D 3 h

1. $Zr(\beta) + O_2 = ZrO_2(\beta)$ 1600 K , $C_p(Zr\beta) = 23.22 + 4.64\times10^{-3}T$, $C_p(Zr(\alpha)) = 21.92 + 11.63\times10^{-3}T$

$C_p(O_2) = 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}$

$\Delta H_1, \Delta S_1$

$Zr(\alpha) + O_2$ at 298 K

$\Delta H_1 = \int_{1600}^{1136} C_p(Zr\beta)\,dT + \int_{1136}^{298} C_p(Zr(\alpha))\,dT - 3960\,J/mol + \int_{1600}^{298} C_p(O_2)\,dT$

$\Delta S_1 = \int_{1600}^{1136} \frac{C_p(Zr\beta)}{T}\,dT + \int_{1136}^{298} \frac{C_p(Zr(\alpha))}{T}\,dT - \frac{\Delta H^{Zr}_{\beta\to\alpha}}{T_{trans}} + \int \frac{C_p(O_2)}{T}\,dT$

$\Delta H_2 = -1100100\,J/mol$

$\Delta S_2 = 56.47\,J/K$

$ZrO_2(\alpha)$ at 298 K

$C_p(ZrO_2(\beta)) = 74.48$, $C_p(ZrO_2(\alpha)) = 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2}$

$\Delta H_3 = \int_{298}^{1478} C_p(ZrO_2(\alpha))\,dT + 5900\,J/mol + \int_{1478}^{1703} + \int_{1478}^{1600} C_p(ZrO_2(\beta))\,dT$

$\Delta H'$

$\Delta S_3 = \int_{298}^{1478} \frac{C_p(ZrO_2(\alpha))}{T}\,dT + \frac{\Delta H^{ZrO_2}_{\alpha\to\beta}}{T_{trans}} + \int_{1478}^{1600} \frac{C_p(ZrO_2(\beta))}{T}\,dT$

$ZrO_2(\beta)$ at 1600 K

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1.080\times10^{6}\,J/mol$ $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -198.5\,J/K\,mol$

2. $Si_3N_4 + 3O_2 = 3SiO_2(\alpha) + 2N_2$ at 800 K

$H_{Si_3N_4,800} = \Delta H^{\circ}_{298,Si_3N_4} + \int_{298}^{800} C_p(Si_3N_4)\,dT$ $C_p(Si_3N_4) = 70.54 + 98.74\times10^{-3}T$

$H_{O_2,800} = \int_{298}^{800} C_p(O_2)\,dT$ $C_p(O_2) = 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}$

$H_{SiO_2,800} = \Delta H^{\circ}_{298} + \int_{298}^{800} C_p(SiO_2)\,dT$ $C_p(SiO_2) = 43.09 + 1\times10^{-3}T - 6.02\times10^{5}T^{-2}$

$H_{N_2,800} = \int_{298}^{800} C_p(N_2)\,dT$ $C_p(N_2) = 27.87 + 4.27\times10^{-3}T$

$\Delta H = 3H_{SiO_2,800} + 2H_{N_2,800} - H_{Si_3N_4,800} - 3H_{O_2,800} = -2004.590\,kJ/mol$

$S_{Si_3N_4,800} = S^{\circ}_{298,Si_3N_4} + \int_{298}^{800} \frac{C_p(Si_3N_4)}{T}\,dT$ $\Delta S = 3S_{SiO_2,800} + 2S_{N_2,800} - S_{Si_3N_4,800} - 3S_{O_2,800} = 232.22\,kJ/K\,mol$

$S_{O_2} = S^{\circ}_{298,O_2} + \int_{298}^{800} \frac{C_p(O_2)}{T}\,dT$ $\Delta G = \Delta H - T\Delta S = +1804.154\,kJ/mol$

$S_{SiO_2} = S^{\circ}_{298,SiO_2} + \int_{298}^{800} \frac{C_p(SiO_2)}{T}\,dT$ if $\Delta C_p = 0$ $\Delta H' \approx \Delta H_{298}$

$S_{N_2} = S^{\circ}_{298,N_2} + \int_{298}^{800} \frac{C_p(N_2)}{T}\,dT$ $= 3H^{\circ}_{SiO_2} + 2H^{\circ}_{N_2} - H^{\circ}_{Si_3N_4} - 3H^{\circ}_{O_2}$ at 298

$= -1909.9\,kJ/mol$

$\Delta S' = \Delta S_{298} = 3S^{\circ}_{SiO_2} + 2S^{\circ}_{N_2} - S^{\circ}_{Si_3N_4} - 3S^{\circ}_{O_2}$ at 298

$= -220.8\,J/K$

$\Delta G' = \Delta H' - T\Delta S' = -1811.26\,kJ/mol$

error $= \left|\frac{\Delta G - \Delta G'}{\Delta G}\right| \times 100 = 0.39\,\%$

i) $Z = \sum e^{-\frac{\varepsilon_i}{kT}}$ $\begin{cases} 0, & \text{(atom} \\ \Delta\mu v & \text{vacu} \end{cases}$ $\Rightarrow Z = e^{-\frac{0}{kT}} + e^{-\frac{\Delta\mu v}{kT}} = 1 + e^{-\frac{\Delta\mu v}{kT}}$

$n = \frac{N e^{-\frac{\Delta\mu v}{kT}}}{Z} \Rightarrow \frac{n}{N} = \frac{e^{-\Delta\mu v/kT}}{1+e^{-\Delta\mu v/kT}} = \frac{1}{1+e^{\Delta\mu v/kT}}$

ii) Varying in $\Rightarrow \Delta E = n\Delta\mu v$ $\Delta S = k \ln \Omega = k \ln \frac{N!}{n!(N-n)!}$

$= k(\ln N! - \ln(n!) - \ln(N-n)!)$

$= k(N\ln(N) - N - (n\ln(n) - n) - ((N-n)\ln(N-n) - (N-n)))$

$= k(N\ln(N) - n\ln(n) - (N-n)\ln(N-n))$

$k(N(\ln(N) - \ln(N-n)) - n(\ln(n) - \ln(N-n)) = k(N\ln\frac{N}{N-n} - n\ln\frac{n}{N-n})$