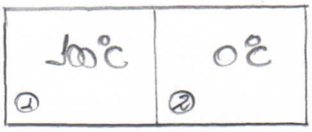
1)



$m_{B_1} = m_{B_2} = 10\,kg$

$C_{Cu} = 0{,}385\ J/Kg$

ΔH ?

ΔS_{TOTAL} ?

UMA VEZ QUE A MASSA DOS BLOCOS SÃO IGUAIS E CAPACIDADE TÉRMICA CONSTANTE :

$$T_f = \frac{(100 + 0)}{2} = 50°C$$

$$C = m\,C_{Cu} \quad (I)$$

$$C = \frac{\delta q}{dT} \therefore \delta q = dH \therefore dH = C\,dT \quad \text{INTEGRANDO}$$

$$\Delta H = C\,\Delta T \quad (II) \qquad \text{SUBSTITUINDO I E II :}$$

$$\Delta H = m\,C_{Cu}\,\Delta T = 10000g \cdot 0{,}385\ J/Kg \cdot (\pm 50K) = \pm 192{,}5\,kJ$$

$$\text{logo } \Delta H_{TOTAL} = 0$$

$$dS = \frac{\delta q}{T} \therefore dS = \frac{dH}{T} \therefore dS = \frac{m\,C_{Cu}\,dT}{T}$$

$$\Delta S = m\,c_u\,ln\left(\frac{T_f}{T_i}\right) \ *$$

$$\Delta S_1 = 10.000 \cdot 0{,}385 \cdot ln\left(\frac{323}{373}\right) = -554{,}12\ J/K$$

$$\Delta S_2 = 10000 \cdot 0{,}385\ ln\left(\frac{323}{273}\right) = 647{,}495\ J/K$$

$$\Delta S_T = \Delta S_1 + \Delta S_2 = 93{,}4\ J/K$$

2) $\Delta S_{SISTEMA}$

$C_{P,m} = \frac{5}{2}R$ MONOATOMICO

$C_{P,m} - C_{V,m} = R$

$C_{V,m} = C_{P,m} - R$

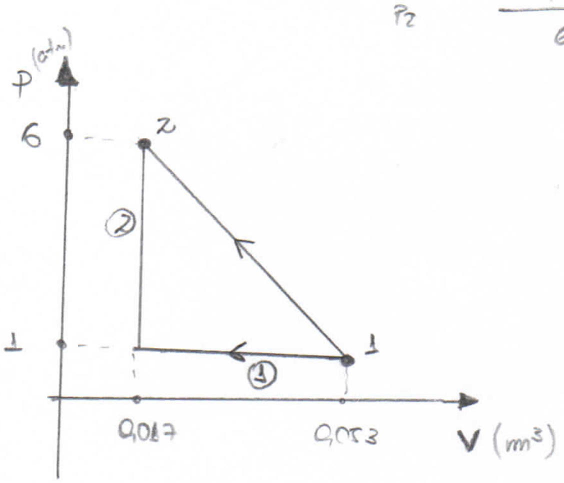
$C_{V,m} = \frac{3}{2}R$

ESTADO 1 : 50°C e 1 atm

$$P_1V_1 = nRT_1 \quad \therefore V_1 = \frac{nRT_1}{P_1} = \frac{2 \cdot 8{,}3144 \cdot 323}{101325} = 0{,}053\ m^3$$

ESTADO 2 : 350°C e 6 atm

$$P_2V_2 = nRT_2 \quad \therefore V_2 = \frac{nRT_2}{P_2} = \frac{2 \cdot 8{,}3144 \cdot 623}{6 \cdot 101325} = 0{,}017\ m^3$$



① P = cte $\quad \delta q_{rev} = \Delta H_p = nC_p\,dT$ $\quad * \; T_f = \frac{101325 \cdot 0{,}017}{2 \cdot 8{,}314} = 103{,}59\ K$

$$ds = \frac{dH}{T} \quad \therefore \quad \Delta S = \int_{T_i}^{T_f} \frac{nC_p\,dT}{T} = \int_{323}^{103{,}6} 2 \cdot \frac{5}{2}R \frac{dT}{T} = 2 \cdot \frac{5}{2} \cdot 8{,}314 \cdot \ln\left(\frac{103{,}6}{323}\right) = -47{,}27\ J/K$$

