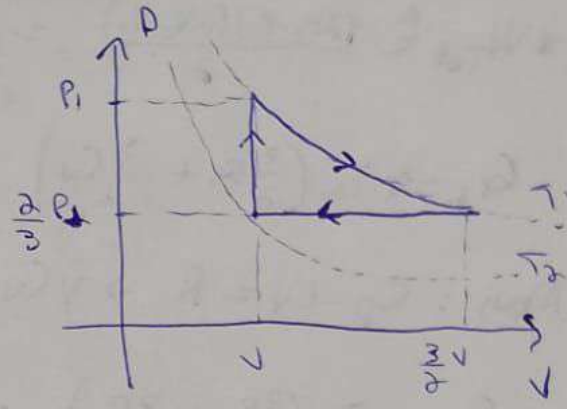
$W = Q_1 - Q_2 = 1 kJ$

c) $\eta_I = 1 - \frac{T_2}{T_1} = 1 - \frac{240{,}56}{721{,}67} = 66{,}67\%$

05 a) i) $P_1 \cdot V = nRT_1$

$\Delta U = 0 : \; Q = W = nRT_1 \cdot \ln \frac{V_F}{V} = nRT_1 \ln 1{,}5$

$= 0{,}405 \cdot nRT_1$



Ao final: $P_1 . V = P_2 \cdot \frac{3}{2} V \rightarrow P_2 = \frac{2}{3} P_1$

ii) $W = P_2 (V - 1{,}5) = -\frac{P_2 V}{2} = -\frac{P_1 V}{3}$

$= -0{,}333\, nRT_1$

$\therefore P_2 \cdot V = nRT_2 \Rightarrow \frac{2}{3} P_1 V = nRT_2$

$\Rightarrow \frac{2}{3} nRT_1 = nRT_2$

$\rightarrow T_2 = \frac{2}{3} T_1$

$Q = nC_p \Delta T = n \cdot \frac{5}{2} R \cdot (T_2 - T_1) = -0{,}833\, nRT_1$

iii) $W = 0$

$\rightarrow Q = nC_v \Delta T = n \cdot \frac{3}{2} R (T_1 - T_2) = 0{,}5\, nRT_1$

Logo $\begin{cases} Q_1 = 0{,}405\, nRT_1 + 0{,}5\, nRT_1 = 0{,}904\, nRT_1 \\ |Q_2| = 0{,}833\, nRT_1 \end{cases}$ $\Rightarrow \eta = 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{0{,}833}{0{,}904}$

$\cong 7{,}8\%$

b) $\eta_c = 1 - \frac{T_2}{T_1} = 1 - \frac{2}{3} = 33{,}3\,\%$

06 a) $P_0 V_0 = nRT_A \rightarrow T_A = \frac{P_0 V_0}{nR}$

$(2P_0)(2V_0) = nRT_B \rightarrow T_B = 4 \cdot \frac{P_0 V_0}{nR} = 4\,T_A$

$P_0 (2V_0) = nRT_C \rightarrow T_C = 2 \cdot \frac{P_0 V_0}{nR} = 2\,T_A$

AB: $W = \frac{(P_0 + 2P_0) \cdot (2V_0 - V_0)}{2} = \frac{3}{2} P_0 V_0 = \frac{3}{2} nRT_A$

$\rightarrow Q_{AB} = nT_A (1{,}5R + 3C_V)$

$\Delta U = nC_V (T_B - T_A) = 3nC_V T_A$

BC: $Q_{BC} = nC_V (T_C - T_B) = nC_V (-2T_A) = -2nC_V T_A$

CA: $Q_{CA} = nC_p (T_A - T_C) = -n\gamma C_V T_A$

$\rightarrow W_{Tot} \stackrel{A}{=} \frac{(2P_0-P_0)(2V_0-V_0)}{2} = \frac{P_0V_0}{2} = \frac{nRT_A}{2}$

$Q_1 = nT_A\left(\frac{3}{2}R + 3C_V\right)$

Mas: $C_p - C_V = R \rightarrow \gamma C_V - C_V = R \rightarrow C_V = \frac{R}{\gamma-1}$

