1.

$$C_p(ZrO_2(\beta)) = 74.48 \ J/mol \cdot K \qquad (1478-2950K)$$

$$C_p(Zr(\alpha)) = 21.97 + 11.63_{\times 10^{-3}} T \ J/mol \cdot K \qquad (298K-1136K)$$

$$C_p(O_2) = 29.96 + 6.18 T_{\times 10^{-3}} - \frac{1.67 \times 10^{-5}}{T^2} J/mol \cdot K$$

$$C_p(ZrO_2(\alpha)) = 69.92 + 7.53_{\times 10^{-3}} T - \frac{14.06 \times 10^{-5}}{T^2} J/mol \cdot K \qquad (298-1478K)$$

$$C_p(Zr(\beta)) = 23.22 + 4.64 T_{\times 10^{-3}} \ J/mol \cdot K$$

$$\begin{tikzcd}
Zr(\beta) + O_2 \arrow[r, "1600K"'] \arrow[d, "1"] & ZrO_2(\beta) \ 1600K \\
Zr(\alpha) + O_2 \arrow[r, "2", "298K"'] & ZrO_2(\alpha) \ 298K \arrow[u, "3"']
\end{tikzcd}$$

$$\Delta H_1 = \int_{1600}^{1136} C_p(Zr(\beta))\,dT + \Delta H(Zr(\beta) \to Zr(\alpha)) + \int_{1136}^{298} C_p(Zr(\alpha))\,dT + \int_{1600}^{298} C_p(O_2)\,dT$$

$$= \left[23.22T + 2.32_{\times 10^{-3}} T^2\right]_{1600}^{1136} + (-3900) + \left[21.97T + \frac{11.63 \times 0.001}{2} T^2\right]_{1136}^{298} + \left[29.96T + 3.09_{\times 10^{-3}} T^2 + \frac{1.67 \times 10^{-5}}{T}\right]_{1600}^{298}$$

$$= -13719 + (-3900) + -25399 - 46644$$

$$= -85762 J$$

$$\Delta H_2 = -1100{,}800 J$$

$$\Delta H_3 = \int_{298}^{1478} 69.92 + 7.53 \times 10^{-3} T - \frac{14.06 \times 10^{-5}}{T^2}\,dT + \int_{1478}^{1600} 74.48\,dT + 5900$$

$$= 90396 + 5900 + 9087 = 105382 J$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1081180 J$$

$-1081180J$

1.

$$\Delta S_1 = \int_{1000}^{1136} \frac{23.22+4.64\times10^{-3}T}{T}dT + \Delta S(Zr(\beta)\to Zr(\alpha)) + \int_{1136}^{298}\frac{21.97+11.63\times10^{-3}T}{T}dT$$

$$+ \int_{1600}^{298} \frac{29.96+6.18\times10^{-3}-\frac{1.67\times10^{-5}}{T^2}}{T}dT$$

$$= -10.11 + \left(-\frac{3900}{1136}\right) + -39.15 - 58.40$$

$$= -111\ J/K$$

$$\Delta S_2 = 50.4 - 39.0 - 205.1 = -193.7$$

$$\Delta S_3 = \int_{298}^{1478} \frac{69.92+17.53\times10^{-3}T}{T} - \frac{14.06\times10^{-5}}{T^3}dT + \int_{1478}^{1600}\frac{74.48}{T}dT + \frac{5900}{1478}$$

$$= 120.8 + 5.91 + 3.992$$

$$= 131\ J/K$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -174\ J/K$$

$-174\ J/K$

2.

$\Delta G = \Delta H - T\Delta S$

$$\begin{tikzcd}
\underset{800K}{Si_3N_4 + 3O_2} \arrow[r] \arrow[d, "1"'] & \underset{800K}{3SiO_2 + 2N_2} \\
\underset{Si_3N_4 + 3O_2}{298K} \arrow[r, "2"] & \underset{3SiO_2 + 2N_2}{298K} \arrow[u, "3"']
\end{tikzcd}$$

$\therefore \Delta G = \Delta H - T\Delta S \quad (T=800)$

$= -1739423\,J$

$-1739423\,J$

$$\Delta H_1 = \int_{800}^{298} 70.54 + 98.74\times10^{-3}\times T + 3\times\left(29.96 + 4.18\times10^{-3}T + \frac{-1.67\times10^{-5}}{T^2}\right) dT$$

$$= -111139\,J$$

$$\Delta H_2 = -910900\times3 + 744800 = -1987900\,J$$

$$\Delta H_3 = 3\int_{298}^{800} 43.89 + 1.00\times10^{-3}T - \frac{6.02\times10^{-5}}{T^2}\,dT + 2\int_{298}^{800} 27.87 + 4.27\times10^{-3}T\,dT$$

$$= 66925\,J + 58316\,J = 125241\,J$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1973798\,J$$

$$\Delta S_1 = \int_{800}^{298} \frac{70.54 + 98.74\times10^{-3}\times T + 3\times\left(29.76 + 4.18\times10^{-3}T + \frac{-1.67\times10^{-5}}{T^2}\right)}{T}\,dT$$

$$= -214\,J/K$$

$$\Delta S_2 = 3\times41.5 - 113.0 - 3\times205.1 + 2\times191.5$$

$$= -225.3\,J/K$$

$$\Delta S_3 = 3\int_{298}^{800} \frac{43.89 + 1.00\times10^{-3}T - \frac{6.02\times10^{-5}}{T^2}}{T}\,dT + 2\int_{298}^{800} \frac{27.87 + 4.27\times10^{-3}T}{T}\,dT$$

$$= 132\,J/K + 59\,J/K = 191\,J/K \quad \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -248\,J/K$$

3.

1) 통계 열역학적 접근 방식

$$Z = \sum_i e^{-\frac{\varepsilon_i}{k_B T}} \text{ (partition function)}$$

~~(partition function)~~

$$(\varepsilon_i = \Delta H_v)$$

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

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

$$= \frac{1}{1 + e^{\frac{\Delta H_v}{k_B T}}} \leftarrow \text{답}$$

2) 고전 열역학적 방식

$$G_m = H_m - S_m T \quad (\text{constant } T)$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$G_{m,f} = G_{m,i} + \Delta H_m - T\Delta S_m$$

Vacancy의 수가 0개일 때 $G_{mi} = 0$

ΔH_m = vacancy n개 생성 $= \frac{n}{N}\Delta H_v$

$$\Delta S = k\left(\frac{n}{N}\ln\left(\frac{n}{N}\right) + \frac{N-n}{N}\ln\left(\frac{N-n}{N}\right)\right)$$

mixing entropy

평형이므로 let $\frac{n}{N} = t$ $\frac{dG}{dt} = 0$

$$\Delta H_m = T\Delta S$$

$$\frac{n}{N}\Delta H_v + kT\left(\frac{n}{N}\ln\left(\frac{n}{N}\right) + \frac{N-n}{N}\ln\left(\frac{N-n}{N}\right)\right) = \Delta G_m$$

$$t\Delta H_v + kT(t\ln t + (1-t)\ln(1-t))$$

$$\Delta H_v + kT\left(\ln\frac{t}{1-t}\right) = 0$$

$$\frac{t}{1-t} = e^{-\frac{\Delta H_v}{kT}}$$

$$t = \frac{e^{-\frac{\Delta H_v}{kT}}}{1+e^{-\frac{\Delta H_v}{kT}}} = \frac{1}{e^{\frac{\Delta H_v}{kT}}+1} \rightarrow \text{답}$$