② V = cte

$$\Delta S = \int_{T_i}^{T_f} \frac{nC_{V,m}\,dT}{T} = 2 \cdot \frac{3}{2}R \cdot \ln\left(\frac{623}{103{,}59}\right) = 44{,}75\ J/K$$

$$\Delta S_{SIST.} = \Delta S_1 + \Delta S_2 = -47{,}27 + 44{,}75 = -2{,}52\ J/K$$

3)

a) SISTEMA ADIABATICO $q = 0$

b) $W = \int P_{ext}\, dV = P_{ext}\, \Delta V = 1{,}5 \cdot 101325 \cdot 0{,}0004 \cdot 0{,}15 = 9{,}12\ J$

c) $\Delta U = q - W \therefore \Delta U = 0 - 9{,}12\ J = -9{,}12\ J$

d) $\Delta U = n C_{V,M} \Delta T \therefore \Delta T = \dfrac{\Delta U}{n C_V}$

$C_{P,M} = 87{,}82 - 2{,}6442 \cdot 10^{-3} T - 9{,}9886 \cdot 10^{2} T^{-0{,}5} + 70{,}641 \cdot 10^{4} T^{-2}$

$87{,}82 - 2{,}6442 \cdot 10^{-3}(298) - 9{,}9886 \cdot 10^{2}(298)^{-0{,}5} + 70{,}641 \cdot 10^{4}(298)^{-2}$

$87{,}82 - 0{,}79 - 57{,}86 + 7{,}96$

$C_{P,M} = 37{,}13\ J/mol\,K$

$C_{P,M} - C_{V,M} = R \therefore C_{V,M} = C_{P,M} - R$

$C_{V,M} = 28{,}82\ J/mol\,K$

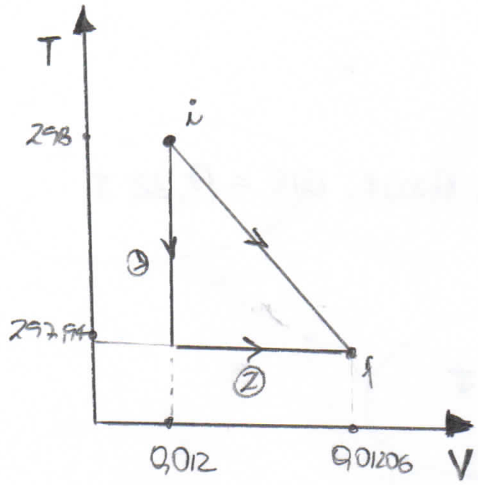
$\Delta T = \dfrac{-9{,}12}{28{,}82 \cdot 5} = -0{,}06\ K$

e) $\Delta T = T_f - T_i \therefore T_f = \Delta T + T_i \therefore T_f = 298 - 0{,}06 = 297{,}94\ K$

$V_i = \dfrac{nRT_i}{P_i} = \dfrac{5 \cdot 8{,}314 \cdot 298}{10 \cdot 101325} = 0{,}012\ m^3$

$V_f = V_i + (A_i \cdot \text{deslocamento}) = 0{,}012 + (0{,}0004 \cdot 0{,}15) = 0{,}01206\ m^3$

$\Delta S_T = \Delta S_1 + \Delta S_2$



① $V = cte$

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{n C_{v,m} dT}{T} = 5 \cdot 28{,}82 \cdot \ln\left(\frac{297{,}94}{298}\right)$$

$$\Delta S_1 = -0{,}029 \ J/K$$

$T = cte$

$$dS = \cancel{\frac{n C_{v,m} dT^{0}}{T}} + \frac{nR\,dV}{V}$$

$$\Delta S_2 = nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_2 = 5 \cdot 8{,}314 \cdot \ln\left(\frac{0{,}01206}{0{,}012}\right)$$

$$\Delta S_2 = 0{,}207 \ J/K$$

$$\Delta S_T = -0{,}029 + 0{,}207 = 0{,}178 \ J/K$$

4)

a) $\Delta H (l \to s) = -\Delta H (s - l)$

$T_f = 1336\ K$

$T_{f_{\text{super resfriado}}} = 1006\ K$

$C_{p_{Au(s)}} = 23{,}68 + 5{,}19 \cdot 10^{-3} T\ [J/mol\,K]$

$C_{p_{Au(l)}} = 29{,}29\ [J/mol\,K]$

$\Delta H_{Au_{1336}} = 12{,}760\ kJ/mol$

$$\begin{tikzcd}
Au(l) \arrow[r, "\Delta H^{l-s}_{1336} = -\Delta H^{s-l}_{1336}"] & Au(s) \\
Au(l) \arrow[u, "\Delta H_{Au(l)}"] \arrow[r, "\Delta H_{l-s_{1006}}"'] \arrow[ur, phantom, "+"] & Au(s) \arrow[u, "\Delta H_{Au(s)}"']
\end{tikzcd}$$

