## 문제 1번

$\Delta H_{1600} = \Delta H_{1600, ZrO_2(\beta)} - \Delta H_{1600, Zr(\beta)} - \Delta H_{1600, O_2}$ 이다.

①　　　②　　　③

각각의 번호의 값을 구하면,

①: $\Delta H_{298, ZrO_2(\alpha)} + \int_{298}^{1478} C_p \cdot dT + \Delta H_{ZrO_2(\alpha \to \beta)} + \int_{1478}^{1600} C_p \cdot dT$

$= -1100800 + \int_{298}^{1478} (69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2})dT$

$+ 5900 + \int_{1478}^{1600} 74.48\, dT$

$= -1100800 + 69.92 \times (1478-298) + 3.765\times10^{-3} \times (1478^2 - 298^2) + 14.06\times10^{5}\left(\frac{1}{1478} - \frac{1}{298}\right) + 5900 + 74.48 \times (1600-1478)$

$\doteq -99.95\times10^{4}$ (J)

②: $\int_{298}^{1136} C_p \cdot dT + \Delta H_{Zr(\alpha \to \beta)} + \int_{1136}^{1600} C_p \cdot dT$

$= \int_{298}^{1136} (21.97 + 11.63\times10^{-3}T)dT + 3900 + \int_{1136}^{1600} (23.22 + 4.63\times10^{-3}T)dT$

$$= 21.97\times(1136-298) + 5.815\times10^{-3}(1136^2-298^2) + 3900$$

$$+23.22\times(1600-1136) + 2.315\times10^{-3}\times(1600^2-1136^2)$$

$$\approx \underline{4.302\times10^4 (J)}$$

③: $\int_{298}^{1600} C_p \cdot dT = \int_{298}^{1600} (29.96 + 4.18\times10^{-3}T - 1.67\times10^5 T^{-2})dT$

$$= 29.96\times(1600-298) + 2.09\times(1600^2-298^2) + 1.67\times10^5\times\left(\frac{1}{1600}-\frac{1}{298}\right)$$

$$\approx 4.396\times10^4 (J)$$

$$\therefore \boxed{\Delta H_{1600} = ① + ② + ③ = \underline{-1.086\times10^6 (J)}}$$

$$\Delta S_{1600} = \underbrace{\Delta S_{1600, ZrO_2(\beta)}}_{①} - \underbrace{\Delta S_{1600, Zr(\beta)}}_{②} - \underbrace{\Delta S_{1600, O_2}}_{③}$$

①: $\Delta S_{298, ZrO_2(\alpha)} + \int_{298}^{1478} \frac{C_p}{T} \cdot dT + \frac{\Delta H_{ZrO_2(\alpha\to\beta)}}{1478} + \int_{1478}^{1600} \frac{C_p}{T} \cdot dT$

$$= 50.4 + 69.92\times \ln\left(\frac{1478}{298}\right) + 7.53\times10^{-3}\times(1478-298) +$$

$$7.03\times10^{5}\left(\frac{1}{1478^{2}}-\frac{1}{298^{2}}\right)+\frac{5900}{1478}+74.48\ln\left(\frac{1600}{1478}\right)$$

$$\approx 173.1(J/K)$$

②: $$\Delta S_{298,Zr(\alpha)}+\int_{298}^{1136}\frac{C_p}{T}dT+\frac{\Delta H_{Zr(\alpha\to\beta)}}{1136}+\int_{1136}^{1600}\frac{C_p}{T}dT$$

$$=39+21.97\times\ln\left(\frac{1136}{298}\right)+11.63\times10^{-3}(1136-298)+\frac{3900}{1136}$$

$$+23.22\ln\left(\frac{1600}{1136}\right)+4.64\times10^{-3}(1600-1136)\approx 91.7(J/K)$$

③: $$\Delta S_{298,O_2}+\int_{298}^{1600}\frac{C_p}{T}dT$$

$$=205.1+29.96\times\left(\frac{1600}{298}\right)+4.18\times10^{-3}(1600-298)$$

$$+0.835\times10^{5}\times\left(\frac{1}{1600^{2}}-\frac{1}{298^{2}}\right)=260(J/K)$$

$$\boxed{\therefore \Delta S_{1600}=173.1-91.7-260\approx -178.6(J/K)}$$ 이다.

## 문제 2번

$$\Delta C_p = 3C_{p\,SiO_2} + 2C_{p\,N_2} - C_{p\,Si_3N_4} - 3C_{p\,O_2}$$

$$= 3\times(41.5) + 2\times(191.5) - 113 - 3\times(205.1)$$

$$= \underline{-220.8\ (J/K)}$$ 이다.

이때,

$$\Delta H_{800} = \Delta H_{298} + \int_{298}^{800} C_p\,dT$$

$$= -1987900 + 26.99\times(800-298) - 49.84\times10^{-3}(800^2-298^2)$$

$$+ 13.05\times10^5\times\left(\frac{1}{800}-\frac{1}{298}\right) \simeq \underline{-2.005\times10^6\ (J)}$$

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

$$= -220.8 + 26.99\times\ln\left(\frac{800}{298}\right) - 99.74\times10^{-3}(800-298)$$

$$+ 6.525\times10^5\left(\frac{1}{800^2}-\frac{1}{298^2}\right) \simeq \underline{-250.5\ (J/K)}$$ 이다.

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

$\Delta G_{800} = -2.005 \times 10^6 (J) - 800 \times (-250.5 (J/k))$

$= -1.805 \times 10^6 (J)$ 이다.

①

또한, $C_p = 0$ 이면, $\Delta H = -1987900 (J)$

$\Delta S = -220.8 (J/k)$ 이므로

이를 대입하면

$\Delta G_{800} = \Delta H - T\Delta S = -1.811 \times 10^6 (J)$ 이다. (for $C_p = 0$)

②

∴ ①과 ②의 오차율을 구하면

$$\left| \frac{(-1.811 \times 10^6) - (-1.805 \times 10^6)}{(-1.805 \times 10^6)} \right| \doteq 0.003$$

$\therefore 0.003 \times 100 = 0.3 (\%)$ 정도이다.

## 문제 3번

(case1) 통계열역학적 방식

$Z = \sum_j e^{-E_j/kT}$ 에서 $E_j = \Delta H_v$ 를 나타낸다.

이때, atom이 채워질 자리에 대한 $E_j = 0$ 이므로,

$$Z = 1 + e^{-\Delta H_v/kT} \rightarrow \frac{n}{N} = \frac{e^{-\Delta H_v/kT}}{Z} = \frac{e^{-\Delta H_v/kT}}{1 + e^{-\Delta H_v/kT}}$$

$$= \frac{1}{1 + e^{\Delta H_v/kT}}$$ 이다.

(case2) 고전열역학적 방식

$$\Delta S_{config} = k \ln \frac{N!}{n!(N-n)!} = k(N\ln N - n\ln N - (N-n)\ln(N-n))$$

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

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

→ $\Delta F$를 $n$에 대해 미분하면

$$\frac{d\Delta F}{dn} = \Delta H_v - Tk\left(-\left(\cancel{\ln N} - \ln(N-n)\right) \cancel{+1} + \cancel{\ln N} - \ln n \cancel{-1}\right)$$

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

$= 0$ 이므로,

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

$$\Leftrightarrow \exp\left(\frac{\Delta H_v}{kT}\right) = \frac{N-n}{n}$$

$$\Leftrightarrow \frac{n}{N} = \frac{1}{1+\exp\left(\frac{\Delta H_v}{kT}\right)}$$ 이므로.

case 1과 case 2의 결과가 동일하다!