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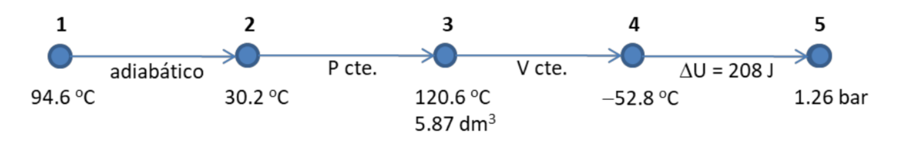
Conteúdo

I – Teste 2019.2.1

Questão 1



Considere que submete 1 mol de um gás perfeito ($C_V = R\,5/2$) ao processo reversível representado.

Q1 a)

Calcule o trabalho posto em jogo no percurso 2→3.

$$W_{(30.2\to 120.6)^\circ\text{C} P_{cnt}} = \int_{Vol_1}^{Vol_2} P_{ext}\,\mathrm{d}Vol = P_{ext}\int_{Vol_1}^{Vol_2} \mathrm{d}Vol = P_{ext}\,\Delta Vol\Big|_{Vol_1}^{Vol_2} =$$

$$= P_{ext}\,(Vol_2 - Vol_1) = P_{ext}\left(\frac{n\,R\,T_2}{P_2} - \frac{n\,R\,T_1}{P_1}\right) = n\,R\,(T_2 - T_1) =$$

$$= (1)\,(8.314)\,((120.6 + 273.15) - (30.2 + 273.15)) \cong 751.627$$

Q1 b)

Calcule o trabalho e o calor postos em jogo no percurso 3→4.

(i)

W

$$W_{vol_{cnt}} = 0$$

(ii)

Q

$$Q_{vol_{cnt},(120.6 \to -52.8)^\circ\mathrm{C}} = \int_{T_3}^{T_4} n\, C_v \,\mathrm{d}T = n\, C_v \int_{T_3}^{T_4} \mathrm{d}T = n\, C_v \,\Delta T\Big|_{T_3}^{T_4} =$$
$$= (1)\ (8.314 * 5/2)\ ((-52.8 + 273.15) - (120.6 + 273.15)) \cong -3.604\,\mathrm{E3}$$

Q1 c)

Calcule a pressão do gás no estado 1.

$$P_1 = \frac{n\,R\,T_1}{vol_1} = \frac{n\,R\,T_1}{vol_1} = \frac{n\,R\,T_1}{vol_2\,\sqrt[\gamma]{P_2/P_1}} = \frac{n\,R\,T_1}{\left(\frac{n\,R\,T_2}{P_2}\right)\ (P_3/P_1)^{C_v/C_P}} =$$

$$= \frac{T_1}{T_2\,P_3^{-1}\,(P_3/P_1)^{5/7}} = \frac{T_1\,P_1^{5/7}}{T_2\,P_3^{5/7-1}} \implies P_1 = \left(\frac{T_1}{T_2\,\left(\frac{n\,R\,T_3}{vol_3}\right)^{5/7-1}}\right)^{1/(1-5/7)} =$$

$$= \left(\frac{T_1}{T_2}\right)^{1/(1-5/7)}\ \frac{n\,R\,T_3}{vol_3} = \left(\frac{94.6+273.15}{30.2+273.15}\right)^{7/2}\ \frac{(1)\,(8.314)\,(120.6+273.15)}{5.87\ \mathrm{E}-6} \cong$$

$$\cong 1.094\ \mathrm{E}9$$

Q1 d)

Calcule ΔS_{viz} para o percurso 4→5.