$\rightarrow Q_1 = nT_A\left(\frac{3R}{2} + \frac{3R}{\gamma-1}\right) = nRT_A\left[\frac{3}{2} + \frac{3}{\gamma-1}\right] = nRT_A \quad \frac{3(\gamma+1)}{2(\gamma-1)}$

Logo, $\eta = \frac{W}{Q_1} = \frac{nRT_A}{2} \cdot \frac{2(\gamma-1)}{3(\gamma+1)nRT_A} = \frac{1}{3} \cdot \frac{\gamma-1}{\gamma+1}$

b) $\begin{cases} T_1 = 4T_A \\ T_2 = T_A \end{cases} \rightarrow$ Carnot: $\eta_C = 1 - \frac{T_2}{T_1} = 1 - \frac{1}{4} = \frac{3}{4}$

$\eta \leq \eta_C \Rightarrow \frac{1}{3}\frac{\gamma-1}{\gamma+1} \leq \frac{3}{4} \Rightarrow 4\gamma - 4 \leq 9\gamma + 9 \Rightarrow -13 \leq 5\gamma$

$\Rightarrow \gamma \geq -2{,}6$, sempre verdade

07

a) $T_A = T_C = T$

i) $Q_{AB} = nC_V(T_B - T)$

Mas: $T_B \cdot V_B^{\gamma-1} = T_C \cdot V_C^{\gamma-1} \rightarrow T_B = T\left(\frac{V_C}{V_B}\right)^{\gamma-1} \rightarrow T_B = T \cdot n^{\gamma-1}$

$\Rightarrow Q_{AB} = nC_VT(n^{\gamma-1} - 1)$

ii) $Q_{BC} = 0$

iii) $Q_{CA} = W = nRT \ln \frac{V_0}{nV_0} = -nRT \ln n$

Assim: $Q_1 = Q_{AB} = nC_VT(n^{\gamma-1} - 1)$ $\therefore$ $C_p - C_V = R \rightarrow \gamma C_V - C_V = R$

$Q_2 = |Q_{CA}| = nRT \ln n$ $\qquad C_V = \frac{R}{\gamma-1}$

$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{nRT \ln n}{\frac{nRT}{\gamma-1}(n^{\gamma-1} - 1)} \rightarrow \eta = 1 - \frac{(\gamma-1) \cdot \ln n}{n^{\gamma-1} - 1}$

b) $T_B = T \cdot r^{\gamma-1} \rightarrow T_1 = T_2 \cdot r^{\gamma-1} \rightarrow r^{\gamma-1} = \frac{T_1}{T_2} = \rho$

$$\rightarrow \eta = 1 - \frac{(\gamma-1)\cdot \ln r}{r^{\gamma-1}-1} = 1 - \frac{\ln r^{\gamma-1}}{r^{\gamma-1}-1} = 1 - \frac{\ln \rho}{\rho - 1}$$

c) $\eta = 1 - \frac{\ln 2^{1,4-1}}{2^{1,4-1}-1} = 13,22\%$

$$\eta_c = 1 - \frac{T_2}{T_1} = 1 - \frac{1}{\rho} = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{1}{2^{1,4-1}} = 24,21\%$$

$\frac{\eta}{\eta_c} = 54,61\%$

08 a) Só há trocas de calor em BC e DA.

$Q_{BC} = nC_V(T_C - T_B) = Q_1$

$Q_{DA} = nC_V(T_A - T_D) = -Q_2$

$$\rightarrow \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{(T_D - T_A)}{T_C - T_B}$$

Adiabáticos: $\begin{cases} T_C \cdot \left(\frac{V_0}{r}\right)^{\gamma-1} = T_D \cdot (V_0)^{\gamma-1} \rightarrow T_C = T_D \cdot r^{\gamma-1} \\ T_A \cdot (V_0)^{\gamma-1} = T_B \left(\frac{V_0}{r}\right)^{\gamma-1} \rightarrow T_B = T_A \cdot r^{\gamma-1} \end{cases}$

$$\rightarrow \eta = 1 - \frac{(T_D - T_A)}{T_D \cdot r^{\gamma-1} - T_A \cdot r^{\gamma-1}} = 1 - \frac{(T_D - T_A)}{r^{\gamma-1}(T_D - T_A)} \rightarrow \eta = 1 - \frac{1}{r^{\gamma-1}}$$

b) $\eta = 1 - \frac{1}{10^{1,4-1}} = 60,19\%$

09 a) Só ocorre trocas de calor em BC e DA:

$Q_{BC} = nC_p(T_C - T_B) \rightarrow Q_1$

$Q_{DA} = nC_V(T_A - T_D) \rightarrow -Q_2$

$$\rightarrow \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{nC_V(T_D - T_A)}{nC_p(T_C - T_B)}$$

$$\eta = 1 - \frac{1}{\gamma}\frac{(T_D - T_A)}{T_C - T_B}$$

$$\text{Adiabáticos: }\begin{cases} CD:\ T_C \cdot V_2^{\gamma-1} = T_D \cdot V_0^{\gamma-1} \rightarrow T_C = T_D \cdot r_e^{\gamma-1} & i) \\ AB:\ T_A \cdot V_0^{\gamma-1} = T_B \cdot V_1^{\gamma-1} \rightarrow T_B = T_A \cdot r_c^{\gamma-1} \end{cases}$$

$$\text{Logo: } \eta = 1 - \frac{1}{\gamma}\,\frac{T_D - T_A}{T_D \cdot r_e^{\gamma-1} - T_A \cdot r_c^{\gamma-1}}$$

$$\text{Mas: } \frac{T_C}{T_B} = \frac{T_D}{T_A}\left(\frac{r_e}{r_c}\right)^{\gamma-1} = \frac{T_D}{T_A}\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{E de } B \rightarrow C:\ \frac{P_1 V_1}{T_B} = \frac{P_1 V_2}{T_C} \rightarrow \frac{T_C}{T_B} = \frac{V_2}{V_1} \quad ii)$$

$$\frac{V_2}{V_1} = \frac{T_D}{T_A}\cdot\left(\frac{V_1}{V_2}\right)^{\gamma-1} \rightarrow T_D = T_A \cdot \left(\frac{V_2}{V_1}\right)^{\gamma} = T_A \cdot \frac{r_c^{\gamma}}{r_e^{\gamma}}$$

$$\text{Assim: } \eta = 1 - \frac{1}{\gamma}\cdot\frac{T_A\left[\frac{r_c^{\gamma}}{r_e^{\gamma}} - 1\right]}{T_A\left[\frac{r_c^{\gamma}}{r_e^{\gamma}}\cdot r_e^{\gamma-1} - r_c^{\gamma-1}\right]} = 1 - \frac{1}{\gamma}\cdot\frac{\frac{r_c^{\gamma} - r_e^{\gamma}}{r_e^{\gamma}}}{\frac{r_c^{\gamma} r_e^{\gamma-1} - r_e^{\gamma} \cdot r_c^{\gamma-1}}{r_e^{\gamma}}}$$

$$\Rightarrow \eta = 1 - \frac{1}{\gamma}\cdot\frac{r_c^{\gamma} - r_e^{\gamma}}{r_c^{\gamma} \cdot r_e^{\gamma-1} - r_e^{\gamma}\cdot r_c^{\gamma-1}} \begin{matrix} \div \frac{1}{r_c^{\gamma} r_e^{\gamma}} \\ \div \frac{1}{r_c^{\gamma} r_e^{\gamma}} \end{matrix} = 1 - \frac{1}{\gamma}\,\frac{\frac{1}{r_e^{\gamma}} - \frac{1}{r_c^{\gamma}}}{\frac{1}{r_e} - \frac{1}{r_c}}$$

$$b)\ \eta = 1 - \frac{1}{1{,}4}\cdot\frac{\frac{1}{5^{1,4}} - \frac{1}{15^{1,4}}}{\frac{1}{5} - \frac{1}{15}} = 1 - \frac{1}{1{,}4}\cdot\frac{0{,}0825}{0{,}1333} \cong 55{,}79\%$$

$$c)\ \text{De } i)\ \begin{cases} T_C > T_D \\ T_B > T_A \end{cases} \rightarrow \eta_C = 1 - \frac{T_A}{T_C}$$

$$\text{E } ii)\ \begin{cases} T_B = T_A \cdot r_c^{\gamma-1} \\ T_B = T_C \cdot \frac{r_e}{r_c} \end{cases} \rightarrow \frac{T_A}{T_C} = \frac{r_e}{r_c^{\gamma}} \rightarrow \eta_C = 1 - \frac{5}{15^{1,4}} \cong 88{,}72\%$$

