Gabarito - Físico-Química I - Exercícios Complementares 3

1. Um gás tem a equação de estado $P(V + b) = nRT$, onde b é uma constante de valor negativo. Ao sofrer uma expansão de Joule-Thomson (ou seja, isoentálpica), a temperatura do gás se eleva, diminui ou fica constante? Justifique sua resposta a partir das seguintes relações:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{Cp}\left\{T\left(\frac{\partial V}{\partial T}\right)_P - V\right\}$$

2. Uma amostra de 1,00 mol de gás ideal monoatômico, com $C_{V,m} = 3R/2$, inicialmente a 27°C e 3,00 atm, expande-se de três maneiras, até a pressão final de 1,00 atm: (a) isotérmica e reversivelmente; (b) adiabática e reversivelmente e (c) adiabaticamente, contra uma pressão externa constante de 1,00 atm. Determinar os valores de Q, W, ΔU, ΔH, ΔS, ΔS_{viz} e ΔS_{total} para cada processo.

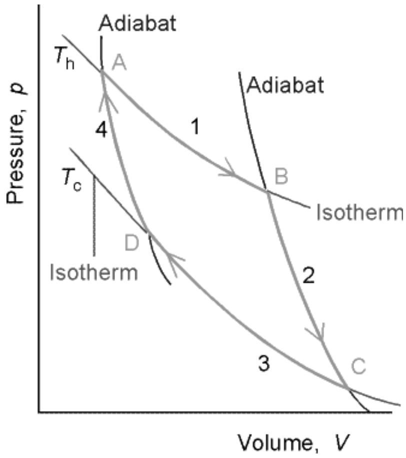
Dados: $C_{P,m} = C_{V,m} + R$
PV^{γ} = cte, onde $\gamma = C_{P,m}/C_{V,m}$ (gás ideal, processo adiabático reversível)
VT^{c} = cte, onde $c = C_{V,m}/R$ (gás ideal, processo adiabático reversível)

3. Calcule o calor padrão de formação (em $kJ.mol^{-1}$) do $NH_{3\,(g)}$ a 300 K, sabendo que, a 1000 K e 1,0 atm:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightarrow 2\,NH_{3\,(g)} \qquad \Delta H = -173{,}70\text{ kJ}$$

	$\Delta H^o_{f,\,300\,K}$ ($kJ.mol^{-1}$)	$C_{P,m}$ ($J.mol^{-1}.K^{-1}$)
$N_{2\,(g)}$	0	$(3{,}2 + 0{,}7\times10^{-3}\,T)\,R$
$H_{2\,(g)}$	0	$(3{,}5 - 0{,}1\times10^{-3}\,T)\,R$
$NH_{3\,(g)}$	?	$(3{,}1 + 4{,}0\times10^{-3}\,T)\,R$

4. Uma máquina de Carnot opera entre $T_h = 25{,}0$°C e $T_c = 0{,}0$°C, usando 1,0 mol de um gás ideal monoatômico ($C_{V,m} = 3R/2$). As condições iniciais de volume e pressão (A) são 24,8 L e 1,00 bar. Durante a expansão isotérmica, o volume muda para 50,0 L. Calcule Q, W, ΔU, ΔH, (em J) e ΔS (em J/K) para cada etapa e para o ciclo completo.



Todos os processos são reversíveis.

Processo adiabático reversível:
PV^{γ} = cte, onde $\gamma = C_{P,m}/C_{V,m}$
VT^{c} = cte, onde $c = C_{V,m}/R$

Gás ideal: $C_{P,m} = C_{V,m} + R$

(1) $P(V+b) = nRT$, $b < 0$ (cte) $\rightarrow V = \frac{nRT}{P} - b$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

$$\mu = \frac{1}{C_P}\left[T\underbrace{\left(\frac{nR}{P}\right)}_{=V+b} - V\right] = \frac{1}{C_P}\left[\cancel{V} + b - \cancel{V}\right] = \frac{b}{C_P} < 0 \text{, pois } b < 0$$

$\mu < 0 \Rightarrow \left(\frac{\partial T}{\partial P}\right)_H < 0$, logo <u>T aumenta</u> quando P diminui, a H cte.