$$\Delta S_{viz} = -\Delta S = -\left(\int n\, C_V \,\frac{\mathrm{d}T}{T} + n\, R\, \ln \frac{V_5}{V_4} \right) = -\int_{T_4}^{T_5} n\, C_V \,\frac{\mathrm{d}T}{T} - n\, R\, \ln \frac{V_f}{V_i} =$$

$$= -n\, C_v\, \ln \frac{T_5}{T_4} - n\, R\, \ln \frac{(n\, R\, T_5/P_5)}{V_4} =$$

$$= -n\, C_v\, \ln \left(\frac{\frac{\Delta U}{n\, C_v} + T_4}{T_4} \right) - n\, R\, \ln \frac{n\, R\, \left(\frac{\Delta U}{n\, C_v} + T_4 \right)}{V_4\, P_5} =$$

$$= -n\, C_v\, \ln \left(\frac{\Delta U}{n\, C_v\, T_4} + 1 \right) - n\, R\, \ln \frac{R\, \left(\frac{\Delta U}{C_v} + T_4 \right)}{V_4\, P_5} =$$

$$= -(1)\,(8.314 * 5/2)\, \ln \left(\frac{208}{(1)\,(8.314 * 5/2)\,(-52.8 + 273.15)} + 1 \right) +$$

$$- (1)\,(8.314)\, \ln \frac{(8.314)\, \left(\frac{208}{8.314 * 5/2} + (-52.8 + 273.15) \right)}{(5.87\ \mathrm{E}-3)\,(1.26\ \mathrm{E}\,5)} \cong -8.8$$

Nota: N aguento mais esses calculos, fazer com variáveis intermediárias é menos preciso porem mais fácil

Q2 a)

Calcule a variação de energia interna associada à passagem da água gasosa, a 138.9 °C e 1.01 bar, a água sólida, a 0 °C e 1.01 bar.

$$\Delta U_{\mathrm{H_2O\,(g)\longrightarrow\,(s)},(138.9\to 0)°\mathrm{C},1.01\mathrm{bar}} \underset{P_{cnt}}{=} \Delta H - P\,\Delta V =$$

$$= \begin{pmatrix} \Delta H_{\mathrm{H_2O\,(s)},(138.9\to 100)°\mathrm{C}} \\ +\,\Delta H_{\mathrm{H_2O(\,(s)\longrightarrow\,(l))},100°\mathrm{C}} \\ +\,\Delta H_{\mathrm{H_2O\,(l)},(100\to 0)°\mathrm{C}} \\ +\,\Delta H_{\mathrm{H_2O(\,(l)\longrightarrow\,(s))},0°\mathrm{C}} \end{pmatrix} - P(V_f - V_i) =$$

$$= \begin{pmatrix} n\,C_{p,(g)}((100+273.15)-(138.9+273.15)) \\ +n\,(-\,\Delta H_{vap}) \\ +n\,C_{p,(l)}((0+273.15)-(100+273.15)) \\ +n\,(-\,\Delta H_{fus}) \end{pmatrix} - P\left(\frac{n}{M}\,\rho_{(s)} - \frac{n\,R\,T_i}{P_i}\right) =$$

$$= n\begin{pmatrix} C_{p,(g)}(100-138.9) \\ +(-\,\Delta H_{vap}) \\ +C_{p,(l)}(-100) \\ +(-\,\Delta H_{fus}) \end{pmatrix} - n\left(\frac{P\,\rho_{(s)}}{M} - R\,T_i\right) \cong$$

$$\cong n\begin{pmatrix} (36)(100-138.9) \\ +(-40.7\ \mathrm{E}\,3) \\ +(75)(-100) \\ +(-6.01\ \mathrm{E}\,3) \end{pmatrix} - n\left(\frac{1.01\ \mathrm{E}\,5 * 18}{0.92\ \mathrm{E}\,6} - 8.314\,(138.9+273.15)\right) \cong$$

$$\cong (n) - 52.186\,\mathrm{E3}$$

Q2 b)

Calcule o trabalho máximo associado à transformação da alínea anterior.