$\boxed{10}$ a) Trocas de calor: $\begin{cases} Q_{BC} = nC_p(T_C - T_B) = Q_1 \\ Q_{DA} = nC_p(T_A - T_D) = -Q_2 \end{cases}$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{(T_D - T_A)}{T_C - T_B} \quad \therefore \text{ Processo adiabático } P^{1-\gamma} T^{\gamma} = cte$$

Adiabáticos: $A \to B$: $P_0^{1-\gamma} . T_A^{\gamma} = (n P_0)^{1-\gamma} . T_B^{\gamma} \to T_A = T_B . n^{\frac{1-\gamma}{\gamma}}$

$C \to D$: $(nP_0)^{1-\gamma} . T_C = P_0^{1-\gamma} . T_D^{\gamma} \to T_D = T_C . n^{\frac{1-\gamma}{\gamma}}$

$$\eta = 1 - \frac{(T_D - T_A)}{T_C - T_B} = 1 - \frac{(T_C . n^{\frac{1-\gamma}{\gamma}} - T_B . n^{\frac{1-\gamma}{\gamma}})}{T_C - T_B} = 1 - n^{\frac{1-\gamma}{\gamma}}$$

$$= 1 - \left(\frac{1}{n}\right)^{\frac{\gamma-1}{\gamma}}$$

b) $\eta = 1 - \left(\frac{1}{10}\right)^{\frac{0,4}{1,4}} = 48,20\%$

$\boxed{11}$ Trocas de calor:

$Q_{BC} = W_{T_1} = nRT_1 . \ln \frac{nV_1}{V_1} = nRT_1 . \ln n$

$Q_{DE} = W_{T_3} = nRT_3 . \ln \frac{nV_2}{V_2} = nRT_3 . \ln n$

$Q_{FA} = W_{T_2} = nRT_2 . \ln \frac{V_A}{V_F}$

Em $E \to F$: $T_3 . (nV_2)^{\gamma-1} = T_2 . V_F^{\gamma-1} \to V_F = \left(\frac{T_3}{T_2}\right)^{\frac{1}{\gamma-1}} . nV_2$

Em $A \to B$: $T_2 . V_A^{\gamma-1} = T_1 . V_1^{\gamma-1} \to V_A = \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} . V_1$

Logo: $\frac{V_A}{V_F} = \left(\frac{T_1}{T_3}\right)^{\frac{1}{\gamma-1}} . \frac{V_1}{nV_2}$

Mas de $C \to D$: $T_1 . (nV_1)^{\gamma-1} = T_3 . (V_2)^{\gamma-1} \to \left(\frac{T_1}{T_3}\right)^{\frac{1}{\gamma-1}} = \frac{V_2}{V_1}$

$\to \frac{V_A}{V_F} = \frac{V_2}{nV_1} . \frac{V_1}{nV_2} = n^{-2} \to Q_{FA} = -2nRT_2 . \ln n$

Logo, $Q_1 = Q_{BC} + Q_{DE} = nR\ln r.(T_1 + T_3)$

$|Q_2| = 2nR\ln r \, . T_2$

$$\eta = 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{2T_2}{T_1+T_3} = 1 - \frac{T_2}{\frac{T_1+T_3}{2}}$$

$\boxed{12}$ $dQ = n . C_V(T) . dT$

Entropia: $dS = \frac{dQ}{T} = \frac{n\, C_V . dT}{T}$

Entropia molar: $ds = \frac{dS}{n} = \frac{464}{T_D^3} . \frac{T^3 dT}{T} = \frac{464}{T_D^3} . T^2 dT$

$$\rightarrow \Delta s = \int_0^{s} \frac{464}{281^3} . T^2 dT = 6{,}971 . 10^{-6} . T^3 \text{ cal/mol.K}$$

$\boxed{13}$ a) $dQ = dU + dW \rightarrow dS = \frac{dQ}{T} = \frac{dU + dW}{T} \rightarrow T.dS = dU + dW$

Mas $T.dS$ é a área de um elemento de área do gráfico.

