1.

$\mathrm{Zr}(\beta) + \mathrm{O}_2 \rightarrow \mathrm{ZrO}_2(\beta)$ $\quad \Delta H_{1600} \quad \Delta S_{1600}$

$$\begin{tikzcd}
\mathrm{Zr}(\beta)+\mathrm{O}_2 \text{ at } 1600^\circ\mathrm{C} \arrow[d] \arrow[dd, bend right=60, "\Delta H_1"'] & \overset{\Delta H}{=} & \mathrm{ZrO}_2(\beta) \text{ at } 1600^\circ & \Delta H_3 = \Delta H_3' + \Delta H_{\alpha\beta} + \Delta H_3'' \\
\mathrm{Zr}(\beta) \rightarrow \mathrm{Zr}(\alpha) \arrow[d] & & \mathrm{ZrO}_2(\alpha) \rightarrow \mathrm{ZrO}_2(\beta) \quad \Delta H_{\alpha\beta} \arrow[u, "\Delta H_3''"'] & \\
\mathrm{Zr}(\beta)+\mathrm{O}_2 \text{ at } 298\mathrm{K} & \overset{\Delta H_2}{=} & \mathrm{ZrO}_2(\alpha) \text{ at } 298\mathrm{K} \arrow[u, "\Delta H_3'"'] \arrow[uu, bend right=60, "\Delta H_3"'] &
\end{tikzcd}$$

$C_p(\mathrm{Zr}(\beta)) = 23.22 + 4.64\times10^{-3}T \quad C_p(\mathrm{Zr}(\alpha)) = 21.97 + 11.63\times10^{-3}T$

$C_p(\mathrm{O}_2) = 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}$

$$\Delta H_1 = \int_{1879}^{1136}(23.22 + 4.64\times10^{-3})dT + \int_{1136}^{298}(21.97 + 11.63\times10^{-3})dT \overset{\Delta H_{\beta\rightarrow\alpha}}{-3900} + \int_{1873}^{298}(29.96 + \underset{\times10^{-3}}{4.18T} - \overset{\times10^{5}}{1.67T^{-2}})dT$$

$$= -22258 - 25398.7 - 3900 - 53862.1$$

$$= -105418.7 \text{ J/mol}$$

$\Delta H_2 = -1100800$ J/mol $\qquad$ (= formation H of ZrO_2)

$C_p(\mathrm{ZrO}_2(\beta)) = 74.48, \quad C_p(\mathrm{ZrO}_2(\alpha)) = 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2}$

$$\Delta H_3 = \int_{298}^{1478}(69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}\cdot T^{-2})dT + 5900 + \int_{1478}^{1873} 74.48\, dT$$

$$= 69.62T + 3.765\times10^{-3}T^2 - \frac{14.06\times10^5}{T}\Bigg|_{298}^{1478} + 5900 + 74.48T\Bigg|_{1478}^{1873}$$

$$= 82151.6 + 7890.24 + 3766.84 + 5900 + 29419.6 = 129128.28$$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1077.1$ kJ/mol

ΔS

$$\begin{tikzcd}
Zr(\beta) + O_2 \text{ at } 1600^\circ C \arrow[dd, "\Delta S_1"'] & = & ZrO_2(\beta) \text{ at } 1600^\circ \\
Zr(\beta) \rightarrow Zr(\alpha) & \Delta S_2 & ZrO_2(\alpha) \rightarrow ZrO_2(\beta) \\
Zr(\beta) + O_2 \text{ at } 298K & = & ZrO_2(\alpha) \text{ at } 298K
\end{tikzcd}$$

$C_p(Zr(\beta)) = 23.22 + 4.64\times10^{-3}T$, $C_p(Zr(\alpha)) = 21.97 + 11.63\times10^{-3}T$

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

$\Delta S_{\beta\rightarrow\alpha} = \Delta H_{\beta\rightarrow\alpha}/T = -3900/1136 = -3.43 \text{ J/mol}\cdot K$

$$\Delta S_1 = \int_{1873}^{1136} \frac{23.22}{T} + 4.64\times10^{-3}\, dT + \int_{1136}^{298} \frac{21.97}{T} + 11.63\times10^{-3}\, dT$$

$$-3.43 + \int_{1873}^{298} \frac{29.96}{T} + 4.18\times10^{-3} - 1.67\times10^{5}\, T^{-3}\, dT$$

$$= -15.03 - 39.15 - 3.43 - 60.74 = -118.35 \text{ J/mol}\cdot K$$

$\Delta S_2 = 50.4 - 39 - 205.1 = -193.7 \text{ J/mol}\cdot K$

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

$C_p(ZrO_2(\beta)) = 74.48$

$\Delta S_{\alpha\rightarrow\beta} = \Delta H_{\alpha\rightarrow\beta}/T = 5900/1478 = 3.99$

$$\Rightarrow \Delta S_3 = \int_{298}^{1478} \frac{C_p(ZrO_2(\alpha))}{T}\, dT + 3.99 + \int_{1478}^{1873} \frac{C_p(ZrO_2(\beta))}{T}\, dT$$

$$= 112.78 + 3.99 + 17.74 = 134.51 \text{ J/mol}\cdot K$$

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -177.54 \text{ J/mol}\cdot K$

2.