$$\max W = \Delta A = \Delta U - \Delta(T\,S) = \Delta U - (T_f\,S_f - T_i\,S_i) = \Delta U - T_f\,S_f + T_i\,S_i =$$
$$= \Delta U - T_f\,\left(S_{(l),25°\mathrm{C},1\mathrm{bar}} + \Delta S_{((l),25°\mathrm{C},1\mathrm{bar})\to f}\right) +$$
$$+ T_i\,\left(S_{(l),25°\mathrm{C},1\mathrm{bar}} + \Delta S_{((l),25°\mathrm{C},1\mathrm{bar})\to i}\right) =$$
$$= \Delta U - T_f\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \Delta S_{((l),25°\mathrm{C},1\mathrm{bar})\to f}\end{pmatrix} + T_i\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \Delta S_{((l),25°\mathrm{C},1\mathrm{bar})\to i}\end{pmatrix} =$$
$$= \Delta U - T_f\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \Delta S_{(l),(25\to 0)°\mathrm{C}} \\ + \Delta S_{(l\to s),0°\mathrm{C}}\end{pmatrix} + T_i\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \Delta S_{(l),(25\to 100)°\mathrm{C}} \\ + \Delta S_{(l\to g),100°\mathrm{C}} \\ + \Delta S_{(g),(100\to 138.9)°\mathrm{C}}\end{pmatrix} =$$
$$\underset{P_{cnt}}{=} \Delta U - T_f\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \int C_{p,(l)}\,\frac{\mathrm{d}T}{T} \\ +(-\Delta H_{fus})/T\end{pmatrix} + T_i\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ + \int C_{p,(l)}\,\frac{\mathrm{d}T}{T} \\ + \Delta H_{vap}/T \\ + \int C_{p,(g)}\,\frac{\mathrm{d}T}{T}\end{pmatrix} =$$
$$= \Delta U - T_f\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ +C_{p,(l)}\ln\frac{0+273.15}{25+273.15} \\ +(-\Delta H_{fus})/T\end{pmatrix} + T_i\begin{pmatrix} S_{(l),25°\mathrm{C},1\mathrm{bar}} \\ +C_{p,(l)}\ln\frac{100+273.15}{25+273.15} \\ + \Delta H_{vap}/T \\ +C_{p,(g)}\ln\frac{138.9+273.15}{100+273.15}\end{pmatrix} \cong$$

Q2 c)

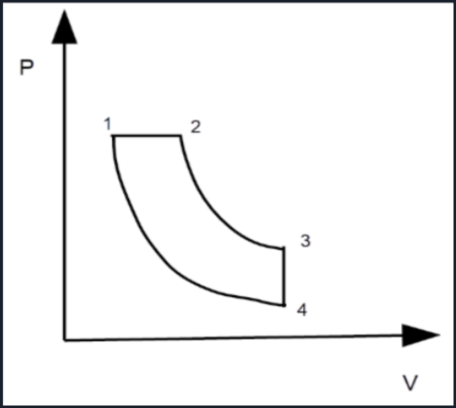
Em que medida a 3a lei da Termodinâmica complementa o sentido da 2a lei?

I – Teste 2022.2.1

Questão 1

Considere que tem 1 mol de um gás perfeito ($C_V = 5/2R$). Na figura estão representados estados deste gás (1, 2, 3 e 4) e transições reversíveis entre eles. $P_1 = 4.0\,\mathrm{bar}, T_1 = 293.15\,\mathrm{K}, T_4 = 197.27\,\mathrm{K}$, as transições $2 \to 3$ e $4 \to 1$ são adiabáticas, o calor envolvido na transição $1 \to 2$ é de $5466\,\mathrm{J}$, e o calor envolvido na transição $3 \to 4$ é de -4100 J.

- $n = 1\,\mathrm{mol}$
- $C_V = 5/2R$
- $P_1 = 4.0\,\mathrm{bar}$
- $T_1 = 293.15\,\mathrm{K}$
- $T_4 = 197.27\,\mathrm{K}$
- $2 \to 3$: Adiabática
- $4 \to 1$: Adiabática
- $\Delta H_{1\to2} = +5466\,\mathrm{J}$
- $\Delta H_{3\to4} = -4100\,\mathrm{J}$



Q1 a)

Calcule T_2

$$\int_1^2 n\,C_P\ \mathrm{d}T = n\,(C_V + R)\ \Delta T = \Delta H_{1\to 2} = Q_{1\to 2} \implies$$

$$\implies T_2 = T_1 + \frac{Q_{1\to 2}}{n\,(C_V + R)} \cong 293.15 + \frac{5466}{1 * 3.5 * 8.31} \cong 480.98$$

