1. $Zr(\beta) + O_2 = ZrO_2(\beta)$

i) According to Appendix, we know $\Delta H^\circ_{298}(ZrO_2) = -1,100,800J$

Zr phase changes α to β at 1136K

ZrO_2 phase changes α to β at 1478K

So. we can change process by following step.

1) Cooling $Zr(\beta)$ & O_2 1600K → 1136K ⇨ $\Delta H_1 = \int_{1600}^{1136} (Cp_{Zr(\beta)} + Cp_{O_2})\,dT$

2) Phase transform of Zr $\beta \rightarrow \alpha$ ⇨ $\Delta H_2 = -\Delta H_{trans}(Zr)$

3) Cooling $Zr(\alpha)$ & O_2 1136K → 298K ⇨ $\Delta H_3 = \int_{1136}^{298} (Cp_{Zr(\alpha)} + Cp_{O_2})\,dT$

4) $Zr(\alpha) + O_2 \rightarrow ZrO_2(\alpha)$ at 298K ⇨ $\Delta H_4 = \Delta H^\circ(ZrO_2) - (\Delta H^\circ(Zr) + \Delta H^\circ(O_2)) = \Delta H^\circ(ZrO_2)$

5) Heating ZrO_2 298K → 1478K ⇨ $\Delta H_5 = \int_{298}^{1478} (Cp_{ZrO_2(\alpha)})\,dT$

6) Phase transform of ZrO_2 $\alpha \rightarrow \beta$ ⇨ $\Delta H_6 = \Delta H_{trans}(ZrO_2)$

7) Heating ZrO_2 1478K → 1600K ⇨ $\Delta H_7 = \int_{1478}^{1600} (Cp_{ZrO_2(\beta)})\,dT$

$\Delta H_{1600} = \sum \Delta H_n$. $\Delta H_{1600} = \Delta H^\circ(ZrO_2) - \Delta H_{trans}(Zr) + \Delta H_{trans}(ZrO_2) + \Delta H_t$

$$\Delta H_t = \int_{298}^{1136} \left(Cp_{ZrO_2(\alpha)} - (Cp_{Zr(\alpha)} + Cp_{O_2})\right) dT$$
$$+ \int_{1136}^{1478} \left(Cp_{ZrO_2(\alpha)} - (Cp_{Zr(\beta)} + Cp_{O_2})\right) dT$$
$$+ \int_{1478}^{1600} \left(Cp_{ZrO_2(\beta)} - (Cp_{Zr(\beta)} + Cp_{O_2})\right) dT$$

$\Delta H^\circ(ZrO_2) = -1100800J$, $\Delta H_{trans}(Zr) = 3900J$, $\Delta H_{trans}(ZrO_2) = 5900J$

→ next page

$$\int_{298}^{1136} \left(Cp_{ZrO_2(\alpha)} - (Cp_{Zr(\alpha)} + Cp_{O_2})\right) dT$$

$$= \int_{298}^{1136} (69.62 - 21.97 - 29.96) + (7.53 - 11.63 - 4.18) \times 10^{-3} T + (-14.06 - 0 + 1.67) \times 10^{5} T^{-2} dT$$

$$= \int_{298}^{1136} (17.69) + (-8.28) \times 10^{-3} T + (-12.39) \times 10^{5} T^{-2} dT$$

$$= \left[(17.69) T + (-4.14) \times 10^{-3} T^{2} + (12.39) \times 10^{5} T^{-1} \right]_{298}^{1136}$$

$$= 14824.22 - 4975.00 - 3067.05 = 6782.17 J$$

$$\int_{1136}^{1478} \left(Cp_{ZrO_2(\alpha)} - (Cp_{Zr(\beta)} + Cp_{O_2})\right) dT$$

$$= \int_{1136}^{1478} (69.62 - 23.22 - 29.96) + (7.53 - 4.64 - 4.18) \times 10^{-3} T + (-14.06 - 0 + 1.67) \times 10^{5} T^{-2} dT$$

$$= \int_{1136}^{1478} (16.44) + (-1.29) \times 10^{-3} T + (-12.39) \times 10^{5} T^{-2} dT$$

$$= \left[(16.44) T + (-0.645) \times 10^{-3} T^{2} + (12.39) \times 10^{5} T^{-1} \right]_{1136}^{1478}$$