$$-\Delta H_{Au(l)} - \left(-\Delta H_{s-l_{1336}}\right) + \Delta H_{l-s_{1006}} + \Delta H_{Au(s)} = 0$$

$$\Delta H_{l-s_{1006}} = \Delta H_{Au(l)} - \Delta H_{s-l_{1336}} - \Delta H_{Au(s)}$$

$$\Delta H_{l-s_{1006}} = +\int_{1106}^{1336} (1)\, 29{,}29\, dT - 12{,}76 \cdot 10^{3} - \int_{1106}^{1336} (1)\left(23{,}68 + 5{,}19 \cdot 10^{-3} T\right) dT$$

$$\Delta H_{l-s_{1006}} = 29{,}29\,(1336 - 1106) - 12{,}76 \cdot 10^{3} - 23{,}68\,(1336 - 1106) - \left[\left(\frac{5{,}19}{2}\right)\left(1336^2 - 1106^2\right)\right]$$

$$\Delta H^{l-s}_{1106} = -12{,}93\ kJ/mol$$

B)

$$\begin{tikzcd}
Au(s) \arrow[r, "\Delta S^f_{1336}"] & Au(l) \\
Au(s) \arrow[u, "\Delta S_{Au(s)}"] \arrow[r, "\Delta S^f_{1106}"'] \arrow[ur, phantom, "+"] & Au(l) \arrow[u, "\Delta S_{Au(l)}"']
\end{tikzcd}$$

$$\Delta S^f_{1106} + \Delta S_{Au(l)} - \Delta S^f_{1336} - \Delta S_{Au(s)} = 0$$

$$\Delta S^{f}_{1106} = -\Delta S_{Au(l)} + \Delta S^{f}_{1336} + \Delta S_{Au(s)}$$

$$\Delta S^{f}_{1106} = -\int_{1106}^{1336} \frac{29,29\,dT}{T} + \frac{\Delta H_{1336}}{T_f} + \int_{1106}^{1336} \frac{23,68 + 5,19 \cdot 10^{-3}T}{T}\,dT$$

$$\Delta S^{f}_{1106} = -29,29\left[\ln\left(\frac{1336}{1106}\right)\right] + \frac{12760}{1336} + \left(23,68\ln\left(\frac{1336}{1106}\right)\right) + 5,19 \cdot 10^{-3}(1336-1106)$$

$$\Delta S^{f}_{1106} = -5,53 + 9,55 + 5,67 = 9,69\ J/mol\,K$$

P/ SABER SE É ESPONTÂNEO

$$\Delta S_T = \Delta S_{SIS} + \Delta S_{viz}$$

$$\Delta S_{viz} = \frac{-\Delta H^{f(l-s)}_{1106}}{T_{viz}} = \frac{-12930}{1106} = -11,69\ J/mol\,K$$

$$\Delta S_T = 9,69 - 11,69 = -2,00\ J/mol\,K$$

$\Delta S_T < 0$

A fusão não é espontânea

em 1106 K

c) $\Delta G_T = \Delta H_T - T\Delta S_T$

$\Delta H^f_{1106, Au} = 12930 \ J/mol$

$\Delta S^f_{1106} = 9{,}69 \ J/mol\,K$

$\Delta G_T = 12930 - 1106\,(9{,}69) = 2213 \ J/mol$

Como $\Delta G^f_{1106} > 0$ a fusão não é espontânea, sendo de acordo com o critério de espontaneidade de entropia.

5) 1ª LEI DA TERMODINÂMICA : $du = \delta q - \delta W$

$$C_{V,m} = \left(\frac{du}{dT}\right)_T \therefore du = nC_{V,m}\,dT \qquad dW = p\,dV$$

PROCESSO adiabático $\delta q = 0$

$$\delta q = nC_{V,m}dT + PdV = 0 \quad (I) \qquad {}^{\#}\, d(PV) = PdV + VdP$$

$$PdV + VdP = nR\,dT$$

ENTÃO : $dT = \frac{PdV}{nR} + \frac{VdP}{nR}$ (II)