Mas, para cada T constante: $dU = 0 \rightarrow T.dS = dW$

$$\rightarrow \oint T.dS = W$$

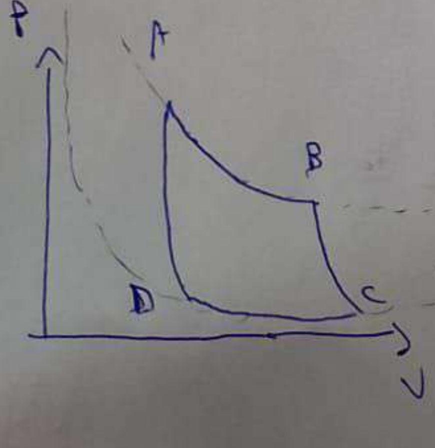
b) Trechos adiabáticos: $Q = 0$

$$\Rightarrow \Delta S = \int \frac{dQ}{T} = 0$$

Trechos isotérmicos: $Q = nRT . \ln \frac{V_F}{V_i}$

$\rightarrow \Delta S = nR\ln \frac{V_F}{V_i}$, se $V_F > V_i$: $\Delta S > 0$

$V_F < V_i$: $\Delta S < 0$



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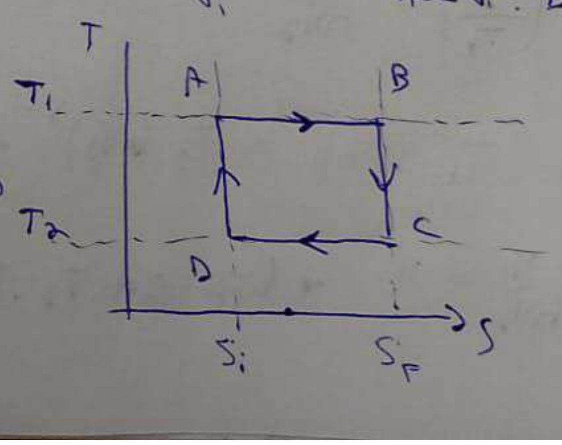

b) $W = \oint T \cdot dS = A = (S_F - S_i)(T_1 - T_2)$

c) $Q_1 = \Delta S \cdot T_1 = (S_F - S_i) \cdot T_1$ $\rightarrow$ $\eta = 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{T_2}{T_1}$

$|Q_2| = \Delta S \cdot T_2 = (S_F - S_i) T_2$

$\boxed{14}$ $S_1 = m \cdot c_G \cdot \ln \frac{T_F}{T_i} = 10^3 \cdot 0,5 \cdot \ln \frac{273}{258} = 28,26$ cal/K

$S_2 = \frac{m \, L_F}{T_F} = \frac{10^3 \cdot 79,6}{273} = 291,58$ cal/K

$S_3 = m \cdot c_a \cdot \ln \frac{T_V}{T_F} = 10^3 \cdot 1 \cdot \ln \frac{373}{273} = 312,11$ cal/K

$S_4 = \frac{m \cdot L_V}{T_V} = \frac{10^3 \cdot 539,6}{373} = 1446,65$ cal/K

+

2078,60 cal/K

$\boxed{15}$ i) $P_1 V_1 = nRT_1$; $P_2 V_2 = nRT_2$ $\Rightarrow$ $1 \cdot 2 = nR \cdot 273$; $1 \cdot 3 = nR \cdot T_2$ $\rightarrow$ $T_2 = 409,5$ K

E: $n = \frac{P_1 V_1}{RT_1} = \frac{1 \cdot 2}{0,082 \cdot 273} = 0,089$ mols

Logo: $S_i = \int_{T_1}^{T_2} \frac{dQ}{T} = n \, C_p \ln \frac{T_2}{T_1} = 0,089 \cdot \frac{7}{2} \cdot 8,314 \ln \frac{409,5}{273} = 1,05$ J/K

ii) $P_1 V_1 = nRT_1$; $P_3 V_3 = nRT_3$ $\rightarrow$ $1 \cdot 2 = nR \cdot 273$; $0,75 \cdot 3 = nR\, T_3$ $\rightarrow T_3 = 307,125$ K

Logo: $S_{ii} = \int_{T_2}^{T_3} \frac{dQ}{T} = n \, C_v \ln \frac{T_3}{T_2} = 0,089 \cdot \frac{5}{2} \cdot 8,314 \cdot \ln \frac{307}{409} = -0,53$ J/K