Q1 b)

Calcule T_3 e V_3

(i) T_3

$$\int_{3\to4} n\,C_V\ \mathrm{d}T = n\,(C_P + R)\,(T_4 - T_3) = Q_{3\to4} \implies$$

$$\implies T_3 = T_4 - \frac{Q_{3\to4}}{n\,(C_V)} \cong 197.27 - \frac{-4100}{1 * 2.5 * 8.31} \cong 394.52$$

(ii) V_3

$$P_3\,V_3^{\gamma} = \left(\frac{n\,R\,T_3}{V_3}\right)\,V_3^{C_P/C_V} = n\,R\,T_3\,V_3^{1.4-1} = n\,R\,T_3\,V_3^{0.4} \underset{\text{adiab. rev.}}{\overset{2\to3}{=}}$$

$$= P_2\,V_2^{\gamma} = P_1\,\left(\frac{n\,R\,T_2}{P_2}\right)^{1.4} = \frac{n^{1.4}\,R^{1.4}\,T_2^{1.4}}{P_1^{1.4-1}} \implies$$

$$\implies V_3 = \left(\frac{n^{0.4}\,R^{0.4}\,T_2^{1.4}}{P_1^{0.4}\,T_3}\right)^{1/0.4} = \frac{n\,R\,T_2^{3.5}}{P_1\,T_3^{2.5}} \cong \frac{1 * 8.31 * (480.98)^{3.5}}{4.0 * 10^5 * (394.52)^{2.5}} \cong 16.41\ \mathrm{E}{-3}$$

Q1 c)

Calcule $W_{4\to 1}$

$$W_{4\to 1} + Q_{4\to 1} = W_{4\to 1} = \Delta U_{4\to 1} = \int_4^1 n\,C_V\ \mathrm{d}T = n\,C_V\ \Delta T \cong$$

$$\cong 1 * 2.5 * 8.31(293.15 - 197.27) \cong 1.99\,\mathrm{E3}$$

Q1 d)

Calcule ΔS_{viz} no processo 1→4→3. (se não resolveu b, considere $T_3 = 400\,\mathrm{K}$)

$$\Delta S_{viz,1\to4\to3} = -\,\Delta S_{1\to3} = -\left(\int_1^3 n\,C_P\ \mathrm{d}T/T + n\,R\,\ln(P_1/P_3)\right) =$$

$$= -n\,3.5\,R\,\ln(T_3/T_1) - n\,R\,\ln\frac{P_1}{\left(\frac{n\,R\,T_3}{V_3}\right)} = -n\,R\left(3.5\,\ln(T_3/T_1) + \ln\frac{P_1}{\left(\frac{n\,R\,T_3}{V_3}\right)}\right) \cong$$

$$\cong 8.31\left(-3.5\,\ln\left(\frac{394.52}{283.15}\right) - \ln\frac{4.0 * 10^5}{\left(\frac{8.31*394.52}{16.41\,\mathrm{E}{-3}}\right)}\right) \cong -15.42$$

Q1 e)

Imagine uma transição isotérmica reversível (realizada a T_4) entre o estado 4 e um estado 5, com $W_{4\to5} = -3986\,\mathrm{J}$. Calcule V_5. (se não resolveu b, considere $T_3 = 400\,\mathrm{K}$ e $V_3 = 15.0\,\mathrm{dm}^3$)

$$- n\,R\,T_4\ln(V_5/V_4) = W_{4\to5} \implies V_5 = V_4\,\exp\left(-\frac{W_{4\to5}}{n\,R\,T_4}\right) \cong$$

$$\cong 16.41\,\mathrm{E}{-3} * \exp\left(-\frac{-3986}{1 * 8.31 * 197.27}\right) \cong 186.42\,\mathrm{E}{-3}$$

Q1 f)

(i)

Imagine uma forma de levar o gás de 1 a 3 de forma irreversível. Represente graficamente essa transição, bem como o trabalho associado.

