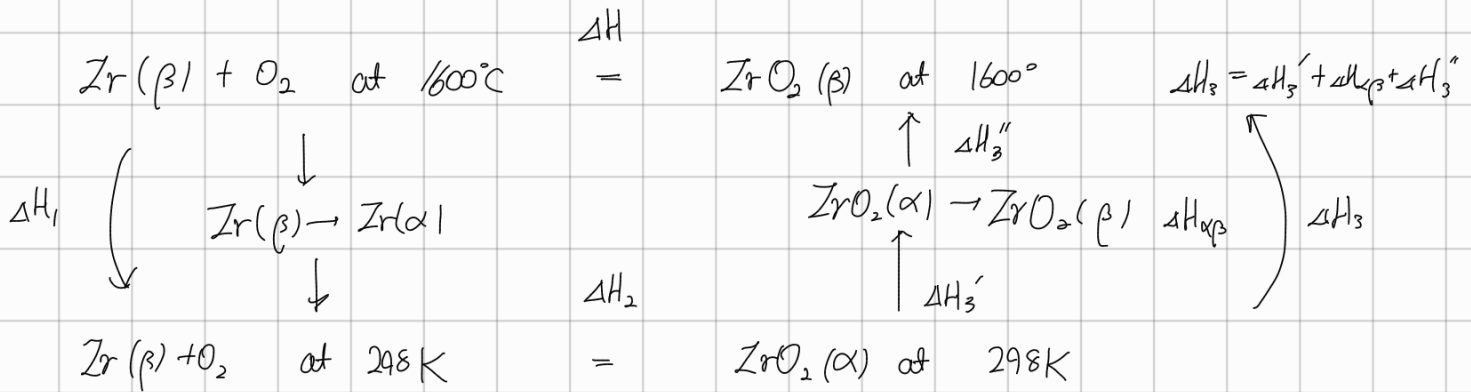
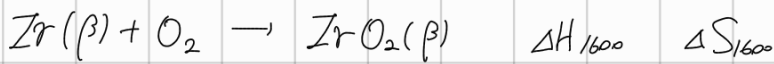


1.



$$C_p(\text{Zr}(\beta)) = 23.22 + 4.64 \times 10^{-3} T \quad C_p(\text{Zr}(\alpha)) = 21.97 + 11.63 \times 10^{-3} T$$

$$C_p(\text{O}_2) = 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^{-2}$$

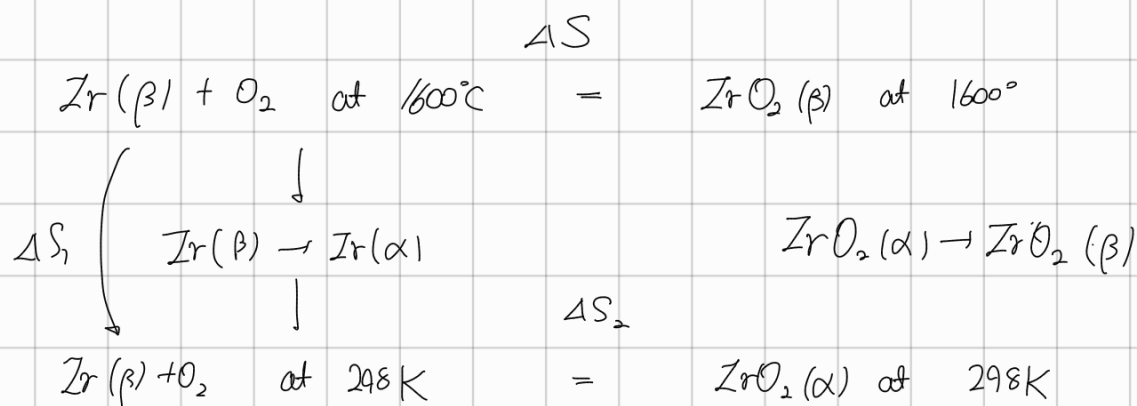
$$\begin{aligned} \Delta H_1 &= \int_{1873}^{1136} (23.22 + 4.64 \times 10^{-3} T) dT + \int_{1136}^{298} (21.97 + 11.63 \times 10^{-3} T) dT - 3900 + \int_{1873}^{298} (29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^{-2}) dT \\ &= -22258 - 25398.7 - 3900 - 53862.1 \\ &= -105418.7 \text{ J/mol} \end{aligned}$$