(2) $T_i = 27°C = 300\,K$ $\qquad C_{V,m} = \frac{3R}{2}$; $C_{p,m} = \frac{3R}{2} + R = \frac{5R}{2}$

$P_i = 3{,}00$ atm $\qquad n = 1{,}00$ mol (gás ideal) $\therefore PV = nRT$

$P_f = 1{,}00$ atm

(a) $\begin{cases} T = \text{cte} ; \text{reversível} \\ \text{gás ideal} \end{cases}$

$\hookrightarrow \Delta U = 0 /\!/ = Q + W \therefore Q = -W = \int P\,dV = \int \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$

$Q = -W = nRT \ln\left(\frac{V_f}{V_i}\right) \qquad P_iV_i = P_fV_f \therefore \frac{V_f}{V_i} = \frac{P_i}{P_f}$

$Q = -W = nRT \ln\left(\frac{P_i}{P_f}\right) = 1{,}00\text{ mol} \times 8{,}314 \frac{J}{mol.K} \cdot 300\,K \ln\left(\frac{3{,}00}{1{,}00}\right) = 2740\,J$

$Q = 2{,}74$ kJ //

$W = -2{,}74$ kJ // $\qquad \Delta H = \Delta U + \underbrace{\Delta(PV)}_{0} \therefore \Delta H = \Delta U = 0$ //

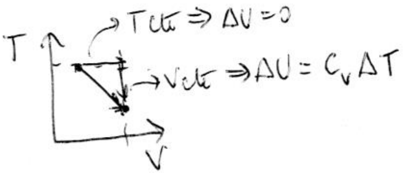
$\Delta S = \int \frac{dQ_{rev}}{T} = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{P_i}{P_f}\right) = \frac{Q_{rev}}{T}$

$\Delta S = \frac{2740\,J}{300\,K} = 9{,}13\ J.K^{-1}$ //

$\Delta S_{viz} = -9{,}13\ J.K^{-1}$ // $\qquad \Bigg\}\ \Delta S_{total} = 0$ //

(b) Adiabático reversível

$\hookrightarrow Q = 0 /\!/ \Rightarrow \Delta U = W$



$V_i T_i^{\,c} = V_f T_f^{\,c}$; $c = \frac{C_{V,m}}{R} = \frac{3R/2}{R} = \frac{3}{2}$

$V_i = \frac{n_i R T_i}{P_i} = \frac{1{,}00\text{ mol} \cdot 0{,}0821\text{ atm}.L.mol^{-1}K^{-1} \cdot 300\,K}{3{,}00\text{ atm}}$

$V_i = 8{,}21\,L$

$P_iV_i^{\gamma} = P_fV_f^{\gamma} \therefore V_f = \left(\frac{P_i}{P_f}\right)^{1/\gamma} V_i$

$$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{5R/2}{3R/2} = \frac{5}{3}$$

$$V_f = \left(\frac{3{,}00}{1{,}00}\right)^{3/5} \cdot 8{,}21\,L = 15{,}9\,L$$

$$T_f = \left(\frac{V_i}{V_f}\right)^{1/c} \cdot T_i = \left(\frac{8{,}21}{15{,}9}\right)^{2/3} \cdot 300\,K = 193\,K //$$

$$\Delta U = C_V \Delta T = \frac{3}{2} \times 8{,}314\,J \cdot mol^{-1} \cdot K^{-1} \times 1{,}00\,mol\,(193 - 300)\,K = -1334\,J$$

$$\Delta U = W = -1{,}33\,kJ //$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = -1334\,J + 1{,}00\,mol \times 8{,}314\,\frac{J}{mol.K} \times (193-300)\,K$$

$$\Delta H = -2223\,J = -2{,}22\,kJ //$$

$$Q_{rev} = 0 \Rightarrow \Delta S = 0 // \text{ e } \Delta S_{viz} = 0 // \Rightarrow \Delta S_{total} = 0 //$$