$$= 5622.48 - 576.62 - 252.37 = 4793.49 J$$

$$\int_{1478}^{1600} \left(Cp_{ZrO_2(\beta)} - (Cp_{Zr(\beta)} + Cp_{O_2})\right) dT$$

$$= \int_{1478}^{1600} (74.48 - 23.22 - 29.96) + (0 - 4.64 - 4.18) \times 10^{-3} T + (0 - 0 + 1.67) \times 10^{5} T^{-2} dT$$

$$= \int_{1478}^{1600} (21.3) + (-8.82) \times 10^{-3} T + (1.67) \times 10^{5} T^{-2} dT$$

$$= \left[(21.3) T + (-4.41) \times 10^{-3} T^{2} + (-1.67) \times 10^{5} T^{-1} \right]_{1478}^{1600}$$

$$= 2598.6 - 1656.03 + 8.62 = 951.19 J$$

$$\Delta H_t = 6782.17 J + 4793.49 J + 951.19 J = 12526.85 J$$

$$\Delta H_{1600} = \Delta H^{\circ}(ZrO_2) - \Delta H_{trans}(Zr) + \Delta H_{trans}(ZrO_2) + \Delta H_t$$

$$\Delta H_{1600} = -1100800 J - 3900 J + 5900 J + 12526.85 J = -1.086 \times 10^{6} J$$

→ next page

ΔS_{1600} 역시 같은 방식으로 구하면, $\Delta S_{1600} = \Delta S_{298} - \Delta S_{trans}(Zr) + \Delta S_{trans}(ZrO_2) + \Delta S_t$

$\Delta S_{298} = S^\circ(ZrO_2) - S^\circ(Zr) - S^\circ(O_2) = 50.4 - 39.0 - 205.1 = -193.7 J/K$

$\Delta S_{trans}(Zr) = \frac{\Delta H_{trans}(Zr)}{T} = \frac{3900}{1136} = 3.43 J/K$

$\Delta S_{trans}(ZrO_2) = \frac{\Delta H_{trans}(ZrO_2)}{T} = \frac{5900}{1478} = 3.99 J/K$

$\Delta S_t = \frac{\Delta H_t}{T}$ 이므로 적분 범위를 위처럼 나눠 계산하면,

$$\int_{298}^{1136} \left(C_{p_{ZrO_2(\alpha)}} - \left(C_{p_{Zr(\alpha)}} + C_{p_{O_2}}\right)\right)\frac{dT}{T}$$

$$= \int_{298}^{1136} (69.62 - 21.97 - 29.96)T^{-1} + (7.53 - 11.63 - 4.18) \times 10^{-3} + (-14.06 - 0 + 1.67) \times 10^5 T^{-3} dT$$

$$= \int_{298}^{1136} (17.69)T^{-1} + (-8.28) \times 10^{-3} + (-12.39) \times 10^5 T^{-3} dT$$

$$= \left[(17.69)\ln T + (-8.28) \times 10^{-3} T + (6.195) \times 10^5 T^{-2}\right]_{298}^{1136}$$

$$= 23.67 - 6.94 - 6.50 = 10.23 J/K$$

$$\int_{1136}^{1478} \left(C_{p_{ZrO_2(\alpha)}} - \left(C_{p_{Zr(\beta)}} + C_{p_{O_2}}\right)\right)\frac{dT}{T}$$

$$= \int_{1136}^{1478} (69.62 - 23.22 - 29.96)T^{-1} + (7.53 - 4.64 - 4.18) \times 10^{-3} + (-14.06 - 0 + 1.67) \times 10^5 T^{-3} dT$$

$$= \int_{1136}^{1478} (16.44)T^{-1} + (-1.29) \times 10^{-3} + (-12.39) \times 10^5 T^{-3} dT$$

$$= \left[(16.44)\ln T + (-1.29) \times 10^{-3} T + (6.195) \times 10^5 T^{-2}\right]_{1136}^{1478}$$

$$= 4.33 - 0.44 - 0.20 = 3.69 J/K$$

$$\int_{1478}^{1600} \left(C_{p_{ZrO_2(\beta)}} - \left(C_{p_{Zr(\beta)}} + C_{p_{O_2}}\right)\right)\frac{dT}{T}$$