SUBSTITUINDO (II) EM (I)

$$\delta q = nC_{V,m}\left(\frac{PdV}{nR} + \frac{VdP}{nR}\right) + PdV = 0$$

$$\delta q = \frac{\cancel{n}C_{V,m}PdV}{\cancel{n}R} + \frac{\cancel{n}C_{V,m}VdP}{\cancel{n}R} + PdV = 0$$

$$\delta q = PdV\underbrace{\left(\frac{C_{V,m}}{R} + 1\right)}_{\frac{C_{V,m}+R}{R}} + \frac{C_{V,m}VdP}{R} = 0$$

$$\delta q = PdV\,(C_{V,m} + R) + C_{V,m}VdP = 0$$

como $C_{P,m} - C_{V,m} = R$ $\qquad \gamma = \frac{C_{P,m}}{C_{V,m}}$

$$\delta q = PdV\,C_{P,m} + VdP\,C_{V,m} = 0 \; (\div PV\,C_{V,m})$$

$$\delta q = \frac{\cancel{P}dV\,C_{P,m}}{\cancel{P}V\,C_{V,m}} + \frac{\cancel{V}dP\,\cancel{C_{V,m}}}{P\cancel{V}\,\cancel{C_{V,m}}} = 0 \therefore \delta q = \frac{dV}{V}\gamma + \frac{dP}{P} = 0$$

INTEGRANDO

$$\gamma \ln V + \ln P = \text{CONSTANTE} \quad \therefore V^{\gamma}P = \text{CONSTANTE!}$$

6) (a) $6Nb + Cr_{23}C_6 \xrightarrow{\Delta G^\circ} 6NbC + 23Cr$

(b)

$$6\,Nb + Cr_{23}C_6 \xrightarrow[1200K]{\Delta G} 6\,NbC + 23\,Cr$$

$$\uparrow 6\Delta G_{Nb} \quad \uparrow \Delta G_{Cr_{23}C_6} \quad + \quad \uparrow 6\Delta G_{NbC} \quad \uparrow 23\Delta G_{Cr}$$

$$6Nb + Cr_{23}C_6 \xrightarrow[1200K]{\Delta G^\circ} 6NbC + 23Cr$$

$$\cancel{-6\Delta G^{*0}_{Nb}} \cancel{-\Delta G^{*0}_{Cr_{23}C_6}} + \Delta G^\circ_{1200K} - \Delta G_{1200K} \cancel{+6\Delta G^{*0}_{NbC}} \cancel{+23\Delta G^{*0}_{Cr}} = 0$$

não há solubilidade, $\Delta G = 0$ (componentes puro)

$$\Delta G_{1200K} = \Delta G^\circ_{1200K}$$

$\frac{23}{6}\langle Cr\rangle + \langle C\rangle = \frac{1}{6}\langle Cr_{23}C_6\rangle$ $\quad -68540 - 6{,}44T \quad (\times -6)$

$\langle Nb\rangle + \langle C\rangle = \langle NbC\rangle$ $\quad -130\,140 + 1{,}67T \quad (\times 6)$

$$\Delta G^\circ_{1200K} = 6\left(-130\,140 + 1{,}64(1200)\right) - 6\left[-68540 - 6{,}44.(1200)\right]$$

$$-769{,}022.10^3 + 457{,}608.10^3$$

$$-311424\ J/mol < 0$$

logo a formação de NbC é favorável

4) $\Delta G° = \Delta H° - T\Delta S°$

a) $\Delta S° = -46,1$ (sólido) $\Delta S°$(gas) > $\Delta S°$(líquido) > $\Delta S°$(sólido)

b) $\Delta S° = -102,1$ (gás)

c) $\Delta S° = -55,4$ (líquido)

8) 1º loop → função de pressão

$$dG = VdP - \cancel{SdT}^{\to 0}$$

T = cte

$$\begin{tikzcd}
Au_{(s)} \arrow[r, "\Delta G^f_{1356K}=0", "P=P"'] \arrow[dr, phantom, "+"] & Au_{(l)} \\
Au_{(s)} \arrow[u, "\Delta G_{Au(s)}"] \arrow[r, "\Delta G^f_{1356K, P=1}"'] & Au_{(l)} \arrow[u, "\Delta G_{Au(l)}"']
\end{tikzcd}$$

$$-\Delta G_{Au(s)} + \Delta G_{Au(l)} - \cancel{\Delta G^f_{1356K, P=P}}^{\to 0} + \Delta G^f_{1356, P=1} = 0$$

$$-\int_1^P V_{Au(s)}\,dP + \int_1^P V_{Au(l)}\,dP + \Delta G^f_{1356, P=1} = 0 \quad (I)$$