(ii)

O coeficiente de Joule-Thomson do H_2 é negativo. Que consequências, em termos da 1º Lei da Termodinâmica, poderão existir no desenho de um motor de combustão, quando o H2 passa através da válvula de saída do depósito a 200K, num processo a entalpia constante?

Questão 2

- $C_{p,L} = 255.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$
- $C_{p,G} = 239.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$
- $\Delta H_{vap,(125.6\,^\circ\mathrm{C},1.01\,\mathrm{bar})} = 41.53\,\mathrm{kJ\,mol^{-1}}$
- $\alpha_{p,liq} \approx 1.4 * 10^{-3}\,\mathrm{K^{-1}}$
- $\rho_{liq} = 0.703\,\mathrm{g\,cm^{-3}}$
- $M_{(n-octano)} = 114.23\,\mathrm{g\,mol^{-1}}$

Q2 a)

Calcule ΔH e ΔG associados à passagem de $200\,\mathrm{g}$ de n-octano do estado ($125.6\,°\mathrm{C}$, gás, $0.5\,\mathrm{bar}$) ao estado ($125.6\,°\mathrm{C}$, líquido, $100\,\mathrm{bar}$)

(i)

$$
\begin{aligned}
&\Delta H = \\
&= \begin{pmatrix} \Delta H_{gas,(0.5\to 1.01)\,\mathrm{bar}} & + \\ +\Delta H_{(gas\to liq),1.01\,\mathrm{bar}} & + \\ +\Delta H_{liq,(1.01\to 100)\,\mathrm{bar}} & \end{pmatrix} = \\
&= \begin{pmatrix} 0 \quad \text{(gas perfeito)} & + \\ +n\ \Delta H_{vap} & + \\ +\displaystyle\int_{P_0}^{P_1} v\,(1-\alpha_p T)\ \mathrm{d}P & \end{pmatrix} = \\
&= \begin{pmatrix} (m/M)\ \Delta H_{vap} & + \\ +(m/\rho)\,(1-\alpha_p T)\,(P_1-P_0) & \end{pmatrix} = \\
&= \begin{pmatrix} (200/114.23) * 41.53 * 10^3 & + \\ +\dfrac{200 * 10^{-3}}{0.703 * 10^3} * (1-(1.4 * 10^{-3}) * (125.6+273.15)) * (100-1.01) * 10^5 & \end{pmatrix} \cong \\
&\cong 73.96\,\mathrm{E3}
\end{aligned}
$$

(ii)

$$
\begin{aligned}
&\Delta G = \\
&= \begin{pmatrix} \Delta G_{gas,(0.5\to 1.01)\,\mathrm{bar}} & + \\ +\Delta G_{(gas\to liq),1.01\,\mathrm{bar}} & + \\ +\Delta G_{liq,(1.01\to 100)\,\mathrm{bar}} & \end{pmatrix} = \\
&= \begin{pmatrix} \displaystyle\int_{P_0}^{P_1} V\ \mathrm{d}P & + \\ +0 & + \\ +\displaystyle\int_{P_1}^{P_2} V\ \mathrm{d}P & \end{pmatrix} = \\
&= \begin{pmatrix} \displaystyle\int_{P_0}^{P_1} \frac{n\,R\,T}{P}\ \mathrm{d}P & + \\ +V\displaystyle\int_{P_1}^{P_2} \mathrm{d}p \quad \text{(vol liq constante em } \Delta P\text{)} & \end{pmatrix} = \\
&= \begin{pmatrix} (m/M)\,R\,T\ \ln(P_1/P_0) & + \\ +(m/\rho)\,(P_2-P_1) & \end{pmatrix} = \\
&= \begin{pmatrix} (200/114.23) * 8.31 * (125.6+273.15) * \ln(1.01/0.5) & + \\ +\dfrac{200 * 10^{-3}}{0.703 * 10^3} * (100-1.01) * 10^5 & \end{pmatrix} \cong \\
&\cong 6897.53
\end{aligned}
$$

Q2 b)