$$= \int_{1478}^{1600} (74.48 - 23.22 - 29.96)T^{-1} + (0 - 4.64 - 4.18) \times 10^{-3} + (0 - 0 + 1.67) \times 10^5 T^{-3} dT$$

$$= \int_{1478}^{1600} (21.3)T^{-1} + (-8.82) \times 10^{-3} + (1.67) \times 10^5 T^{-3} dT$$

$$= \left[(21.3)\ln T + (-8.82) \times 10^{-3} T + (-0.835) \times 10^5 T^{-2}\right]_{1478}^{1600}$$

$$= 1.69 - 1.08 + 0.01 = 0.62 J/K$$

$\Delta S_{1600} = \Delta S_{298} - \Delta S_{trans}(Zr) + \Delta S_{trans}(ZrO_2) + \Delta S_t = -193 - 3.43 + 3.99 + 10.23 + 3.69 + 0.62 = -178.6 J/K$

End of Problem 1.

2. $\Delta G_{800} = \Delta H_{800} - T\Delta S_{800}$

So we have to know the value of ΔH_{800}, ΔS_{800}

298K에서의 $\Delta H°$를 알고 있으므로

$\Delta H_{800} = \left(\Delta H°_{298} + \int_{298}^{800} C_p dT\right)_{생성물} - \left(\Delta H°_{298} + \int_{298}^{800} C_p dT\right)_{반응물}$ 로 구할 수 있다.

① Si_3N_4 : $\Delta H° + \int_{298}^{800} (70.54) + (98.74)\times10^{-3}T\ dT$

$= -744800 + \left[(70.54)T + (49.37)\times10^{-3}T^2\right]_{298}^{800}$

$= -744800 + 35411.08 + 27212.55 = -682176.37J$

② $3O_2$: $3\left(\Delta H° + \int_{298}^{800} (29.96) + (4.18)\times10^{-3}T + (-1.67)\times10^{5}T^{-2}\ dT\right)$

$= 3\left(0 + \left[(29.96)T + (2.09)\times10^{-3}T^2 + (1.67)\times10^{5}T^{-1}\right]_{298}^{800}\right)$

$= 3(15039.92 + 1152.00 - 351.65) = 47520.81J$

③ $3SiO_2$: $3\left(\Delta H° + \int_{298}^{800} (43.89) + 10^{-3}T + (-6.02)\times10^{5}T^{-2}\ dT\right)$

$= 3\left(-910900 + \left[(43.89)T + (0.5)\times10^{-3}T^2 + (6.02)\times10^{5}T^{-1}\right]_{298}^{800}\right)$

$= 3(-910900 + 22032.78 + 275.60 - 1267.63) = -2669577.75J$

④ $2N_2$: $2\left(\Delta H° + \int_{298}^{800} (27.87) + (4.27)\times10^{-3}T\ dT\right)$

$= 2\left(0 + \left[(27.87)T + (2.135)\times10^{-3}T^2\right]_{298}^{800}\right)$

$= 2(13990.74 + 1176.80) = 30335.08$

$\Delta H_{800} = -2669577.75J + 30335.08J + 682176.37J - 47520.81J = -2004587.11J$

→ next page

$\Delta S_{800} = \left(\Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT\right)_{생성물} - \left(\Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT\right)_{반응물}$ 로 구할 수 있다.

① Si_3N_4 : $\Delta S^\circ + \int_{298}^{800} (70.54) \times T^{-1} + (98.74) \times 10^{-3} dT$

$= 113.0 + \left[(70.54) \ln T + (98.74) \times 10^{-3} T\right]_{298}^{800}$

$= 113.0 + 69.66 + 49.57 = 232.23 J/K$

② $3O_2$: $3\left(\Delta S^\circ + \int_{298}^{800} (29.96) T^{-1} + (4.18) \times 10^{-3} + (-1.67) \times 10^5 T^{-3} dT\right)$

$= 3\left(205.1 + \left[(29.96) \ln T + (4.18) \times 10^{-3} T + (0.835) \times 10^5 T^{-2}\right]_{298}^{800}\right)$

$= 3(205.1 + 29.59 + 2.10 - 0.81) = 707.94 J/K$

③ $3SiO_2$: $3\left(\Delta S^\circ + \int_{298}^{800} (43.89) T^{-1} + 10^{-3} + (-6.02) \times 10^5 T^{-3} dT\right)$

