$\left(\frac{\partial F}{\partial U}\right)_S = M dU + N dS$; $\boxed{F(U,S)}$ — $MTdS - MPdV + NdS^{(1)}$. Precisamos de $S(T,V)$. (a)

$dU = TdS - PdV$ — Livro DeHoff fez como exemplo (4.2).

$S(T,V) = M dT + N \underbrace{(\alpha V dT - V\beta dP)}_{dV}$ $\rightsquigarrow$ $dS = (M + NV\alpha)dT - NV\beta dP$

Temos $S(T,P) \rightarrow \frac{C_p}{T} dT - \alpha V dP$ (vem da $dG = VdP - SdT$ $\Rightarrow$ $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$)

e $\left(\delta Q_{rev,P} = T\left(\frac{\partial S}{\partial T}\right) dT \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}\right)$. Juntando os termos:

$M + NV\alpha = \frac{C_p}{T}$; $-\beta V N = -\alpha V$; $N = \frac{\alpha}{\beta}$; $M = -\frac{V\alpha^2}{\beta} + \frac{C_p}{T}$

$M = \frac{1}{T}\left(C_p - \frac{TV\alpha^2}{\beta}\right) \rightarrow dS = \frac{1}{T}\underbrace{\left(C_p - \frac{TV\alpha^2}{\beta}\right)}_{C_V} dT + \frac{\alpha}{\beta} dV$

$dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV$. Utilizando esta relação em (1)

$MT\frac{C_V}{T} dT + \frac{MT\alpha}{\beta} dV - MPdV + N\frac{C_V}{T} dT + N\frac{\alpha}{\beta} dV =$

$= dT\left(MT\frac{C_V}{T} + N\frac{C_V}{T}\right) + dV\left(\frac{MT\alpha}{\beta} - MP + N\frac{\alpha}{\beta}\right)$

$dF = -SdT - PdV$

$-S = MT\frac{C_V}{T} + N\frac{C_V}{T}$ e $-P = M\left(\frac{T\alpha}{\beta} - P\right) + N\frac{\alpha}{\beta}$

$\frac{N\alpha}{\beta} = -M\left(\frac{T\alpha}{\beta} - P\right) - P \rightarrow N = \frac{\beta}{\alpha}\left[M\left(P - \frac{T\alpha}{\beta}\right) - P\right]$

$-S = \frac{C_V}{T} MT + \frac{\beta}{\alpha} MP - TM - \frac{\beta}{\alpha} P$

$M\left(C_V + \frac{\beta}{\alpha}P - T\right) = \frac{\beta}{\alpha}P - S \rightarrow M = \frac{\frac{\beta}{\alpha}P - S}{\left(C_V + \frac{\beta}{\alpha}P - T\right)} = \left(\frac{\partial F}{\partial U}\right)_S$

Gás ideal: (b)

$$\frac{\frac{\beta}{2}P - S}{\left(C_v + \frac{\beta}{2}P - T\right)} \rightsquigarrow \frac{\left(\frac{1}{\rho}\cdot P - S\right)}{\left(\frac{3}{2}R + \frac{T}{\rho}P - T\right)} = \frac{T-S}{\frac{3}{2}R} = \frac{2}{3}\left(\frac{T-S}{R}\right)$$

(c)

Estas expressões não seriam úteis de serem utilizadas pois estamos trabalhando com relações parciais de energia. Normalmente utiliza-se valores de entalpia pura. Tal derivada parcial indicaria uma proporção específica entre a energia livre de Helmholtz e interna (a entropia constante) o que é muito difícil de obter experimentalmente.

2) ii)

a) $V = \ln(Sx^2) - Sx + 50 > 1 \{\mathbb{R}, x > 1\}$ x = Pressão

$V_F = 10L$

$V_0 = 2L$

$P_0 V_0 = nRT$

$T = \frac{P_0 V_0}{nR} =$

$\begin{cases} P_0 = 56,0526 \\ P_F = 47,7312 \end{cases}$ [S=1] $\rightarrow$ $\begin{cases} T_0 = 1366,13697 \\ T_F = 5816,62198 \end{cases}$

$\begin{cases} P_0 = 27,6668 \\ P_F = 23,5037 \end{cases}$ [S=2] $\rightarrow$ $\begin{cases} T_0 = 674,3060\,K \\ T_F = 2864,2091 \end{cases}$

$\begin{cases} P_0 = 18,3043 \\ P_F = 15,528 \end{cases}$ [S=3] $\rightarrow$ $\begin{cases} T_0 = 446,1199\,K \\ T_F = 1892,2739 \end{cases}$

$\begin{cases} P_0 = 13,6536 \\ P_F = 11,5708 \end{cases}$ [S=4] $\rightarrow$ $\begin{cases} T_0 = 332,7711\,K \\ T_F = 1410,0414 \end{cases}$

$\begin{cases} P_0 = 10,8765 \\ P_F = 9,21 \end{cases}$ [S=5] $\rightarrow$ $\begin{cases} T_0 = 265,0865\,K \\ T_F = 1122,3495\,K \end{cases}$