(c) Adiabático ; irreversível ($P_{ext} = 1{,}00\,atm = cte$)

$$\hookrightarrow Q = 0 // \quad \therefore \quad \Delta U = W \rightarrow \int C_V\,dT = \int -P_{ext}\,dV \quad \therefore$$

$$\therefore \; C_V \Delta T = -P_{ext} \Delta V \quad \therefore \quad C_V (T_f - T_i) = -P_{ext}\left(\frac{nRT_f}{P_f} - V_i\right)$$

$$1{,}00\,mol \times \frac{3}{2} \times 8{,}314\,\frac{J}{mol.K}\,(T_f - 300)\,K = -1{,}00\,atm \left(\frac{1{,}00\,mol \times 0{,}0821\,atm \cdot L \cdot mol^{-1} \cdot K^{-1} \cdot T_f}{1{,}00\,atm} - 8{,}21\,L\right)$$

$$12{,}471\,(T_f - 300)\,[J] = (-0{,}0821 \cdot T_f + 8{,}21)\,[atm \cdot L] \times 101\,325\,\frac{Pa}{atm} \times 10^{-3}\,\frac{m^3}{L}$$

$$12{,}471\,(T_f - 300) = -8{,}319\,T_f + 831{,}9$$

$$20{,}79\,T_f = 4573{,}2$$

$$T_f = 220\,K //$$

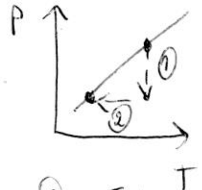
$$\Delta U = C_v \Delta T = 1{,}00\ \text{mol} \times \frac{3}{2} \times 8{,}314 \frac{J}{\text{mol.K}} \cdot (220-300)\ K = -997{,}7\ J$$

$$\Delta U = W = -1{,}00\ kJ$$ //

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = -997{,}7 + 1{,}00 \times 8{,}314 \times (220-300)$$

$$\Delta H = -997{,}7 - 88{,}3 = -1086\ J$$

$$\Delta H = -1{,}09\ kJ$$ //



① e ② são reversíveis

① T cte (rev.): $dU = dQ + dW = 0 \therefore dQ = -dW \overset{\text{reversível}}{=} PdV = nRT\frac{dV}{V}$

$$\Delta S_1 = \int \frac{dQ_{rev}}{T} = nR\int \frac{dV}{V} = nR \ln\left(\frac{V_f}{V_i}\right) \underset{T\ cte}{=} nR \ln\left(\frac{P_i}{P_f}\right)$$

② P cte: $dQ = C_p\, dT$

$$\Delta S_2 = \int \frac{dQ_{rev}}{T} = \int C_p \frac{dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right)$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 1{,}00\ \text{mol} \times 8{,}314 \frac{J}{\text{mol.K}} \ln\left(\frac{3{,}00}{1{,}00}\right) + 1{,}00\ \text{mol} \times \frac{5}{2} \times 8{,}314 \frac{J}{\text{mol.K}} \ln\left(\frac{220}{300}\right)$$

$$\Delta S = 9{,}13 - 6{,}45 = 2{,}69\ J.K^{-1}$$ //

$$\Delta S_{viz} = \frac{Q_{viz}}{T} = \frac{-Q}{T} = 0$$ //

$$\Delta S_{total} = \Delta S + \Delta S_{viz} = +2{,}69\ J.K^{-1}$$ //

3ª QUESTÃO:

$$\begin{tikzcd}[column sep=huge]
\underset{1000\,K}{N_2 + 3H_2} \arrow[r, "\Delta H_2"] & \underset{1000\,K}{2NH_3} \arrow[d, "\Delta H_3"] \\
\underset{(300\,K)}{N_2(g) + 3H_2(g)} \arrow[u, "\Delta H_1"] \arrow[r, "1"'] & \underset{(300\,K)}{2NH_3(g)}
\end{tikzcd}$$

