

1.

$$C_p(ZrO_2(\beta)) = 74.48 \text{ J/mol} \cdot K$$

$$(1478 - 2950 \text{ K})$$

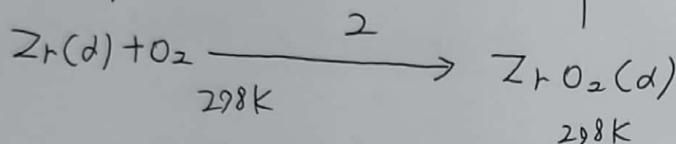
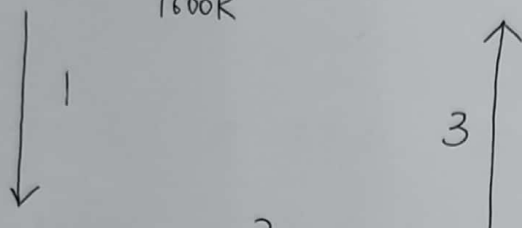
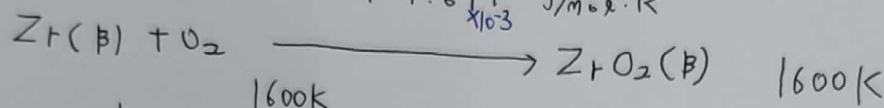
$$C_p(Zr(\alpha)) = 21.97 + 11.63 \times 10^{-3} T \text{ J/mol} \cdot K$$

$$(298 \text{ K} - 1136 \text{ K})$$

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

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

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



$$\begin{aligned} \Delta H_1 &= \int_{1600}^{1136} C_p(Zr(\beta)) dT + \Delta H(Zr(\beta) \rightarrow Zr(\alpha)) + \int_{1136}^{298} C_p(Zr(\alpha)) dT \\ &\quad + \int_{1600}^{298} C_p(O_2) dT \\ &= \left[23.22T + 2.32 \times 10^{-3} T^2 \right]_{1600}^{1136} + (-3900) + \left[21.97T + \frac{11.63 \times 10^{-3}}{2} T^2 \right]_{1136}^{298} \\ &\quad + \left[29.96T + 3.09 \times 10^{-3} T^2 - \frac{1.67 \times 10^{-5}}{T} \right]_{1600}^{298} \end{aligned}$$

$$\begin{aligned} &= -13719 + (-3900) + -2539 - 46644 \\ &= -85762 \text{ J} \end{aligned}$$

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

$$\begin{aligned} \Delta H_3 &= \int_{298}^{1478} 69.92 + 7.53 \times 10^{-3} T - \frac{14.06 \times 10^{-5}}{T^2} dT + \int_{1478}^{1600} 74.48 dT + 5900 \\ &= 90396 + 5900 + 9087 = 105382 \text{ J} \end{aligned}$$

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

$$(-1081180 \text{ J})$$

1.

$$\Delta S_1 = \int_{1600}^{1136} \frac{23.22 + 4.64 \times 10^{-3} T}{T} dT + \Delta S(Zr(\beta) \rightarrow Zr(\alpha)) + \int_{1136}^{298} \frac{21.97 + 11.63 \times 10^{-3} T}{T} dT$$

$$+ \int_{1600}^{298} \frac{22.96 + 6.18 \times 10^{-3} - \frac{1.67 \times 10^{-5}}{T^2}}{T} dT$$

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

$$= -111 \text{ J/K}$$

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

$$\Delta S_3 = \int_{298}^{1478} \frac{62.92 + 7.53 \times 10^{-3} T - \frac{14.06 \times 10^{-5}}{T^3}}{T} dT + \int_{1478}^{1600} \frac{174.48}{T} dT + \frac{5900}{1478}$$

$$= 120.8 + 5.91 + 3.992$$

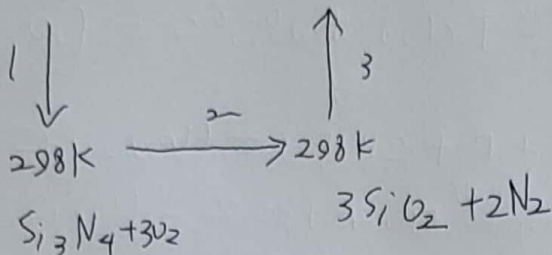
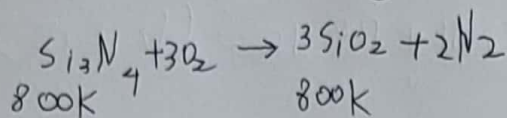
$$= 131 \text{ J/K}$$

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

-174 J/K

2.

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



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

$$= -1730423 \text{ J}$$

$$\boxed{-1730423 \text{ J}}$$

$$\Delta H_1 = \int_{800}^{298} 70.54 + 98.14 \times 10^{-3} \times T + 3 \times \left(29.76 + 4.18 \times 10^{-3} T + \frac{-1.67 \times 10^{-5}}{T^2} \right) dT$$

$$= -111139 \text{ J}$$

$$-1987900 \text{ J}$$

$$\Delta H_2 = -910200 \times 3 + 144200 =$$

$$\Delta H_3 = 3 \int_{298}^{800} 43.89 + 1.00 \times 10^{-3} T - \frac{6.02 \times 10^{-5}}{T^2} dT + 2 \int_{298}^{800} 27.87 + 4.27 \times 10^{-3} T dT$$

$$= 66925 \text{ J} + 58316 \text{ J} = 125241 \text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1973798 \text{ J}$$

$$\Delta S_1 = \int_{800}^{298} \frac{70.54 + 98.14 \times 10^{-3} \times T + 3 \times \left(29.76 + 4.18 \times 10^{-3} T + \frac{-1.67 \times 10^{-5}}{T^2} \right)}{T} dT$$

$$= -214 \text{ J/K}$$

$$\Delta S_2 = 3 \times 41.5 - 113.0 - 3 \times 205.1 + 2 \times 191.5$$

$$= -225.3 \text{ J/K}$$

$$\Delta S_3 = 3 \int_{298}^{800} \frac{43.89 + 1.00 \times 10^{-3} T - \frac{6.02 \times 10^{-5}}{T^2}}{T} dT + 2 \int_{298}^{800} \frac{27.87 + 4.27 \times 10^{-3} T}{T} dT$$

$$= 132 \text{ J/K} + 57 \text{ J/K} = 191 \text{ J/K} \quad \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -248 \text{ J/K}$$

3.

1) 통계역학적 접근 방식

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

$$(\epsilon_i = \Delta H_i)$$

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

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

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

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 $G_{mi} = 0$

$$\Delta H_m = \text{vacancy } n\text{개 생성} = \frac{n}{N} \Delta H_v$$

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

Mixing
entropy

평형상태의 조건 $\left(\text{let } \frac{n}{N} = t \right) \quad \frac{dG}{dt} = 0$

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

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

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

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

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

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