$$\Delta H_2 = -1100800 \text{ J/mol} \quad (= \text{formation H of } \text{ZrO}_2)$$

$$C_p(\text{ZrO}_2(\beta)) = 74.48, \quad C_p(\text{ZrO}_2(\alpha)) = 69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^{-5} T^{-2}$$

$$\begin{aligned} \Delta H_3 &= \int_{298}^{1478} (69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^{-5} T^{-2}) dT + 5900 + \int_{1478}^{1873} 74.48 dT \\ &= 69.62T + 3.765 \times 10^{-3} T^2 - \frac{14.06 \times 10^{-5}}{T} \bigg|_{298}^{1478} + 5900 + 74.48T \bigg|_{1478}^{1873} \\ &= 82151.6 + 7890.24 + 3766.84 + 5900 + 29419.6 = 129128.28 \end{aligned}$$

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



$$C_p(\text{Zr}(\beta)) = 23.22 + 4.64 \times 10^{-3}T, \quad C_p(\text{Zr}(\alpha)) = 21.97 + 11.63 \times 10^{-3}T$$

$$C_p(\text{O}_2) = 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{-5}T^{-2}$$

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

$$\begin{aligned}
 \Delta S_1 &= \int_{1873}^{1136} \frac{23.22}{T} + 4.64 \times 10^{-3} dT + \int_{1136}^{298} \frac{21.97}{T} + 11.63 \times 10^{-3} dT \\
 &\quad - 3.43 + \int_{1873}^{298} \frac{29.96}{T} + 4.18 \times 10^{-3} - 1.67 \times 10^{-5} T^{-2} dT \\
 &= -15.03 - 39.15 - 3.43 - 60.74 = -118.35 \text{ J/mol}\cdot\text{K}
 \end{aligned}$$

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

$$C_p(\text{ZrO}_2(\alpha)) = 69.62 + 7.53 \times 10^{-3}T - 14.06 T^{-2}$$

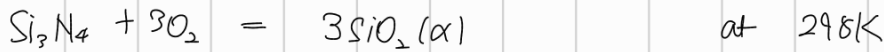
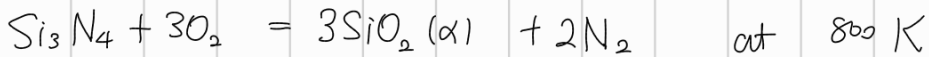
$$C_p(\text{ZrO}_2(\beta)) = 74.48$$

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

$$\begin{aligned}
 \Rightarrow \Delta S_3 &= \int_{298}^{1478} \frac{C_p(\text{ZrO}_2(\alpha))}{T} dT + 3.99 + \int_{1478}^{1873} \frac{C_p(\text{ZrO}_2(\beta))}{T} dT \\
 &= 112.78 + 3.99 + 17.74 = 134.51 \text{ J/mol}\cdot\text{K}
 \end{aligned}$$

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

2.



$$\Delta H_{\text{rxn}} = 3H_{\text{SiO}_2} - H_{\text{Si}_3\text{N}_4} = -1987900 \text{ J/mol}$$

$$\Delta S_{\text{rxn}} = 3S_{\text{SiO}_2} + 2S_{\text{N}_2} - S_{\text{Si}_3\text{N}_4} - 3S_{\text{O}_2} = -220.8 \text{ J/mol}\cdot\text{K}$$

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

$$\Delta C_p = 2C_p(\text{N}_2) + 3C_p(\text{SiO}_2(\alpha)) - C_p(\text{Si}_3\text{N}_4) - 3C_p(\text{O}_2)$$

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

$$C_p(\text{N}_2) = 27.87 + 4.27 \times 10^{-3} T$$

$$C_p(\text{SiO}_2(\alpha)) = 43.89 + 1 \times 10^{-3} T - 6.02 \times 10^5 T^{-2}$$

$$C_p(\text{Si}_3\text{N}_4) = 70.54 + 98.74 \times 10^{-3} T$$

$$C_p(\text{O}_2) = 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2}$$

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

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

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

$$\Delta C_p = 0 \quad 0/2 \quad \text{true}$$

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

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

3.

i) classical

생성 $E = \Delta H_v$

n 개 생성되면 $n \cdot \Delta H_v$

전체 lattice N 개, vacancy n 개 atom $N-n$ 개

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

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

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

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

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

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

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

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

ii) statistical

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

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

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