$\Delta H^\circ_f(NH_3)_{300K}$

$$\Delta H^\circ_f(NH_3(g))_{300K} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_2 = -173,70\ kJ$$

$$dH = C_p\,dT \quad \therefore \quad \Delta H = \int_{T_i}^{T_f} C_p\,dT \qquad P = 1,0\ atm = cte$$

$$\Delta H_1 = \int_{300}^{1000} [C_p(N_2) + 3\,C_p(H_2)]\,dT = \int_{300}^{1000} [3,2 + 0,7\times10^{-3}T + (3.3,5) - 0,3\times10^{-3}T]\,R\,dT$$

$$\Delta H_1 = \int_{300}^{1000} [13,7 + 0,4\times10^{-3}T]\,R\,dT = R\,[13,7T + 0,2\times10^{-3}T^2]_{300}^{1000}$$

$$\Delta H_1 = R\,[13,7(1000-300) + 0,2\times10^{-3}(1000^2 - 300^2)] = R.[9590 + 182] = 9772.R$$

$$\Delta H_1 = 9772\overset{(mol.K)}{.}\ 8,314\ J/_{mol.K} = 81,24\ kJ$$

$$\Delta H_3 = \int_{1000}^{300} 2\,C_p(NH_{3(g)})\,dT = \int_{1000}^{300} 2\,(3,1 + 4,0\times10^{-3}T)\,R\,dT = \int_{1000}^{300} (6,2 + 8,0\times10^{-3}T)\,R\,dT$$

$$\Delta H_3 = [(6,2T + 4,0\times10^{-3}T^2)R]_{1000}^{300} = [6,2\,(300-1000) + 4,0\times10^{-3}(300^2 - 1000^2)]\,R$$

$$\Delta H_3 = [-4340 - 3640]\,R = -7980\,R = -7980.\ 8,314\ J$$

$$\Delta H_3 = -66,35\ kJ$$

$$\Delta H^\circ_f(NH_3(g))_{300K} = (81,24 - 173,70 - 66,35)/_{2\,moles} = -79,4\ kJ/_{mol}$$

//

4ª QUESTÃO:

$T_A = T_B = 25°C = 298\ K$ $\qquad$ $n = 1,0\ mol \rightarrow C_{v,m} = 3R/2$

$T_C = T_D = 0°C = 273\ K$ $\qquad$ (gás ideal) $\qquad C_{p,m} = 5R/2$

$\begin{cases} P_A = 1,00\ bar \\ V_A = 24,8\ L \end{cases} \xrightarrow[T\ cte]{①} \begin{matrix} P_B = ? \\ V_B = 50,0\ L \end{matrix} \rightarrow PV = cte$

$$P_B = \frac{P_A V_A}{V_B} = \frac{1,00\ bar \cdot 24,8\ L}{50,0\ L} = 0,496\ bar$$

① Expansão $\begin{cases} \text{isotérmica reversível} \\ \text{gás ideal} \end{cases}$

$\hookrightarrow \Delta U = 0$; $H = U + PV \therefore \Delta H = \Delta U + \Delta(PV) = \cancel{\Delta U}^{0} + nR\cancel{\Delta T}^{0} \therefore \Delta H = 0$

$$dU = dQ + dW = 0 \therefore -dQ = dW = -P_{ext}\,dV = -P\,dV$$

$$W = -\int_{V_i}^{V_f} P\,dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT \ln\frac{V_f}{V_i}$$

$$W = -1,0\ mol \cdot 8,314\ \frac{J}{mol.K} \cdot 298\ K \ \ln\frac{50}{24,8} \therefore W = -1737,2\ J$$

$$Q = +1737,2\ J$$

$$dS = \frac{dQ_{rev}}{T} \therefore \Delta S = \int \frac{dQ_{rev}}{T} \xrightarrow{T\ cte} \Delta S = \frac{Q}{T} = \frac{1737,2\ J}{298\ K} \therefore \Delta S = 5,83\ J/K$$