$\begin{cases} P_0 = 9,03223 \\ P_F = 7,64323 \end{cases}$ [S=6] $\rightarrow$ $\begin{cases} T_0 = 220,1372\,K \\ T_F = 931,41989 \end{cases}$

$\begin{cases} P_0 = 7,71904 \\ P_F = 6,52832 \end{cases}$ [S=7] $\rightarrow$ $\begin{cases} T_0 = 188,1316\,K \\ T_F = 795,5344 \end{cases}$

$\begin{cases} P_0 = 6,73688 \\ P_F = \ldots \end{cases}$ [S=8] $\begin{cases} T_0 = 164,1940\,K \\ T_F = 693,98245 \end{cases}$

$\begin{cases} P_0 = 5,97447 \\ P_F = 5,04837 \end{cases}$ $[S=9] \rightarrow \begin{cases} T_0 = 145,6178 \\ T_F = 613,2047 \end{cases}$ (2)

$\begin{cases} P_0 = 5,36629 \\ P_F = 4,53251 \end{cases}$ $[S=10] \rightarrow \begin{cases} T_0 = 130,7894 \\ T_F = 552,3409 \end{cases}$ atm L

b) $\delta Q_{rev} = T dS = C_V \frac{V}{R} dP + C_P \frac{P}{R} dV$ $\quad I = \ln(sp^2) - sp + 50$

$\delta Q_{rev} = \frac{C_V}{R}\left[\ln(sp^2) - sp + 50\right] dP + \frac{C_P \cdot P}{R}\left(\frac{2}{P} - s\right) dP \quad dV = \left(\frac{2}{P} - s\right) dP$

$C_V = \frac{3}{2}R$ $\quad \delta Q_{rev} = \left[\frac{3}{2}\frac{R}{R}\left[\ln sp^2 - sp + 50\right] + \frac{5}{2}\frac{R}{R}P\left(\frac{2}{P} - s\right)\right] dP$

$C_P = \frac{5}{2}R$ $\quad \delta Q_{rev} = \left[\frac{3}{2}\ln sp^2 - \frac{3}{2}sp + \frac{3}{2}50 + 5 - \frac{5}{2}sp\right] dP$

$Q = \int_{P_0}^{P_F} \left(\frac{3}{2}\ln(sp^2) - 4sp + 80\right) dP$

$\Delta Q = \frac{1}{2} P\left(3\ln(sp^2) - 4sp + 154\right)$

$\Delta Q_{S=1} = 962,98$ L atm

$\Delta Q_{S=2} = 474,258$ L atm $= 48,054$ J/mol $\quad 0,101325$ J

$\Delta Q_{S=3} = 313,346$ L atm $= 31,74978345$ J/mol

$\Delta Q_{S=4} = 233,513$ L atm $= 23,6607$ J/mol

$\Delta Q_{S=5} = 185,871$ L atm $= 18,83338$ J/mol

$\Delta Q_{S=6} = 154,261$ L atm $= 15,63049$ J/mol

$\Delta Q_{S=7} = 131,762$ L atm $= 13,35078$ J/mol

$\Delta Q_{S=8} = 114,95$ L atm $= 11,6473$ J/mol

$\Delta Q_{S=9} = 101,899$ L atm $= 10,32453$ J/mol

$\Delta Q_{S=10} = 91,4889$ L atm $= 9,27011$ J/mol

c) Trabalho?

$W = \int P dV \rightarrow dV = \left(\frac{2}{P} - 5\right) dP \rightarrow W = -\int (2 - 5P)\, dP$ (3)

$\Delta W = -\left[2P + 5P^2\right]_{P_0}^{P_F} =$

$\Delta W_{S=1} = -415,17$ L.atm =

$\Delta W_{S=2} = -204,702$ L.atm

$\Delta W_{S=3} = -135,34$ L.atm

$\Delta W_{S=4} = -100,909$ L.atm

$\Delta W_{S=5} = -80,3524$ L.atm

$\Delta W_{S=6} = -66,7086$ L.atm

$\Delta W_{S=7} = 440,926$ L.atm

$\Delta W_{S=8} = 335,804$ L.atm

$\Delta W_{S=9} = 264,054$ L.atm

$\Delta W_{S=10} = 212,984$ L.atm

d) ΔS? Variação da entropia

$dS = \frac{C_p}{T} dT - V\alpha\, dP = \frac{C_p}{T} dT - \frac{R}{P} dP$

$\Delta S_I = C_p \ln\left(\frac{T_F}{T_0}\right)$ $\Delta S_{II} = -R \ln\left(\frac{P_f}{P_0}\right)$ Pascal transf. $\times 101\,325$

$\Delta S_T = \Delta S_I + \Delta S_{II}$

$\Delta S_{S=1} = 31,45$ J/(mol K)