$S_i + S_{ii} = 0,52$ J/K

16 a) Fusão: $Q_1 = m_G \cdot L_F$

Aquecimento do "gelo": $Q_2 = m_G \cdot c_A \cdot (T-0) = m_G \cdot c_A \cdot T$

Resfriamento da "água": $Q_3 = m_A \cdot c_A \cdot (T - 30^\circ)$

$$Q_1 + Q_2 + Q_3 = 0 \Rightarrow 500 \cdot 80 + 500 \cdot T + 2000 \cdot 1 \cdot (T-30) = 0$$

$$\Rightarrow 2500T = 20\,000 \Rightarrow T = 8^\circ C$$

b) $S_1 = \int \frac{dQ_1}{T} = \frac{m_G \cdot L_F}{T_F} = \frac{500 \cdot 80}{273} = 146{,}52 \text{ cal/K}$

$S_2 = m_G \cdot c_A \cdot \ln \frac{T}{T_F} = 500 \cdot 1 \cdot \ln \frac{281}{273} = 14{,}44 \text{ cal/K}$ +

$S_3 = m_A \cdot c_A \cdot \ln \frac{T}{303} = 2000 \cdot 1 \cdot \ln \frac{281}{303} = -150{,}76 \text{ cal/K}$ / $10{,}20$ cal/K

17 $Q = mL = 10^3 \cdot 539{,}6$

$= 5{,}4 \cdot 10^5$ cal

$$S_a = \frac{Q}{T_{100}} + \frac{(-Q)}{T_{100}} = 0 \quad \text{(reversível)}$$

$$S_b = \frac{Q}{T_{100}} + \frac{(-Q)}{T_{200}} = 5{,}4 \cdot 10^5 \left(\frac{1}{373} - \frac{1}{473}\right) = 305{,}85 \text{ cal/K}$$

(irreversível)

18 $n = \frac{m}{M} = \frac{1000}{4} = 250$ mols

$$PV = nRT \rightarrow VdP + PdV = nR\,\cancel{dT}^{\,cte} = 0 \rightarrow PdV = -V \cdot dP$$

Mas: $V = \frac{nRT}{P} \rightarrow PdV = -nRT\frac{dP}{P}$

$\rightarrow \Delta U = Q - W = 0$ (mesma temperatura) $\rightarrow W = Q$

$$W = \int PdV = -\int_{150\,atm}^{1\,atm} VdP = -nRT \ln \frac{1}{150} = 250 \cdot 8{,}314 \cdot 290 \cdot \ln 150 = 3 \cdot 10^6 \text{ J}$$

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{3 \cdot 10^6}{290} \cong 10^4 \text{ J/K}$$

19 a) $\Delta S_c = \int \frac{dQ}{T} = mc \int \frac{dT}{T} = 10^3 \cdot 1 \cdot \ln \frac{293}{373} = -241,41$ cal/K

b) Calor recebido pela piscina: $Q_p = mc(100-20) = 8 \cdot 10^4$ cal

$\rightarrow \Delta S_p = \frac{8 \cdot 10^4}{293} = 273,04$ cal/K

$\rightarrow \Delta S_U = \Delta S_c + \Delta S_p = -241,41 + 273,04 = 31,63$ cal/K

20 a) $F = U - TS$

$\rightarrow dF = dU - TdS - SdT$

Isotérmico: $\begin{cases} dU = 0 \\ dT = 0 \end{cases}$ $\rightarrow dF = -T \cdot dS$

Mas: $U = Q - W \rightarrow dU = dQ - pdV = 0 \rightarrow dQ = pdV = dW$

$dS = \frac{dQ}{T} \rightarrow dW = T \cdot dS \rightarrow dF = -dW \Rightarrow \boxed{dW = -dF}$

b) Irreversível: $dS > \frac{dQ}{T} \rightarrow dQ < T \cdot dS$

$\rightarrow dW < -dF$

c) $dF = dU - TdS - SdT$

Expansão livre: $\begin{cases} dU = 0 \\ dS > 0 \\ dT = 0 \end{cases}$ $\rightarrow dF = -T \cdot dS$

. O decréscimo na energia livre de Helmholtz é o trabalho desperdiçado:

$-dF = T \cdot dS \quad , \quad dF < 0$