② Expansão adiabática reversível

$\hookrightarrow Q = 0 \therefore \Delta S = 0$ $\leftarrow Q_{rev} = 0$

$$dU = \underbrace{dQ}_{0} + dW \therefore \underbrace{dU}_{C_v dT} = dW \therefore W = \Delta U = C_v \Delta T$$

$$V_B T_B^{\,c} = V_C T_C^{\,c} \ , \quad c = C_v/R = \frac{3R}{2}\cdot\frac{1}{R} = 1,5 \ ; \quad PV^\gamma = cte \ , \quad \gamma = \frac{C_p}{C_v} = \frac{5R/2}{3R/2} = \frac{5}{3}$$

$$W = \Delta U = \frac{3R}{2}(T_C - T_B) = \frac{3}{2}\, 8,314\ \frac{J}{mol.K} \cdot 1,0\ mol \cdot (273-298)K$$

$$W = \Delta U = -311,8\ J$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T$$

$$\Delta H = -311,8\ J + 1,0\ mol \cdot 8,314\ \frac{J}{mol.K}(273-298)K = -311,8\ J - 207,85$$

$$\Delta H = -519,7\ J$$

$$V_C = \frac{V_B T_B^{\,c}}{T_C^{\,c}} = 50,0\ L \cdot \left(\frac{298}{273}\right)^{1,5} \therefore V_C = 57,0\ L$$

$$P_C = P_B\left(\frac{V_B}{V_C}\right)^\gamma = 0,496\ bar \left(\frac{50}{57}\right)^{5/3} \therefore P_C = 0,399\ bar$$

③ Compressão $\begin{cases} \text{isotérmica reversível} \\ \text{gás ideal} \end{cases}$ $\rightsquigarrow PV = \text{cte}$ $\quad T = 273\,K = \text{cte}$

$\hookrightarrow \Delta U = 0$ // e $\Delta H = 0$ //

$$W = -nRT \ln \frac{V_D}{V_C} = -Q$$

$$V_A T_A^{\,c} = V_D T_D^{\,c} \therefore V_D = V_A \left(\frac{T_A}{T_C}\right)^c = 24{,}8\,L \left(\frac{298}{273}\right)^{1{,}5} \therefore V_D = 28{,}3\,L$$

$$W = -1{,}0 \cdot 8{,}314 \cdot 273 \ln\left(\frac{28{,}3}{57{,}0}\right) \therefore W = 1589{,}2 \,//$$

$$Q = -1589{,}2 \,//$$

$$\Delta S = \frac{Q}{T} = -\frac{1589{,}2\,J}{273\,K} \therefore \Delta S = -5{,}82\,J/K \,//$$

④ Compressão adiabática reversível

$\hookrightarrow Q = 0$ // $\therefore \Delta S = 0$ //

$$T_D = \left(\frac{V_A T_A^{\,c}}{V_D}\right)^{1/c} = \left(\frac{V_A}{V_D}\right)^{1/c} \cdot T_A$$

$$T_D = 273\,K$$

$$W = \Delta U = C_V \Delta T = \frac{3}{2} \cdot 8{,}314 \cdot (\underset{298-273}{T_A - T_D})$$

$$W = \Delta U = 311{,}8\,J \,//$$

$$\Delta H = \Delta U + nR\Delta T = 311{,}8 + 1{,}0 \cdot 8{,}314 \cdot (298-273) \therefore \Delta H = 519{,}7\,J \,//$$

CICLO

$\Delta U = 0 - 311{,}8 + 0 + 311{,}8 = 0$ // (O.K.)
$\Delta H = 0 - 519{,}7 + 0 + 519{,}7 = 0$ // (O.K.)
$\Delta S = 5{,}83 + 0 - 5{,}82 + 0 \hat{=} 0$ // (O.K.)

Funções de estado em ciclos tem variação nula (estado inicial = final)

$Q = 1737{,}2 + 0 - 1589{,}2 + 0 = 148{,}0\,J$ //
$W = -1737{,}2 - 311{,}8 + 1589{,}2 + 311{,}8 = -148{,}0\,J$ //

$Q = -W$ (O.K.)