$= 3\left(41.5 + \left[(43.89) \ln T + 10^{-3} T + (3.01) \times 10^5 T^{-2}\right]_{298}^{800}\right)$

$= 3(41.5 + 43.34 + 0.50 - 2.92) = 247.26 J/K$

④ $2N_2$: $2\left(\Delta S^\circ + \int_{298}^{800} (27.87) T^{-1} + (4.27) \times 10^{-3} dT\right)$

$= 2\left(191.5 + \left[(27.87) \ln T + (4.27) \times 10^{-3} T\right]_{298}^{800}\right)$

$= 2(191.5 + 27.52 + 2.14) = 442.32 J/K$

$\Delta S_{800} = 247.26 + 442.32 - 232.23 - 707.94 = -250.59 J/K$

$\Delta G_{800} = \Delta H_{800} - T\Delta S_{800}$

$= -2004587.11 J - (800 K) \cdot (-250.59 J/K) = -1804115.11 J$

→ next page

If $\Delta C_p = 0$,

$\Delta H_{800} = \Delta H^\circ_{생성물} - \Delta H^\circ_{반응물}$, $\Delta S_{800} = \Delta S^\circ_{생성물} - \Delta S^\circ_{반응물}$

$\Delta H_{800} = 3(-910990) - (-744800) = -1988170\,J$

$\Delta S_{800} = 3(41.5) + 2(191.5) - (113.0) - 3(205.1) = -220.8\,J/k$

$\Delta G_{800} = \Delta H_{800} - T\Delta S_{800} = -1988170\,J - (800K)\cdot(-220.8\,J/k) = -1811530\,J$

$\text{Error} : \left(\dfrac{-1811530\,J}{-1804115.11\,J} - 1\right) \times 100\,(\%) = 0.41\%$ error.

End of Problem 2.

3. 1) 고전열역학적 접근 방식.

vacancy 수를 n, atom 수를 $N-n$이라 할 때

vacancy와 atom의 배열 엔트로피는

$$\Delta S_{conf} = k_B \ln \frac{N!}{n!(N-n)!} = k_B \left[N\ln N - N - \left(n\ln n - n + (N-n)\ln(N-n) - (N-n)\right)\right]$$

$$= k_B \left[N\ln N - n\ln n - (N-n)\ln(N-n)\right]$$

$$= Nk_B \left[\ln N - \frac{n}{N}\ln n - \left(1-\frac{n}{N}\right)\ln(N-n)\right]$$

$$G = G_0 + \Delta G$$

$$\Delta G = \Delta H + T\Delta S = n\Delta H + Nk_B T \left[\ln N - \frac{n}{N}\ln n - \left(1-\frac{n}{N}\right)\ln(N-n)\right]$$

$\frac{\delta G}{\delta n} = 0$인 상태가 stable 하므로 $\frac{dG}{dn} = 0$이어야 한다.

$$\frac{\delta G}{\delta n} = \Delta H + k_B T\left[-\ln n + \ln(N-n)\right] = 0$$

$$\frac{\delta G}{\delta n} = \Delta H + k_B T \ln\left(\frac{N-n}{n}\right) = \Delta H + k_B T \ln\left(\frac{N}{n} - 1\right) = 0$$

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

$$\therefore \frac{n}{N} = \frac{1}{1 + \exp\left(\frac{-\Delta H}{k_B T}\right)}$$

2) 통계열역학적 방법

$$Z = \sum_i \exp\left(\frac{-E_i}{kT}\right) = \exp\left(\frac{-\Delta H_A}{kT}\right) + \exp\left(\frac{-\Delta H_v}{kT}\right),$$

ΔH_A = Atom의 ΔH
ΔH_v = vacancy의 ΔH

$$= 1 + \exp\left(\frac{-\Delta H_v}{kT}\right) \quad (\Delta H_A = 0)$$

$P = \frac{1}{Z}\exp\left(\frac{-E_i}{kT}\right)$이므로, $P_v = \frac{n}{N} = \frac{\exp\left(-\frac{\Delta H_v}{kT}\right)}{1+\exp\left(-\frac{\Delta H_v}{kT}\right)} = \frac{\exp\left(\frac{\Delta H_v}{kT}\right)}{\exp\left(\frac{\Delta H_v}{kT}\right)+1}$