$\Delta S_{S=2} = 31,42$ J/mol K

$\Delta S_{S=3} = 31,4028$ J/mol K

$\Delta S_{S=4} = 31,389875$ J/mol K

$\Delta S_{S=5} = 31,37994$

$\Delta S_{S=6} = 28,59496$

$\Delta S_{S=7} = 31,364656$

$\Delta S_{S=8} = 31,35842$

$\Delta S_{S=9} = 31,35308$

$\Delta S_{S=10} = 31,34818$

(4)

$\Delta F = ?$ $-SdT - PdV$ $S(T)$ $dS = \frac{C_V}{T}dT + \frac{\alpha}{\beta}dV$ $P \frac{1}{T}$ $\frac{P}{T}($

$PV = RT$

$\frac{P}{T} = \frac{R}{V}$

$P = \frac{mRT}{V}$

$$S(T) = S_{298} + \int_{298}^{T} \frac{C_V}{T} dT = 126{,}04 + \frac{3}{2}R$$

S_{298} He

$$S(T) = 126{,}04 + \frac{3}{2}R \ln\left(\frac{T}{298}\right) = \frac{3}{2}R \ln T - 54{,}99$$

$$\Delta F_I = -\int_{T_0}^{T_F} S(T)\,dT = \int_{T_0}^{T_F} \left[\frac{3}{2}R \ln T + 54{,}99\right] dT =$$

$$\Delta F_{II} = -\int_{V_0}^{V_F} \frac{RT_F}{V}\,dV = -R(T_F) \ln\left(\frac{V_F}{V_0}\right) =$$

$\Delta F = \Delta F_I + \Delta F_{II}$

$\Delta F_{S=1} = -205593 - 77836.1248 =$

$\Delta F_{S=2} = -81833.1 - 38327.9053 =$

$\Delta F_{S=3} = -46571.3 - 25321.78776 =$

$\Delta F_{S=4} = -30743.5 - 18868.7108 =$

$\Delta F_{S=5} = -22027{,}5 - 15018.912 =$

$\Delta F_{S=6} = -16623.4 - 12463.952 =$

$\Delta F_{S=7} = -13003.3 - 10645.847 =$

$\Delta F_{S=8} = -10439.7 - 9286.64 =$

$\Delta F_{S=9} = -8548.44 - 8232.4672 =$

$\Delta F_{S=10} = -7107.86 - 7391.2245 =$

ii) $\Delta F = ?$

$$F_2 - F_1 \Rightarrow F = -N_0 k T \ln 8 = -N_0 k T \left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T\right]$$

$$N_0 k = R \Rightarrow \Delta F = -RT\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T\right] \Bigg| \begin{matrix} F_1(T_1, V_1) \\ F_2(T_2, V_2) \end{matrix}$$

$$\Delta F = -RT_2\left[\ln V_2 + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T_2\right] + RT_1\left[\ln V_1 + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T_1\right].$$

$k = 1{,}38 \cdot 10^{-23}$ (J/atm K) e 1 mol He $\sim m = 4.002602\,g$.

$R = 8.314313$ (J/mol K) $R = 82{,}0589$ (cc atm / mol K) $m = 4 \times 10^{-3}$ kg

$\Delta F =$ Substituindo valores para cada $S = 1, 2, 3, 4, 5, 6$

~~ΔF = 82.0589 (cc atm/mol k) . T2(1) (ln V2(1)) + 8.314313 x~~

$$\Delta F_1 = \left[\frac{-8.314}{0.008206} \times T_{2(1)} \left(\ln V_{2(1)}\right) + \left(\frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) \times -8.314\right) \times T_{2(1)} - 8.314 \times T_{2(1)} \times \frac{3}{2}\ln T_{2(1)}\right] + \frac{8.314}{0.008206} T_{1(1)} \ln V_{1(1)} + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) \times 8.314 \times T_{1(1)} + \frac{3}{2} 8.314 \times T_{1(1)} \times \ln T_{1(1)} \ldots$$

$\Delta F_1 = -3.67075 \times 10^9 +$ ~~$7.7\ldots \times 10^5$~~ $= -694\,038\,000$ J/mol

$9.07038 \times 10^8 - 2.13037 \times 10^8 \ldots$ 283429 (Fenomenológica).

ΔS ?

$$S = N_0 k \ln\left[V\left(\frac{2\pi k T}{m}\right)^{3/2}\right] + \frac{3}{2} N_0 k$$

$N_0 k \to R$ $\quad \Delta S \neq 0$

$$\Delta S = R \ln V + \frac{3}{2} R \ln\left(\frac{2\pi k T}{m}\right).$$

$$\Delta S = R \ln\left(\frac{10}{2}\right) + \frac{3}{2} R \ln\left(\frac{T_{2(5)}}{T_{1(5)}}\right)$$

$\Delta S_1 = 31.4479 \sim 31.45$ J/mol K da Fenomenológica.

$\Delta S_5 = 3$ ~~1.37 8~~ 31.3732 J/mol K ~ 31.37994 "

$\Delta S_6 = 31.3719$ J/mol K ~ 28.59496 da Fenomenológica

Os valores são parecidos pois estamos apenas utilizando
outro formalismo matemático para encontrar o
valor final. Há variação pois utilizamos constantes
diferentes, que interferem no valor final