2º loop → ENTALPIA DE FUSÃO A 1356 K

$$\begin{tikzcd}
Au_{(s)} \arrow[r, "\Delta H^f_{1356K}"] \arrow[dr, phantom, "+"] & Au_{(l)} \\
Au_{(s)} \arrow[u, "\Delta H_{Au(s)}"] \arrow[r, "\Delta H^f_{1336K}"'] & Au_{(l)} \arrow[u, "\Delta H_{Au(l)}"']
\end{tikzcd}$$

$$\Delta H^f_{1336K} = 12{,}760\ kJ/mol$$

$$-\Delta H_{Au(s)} + \Delta H_{Au(l)} - \Delta H^f_{1356K} + \Delta H^f_{1336K} = 0$$

$$-\int_{1336}^{1356}(22{,}68 + 5{,}19\cdot 10^{-3}T)\,dT + \int_{1336}^{1356} 29{,}29\,dT - \Delta H^f_{1356K} + 12760 = 0$$

$$-613{,}6 + 585{,}8 + 12760 = \Delta H^f_{1356K}$$

$$\Delta H^f_{1356K} = 12{,}73\cdot 10^3\ J/mol$$

3° LOOP $\longrightarrow$ ENTROPIA DE FUSÃO 1356 K

$$\begin{tikzcd}
Au_{(s)} \arrow[r, "\Delta S^{f}_{1356K}"] & Au_{(l)} \\
Au_{(s)} \arrow[u, "\Delta S_{Au_{(s)}}"] \arrow[r, "\Delta S^{f}_{1336K}"'] \arrow[ur, phantom, "+"] & Au_{(l)} \arrow[u, "\Delta S_{Au_{(l)}}"']
\end{tikzcd}$$

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

$$\Delta S_f = \frac{12760}{1336}$$

$$\Delta S_{f_{1336}} = 9,55 \text{ J/K}$$

$$-\Delta S_{Au(s)} + \Delta S_{Au(l)} - \Delta S^{f}_{1356K} + \Delta S^{f}_{1336K} = 0$$

$$-\int_{1336}^{1356}\left(\frac{23,68}{T} + 5,19.10^{-3}\right)dT + \int_{1336}^{1356}\frac{29,29}{T}\,dT - \Delta S^{f}_{1356K} + \Delta S^{f}_{1336K} = 0$$

$$-\left[\left(23,68 \ln (1356/1336)\right) + \left(5,19.10^{-3}(1356-1336)\right)\right] + 29,29 \ln\left(\frac{1356}{1336}\right)$$

$$+ 9,55 = \Delta S^{f}_{1356K}$$

$$\Delta S^{f}_{1356K} = 9,55 + 0,435 - 0,456 = 9,529 \text{ J/mol K}$$

SABE-SE QUE $\Delta G = \Delta H - T\Delta S$

$$\Delta G^{f}_{1356K} = \Delta H^{f}_{1356K} - T_f\,\Delta S^{f}_{1356K}$$

$$\Delta G^{f}_{1356} = 12,43.10^{3} - 1356.(9,529) = -191,3 \text{ J/mol} \; *$$

SUBSTITUINDO * EM (I)

$$-191,3 + V_{Au_{(l)}}\int_{1}^{P} dP - V_{Au(s)}\int_{1}^{P} dP = 0$$

$$-191{,}3 + V_{Au_l}(P-1) - V_{Au_s}(P-1) = 0$$

$$\rho_{Au_l} = 17{,}0\ g/cm^3$$

$$\rho_{Au_s} = 19{,}3\ g/cm^3$$

$$M = 197\ g/mol$$

$$V_{Au_l} = \frac{197}{17} = 11{,}59\ \frac{cm^3}{mol} = 1{,}159 \cdot 10^{-5}\ \frac{m^3}{mol}$$

$$V_{Au_s} = \frac{197}{19{,}3} = 10{,}21\ \frac{cm^3}{mol} = 1{,}021 \cdot 10^{-5}\ \frac{m^3}{mol}$$

$$-191{,}3 + 1{,}159 \cdot 10^{-5}(P-1) - 1{,}021 \cdot 10^{-5}(P-1) = 0$$

$$-191{,}3 + 1{,}159 \cdot 10^{-5}P - 1{,}159 \cdot 10^{-5} - 1{,}021 \cdot 10^{-5}P + 1{,}021 \cdot 10^{-5} = 0$$

$$1{,}38 \cdot 10^{-6}P = 191{,}3$$

$$P = 138{,}62 \cdot 10^{6}\ Pa$$

$$P \approx 1368\ atm$$