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

$Si_3N_4 + 3O_2 = 3SiO_2(\alpha)$ at 298K

$\Delta H_{rxn} = 3H_{SiO_2} - H_{Si_3N_4} = -1987900$ J/mol

$\Delta S_{rxn} = 3S_{SiO_2} + 2S_{N_2} - S_{Si_3N_4} - 3S_{O_2} = -220.8$ J/mol·K

$\Rightarrow \Delta G_{rxn} = \Delta H_{rxn} - 298\Delta S_{rxn} = -1.9221 \times 10^6$

$\Delta C_p = 2C_p(N_2) + 3C_p(SiO_2(\alpha)) - C_p(Si_3N_4) - 3C_p(O_2)$

$$\Delta G_{800} = \Delta H_{rxn} - 800\Delta S_{rxn} + \int_{298}^{800} \Delta C_p \, dT - 800\int_{298}^{800} \frac{\Delta C_p}{T} dT$$

$C_p(N_2) = 27.87 + 4.27 \times 10^{-3}\, T$

$C_p(SiO_2(\alpha)) = 43.89 + 1 \times 10^{-3} T - 6.02 \times 10^5\, T^{-2}$

$C_p(Si_3N_4) = 70.54 + 98.74 \times 10^{-3} T$

$C_p(O_2) = 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2}$

$\Delta C_p = 26.99 - 99.74 \times 10^{-3} T - 13.05 \times 10^5 T^{-2}$

$$\int_{298}^{800} \Delta C_p \, dT = -16687.1 \quad , \quad \int_{298}^{800} \frac{\Delta C_p}{T} dT = -29.7445$$

$\Rightarrow \Delta G_{800} = -1.8163 \times 10^6$

$\Delta C_p = 0$ 이라 하면

$\Delta G_{800} = \Delta H_{rxn} - 800\Delta S_{rxn} = -1.81126 \times 10^6$

$$err = \frac{\Delta G_{simpled} - \Delta G_{800}}{\Delta G_{800}} \cdot 100 = \underline{-0.278\ \%}$$

3.

i) classical

생성 $E = \Delta H_v$

n 개 생성되면 $n \cdot \Delta H_v$ 전체 lattice N개, vacancy n개 atom $N-n$ 개

$$S = k_B \ln \frac{N!}{(N-n)!\,n!} = k_B \left(N\ln N - (N-n)\ln(N-n) - n\ln n \right)$$

$$= k_B \left((N-n)\ln \frac{N}{N-n} + n\ln \frac{N}{n} \right)$$

$$\Delta F = \Delta U - T\Delta S = \Delta H_v \cdot n - T \cdot k_B \cdot \left((N-n)\ln \frac{N}{N-n} + n \ln \frac{N}{n} \right)$$

$$\frac{d\Delta F}{dn} = \Delta H_v - k_B T \frac{d}{dn_v} \left((N-n)(\ln N - \ln(N-n)) + n(\ln N - \ln n) \right)$$

$$= \Delta H_v - k_B T \left(-1(\ln N - \ln(N-n)) + 1 + \ln N - \ln n - 1 \right)$$

$$= \Delta H_v - k_B T \left(\ln(N-n) - \ln n \right)$$

$$= \Delta H_v - k_B T \ln \frac{N-n}{n} = 0$$ 일때 평형.

$$\frac{N-n}{n} = \exp\left(\frac{\Delta H_v}{k_B T}\right) \qquad \frac{n}{N} = \frac{1}{1+\exp(\Delta H_v / k_B T)}$$

ii) statistical

N개의 lattice $\begin{cases} \Delta H_v & (\text{vacancy}) \\ 0 & (\text{atom}) \end{cases}$

$$Z = \sum_i e^{-\varepsilon_i/k_B T} = 1 + e^{-\Delta H_v/k_B T}$$

$$n_i = n = \frac{N e^{-\Delta H_v/k_B T}}{Z} \Rightarrow \frac{n}{N} = \frac{e^{-\Delta H_v/k_B T}}{1 + e^{-\Delta H_v/k_B T}} = \frac{1}{1 + e^{\Delta H_v/k_B T}}$$