Calcule ΔS e ΔU associados à passagem de $200\,\mathrm{g}$ de n-octano do estado ($50\,°\mathrm{C}$, líquido, $1.01\,\mathrm{bar}$) ao estado ($200\,°\mathrm{C}$, gás, $0.5\,\mathrm{bar}$)

(i)

$$\begin{aligned}
&\Delta S = \\
&= \begin{pmatrix} \Delta S_{liq,1.01\mathrm{bar},(50\to125.6)°\mathrm{C}} & + \\ + \Delta S_{(liq\to gas),1.01\mathrm{bar},125.6°\mathrm{C}} & + \\ + \Delta S_{gas,1.01\mathrm{bar},(125.6\to200)°\mathrm{C}} & + \\ + \Delta S_{gas,(1.01\to0.5)\mathrm{bar},200°\mathrm{C}} & \end{pmatrix} = \\
&= \begin{pmatrix} \int_{T_0}^{T_1} n\, C_{p,liq}\ \mathrm{d}T/T + 0 & + \\ +n\ \Delta H_{vap}/T_1 & + \\ + \int_{T_1}^{T_2} n\, C_{p,gas}\ \mathrm{d}T/T + 0 & + \\ +0 + n\, R \int_{P_2}^{P_3} \mathrm{d}P/P & \end{pmatrix} = \\
&= \begin{pmatrix} n\, C_{p,liq} \ln(T_1/T_0) & + \\ +n\ \Delta H_{vap}/T_1 & + \\ +n\, C_{p,gas}\ \ln(T_2/T_1) & + \\ +n\, R\ \ln(P_3/P_2) & \end{pmatrix} = \\
&= \begin{pmatrix} 255.7 * \ln\left(\dfrac{125.6+273.15}{50+273.15}\right) & + \\ +41.53 * 10^3/(125.6+273.15) & + \\ +239.0 * \ln\left(\dfrac{200+273.15}{125.6+273.15}\right) & + \\ +8.31 * \ln(0.5/1.01) & \end{pmatrix} * (200/114.23) \cong \\
&\cong 337.82
\end{aligned}$$

(ii)

$$\begin{aligned}
&\Delta U = \Delta H - \Delta(P\,V) = \\
&= \begin{pmatrix} \Delta H_{liq,1.01\mathrm{bar},(50\to125.6)°\mathrm{C}} & + \\ + \Delta H_{(liq\to gas),1.01\mathrm{bar},125.6°\mathrm{C}} & + \\ + \Delta H_{gas,1.01\mathrm{bar},(125.6\to200)°\mathrm{C}} & + \\ + \Delta H_{gas,(1.01\to0.5)\mathrm{bar},200°\mathrm{C}} & \end{pmatrix} - \Delta(P\,V) = \\
&= \begin{pmatrix} \int_{T_0}^{T_1} n\, C_{P,l}\ \mathrm{d}T & + \\ +n\ \Delta H_{vap} & + \\ + \int_{T_1}^{T_2} n\, C_{P,g}\ \mathrm{d}T & + \\ +0 & \end{pmatrix} - (P_3\,V_3 - P_0\,V_0) = \\
&= \begin{pmatrix} n\, C_{P,l}\,(T_1 - T_0) & + \\ +n\ \Delta H_{vap} & + \\ +n\, C_{P,g}\,(T_2 - T_1) & \end{pmatrix} - P_3\, \left(\frac{n\, R\, T_3}{P_3}\right) + P_0\,(m/\rho_{liq}) = \\
&= \begin{pmatrix} C_{P,l}\,(T_1 - T_0) & + \\ + \Delta H_{vap} & + \\ +C_{P,g}\,(T_2 - T_1) & + \\ -R\, T_3 & + \\ +P_0\, M/\rho_{liq} & \end{pmatrix} (m/M) = \\
&= \begin{pmatrix} 255.7 * (125.6 - 50) & + \\ +41.53 * 10^3 & + \\ +239.0 * (200 - 125.6) & + \\ -8.31 * (200 + 273.15) & + \\ +1.01 * 114.23/(0.703 * 10^6) & \end{pmatrix} (200/114.23) \cong \\
&\cong 130\,803.70
\end{aligned}$$