HW1 20200809 유경환

1.

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

i) ΔH_{1600}

$$\Delta H_{298} = \Delta H^\circ_{298,ZrO_2} - (\Delta H^\circ_{298,Zr} + \Delta H^\circ_{298,O_2})$$
$$= -1,100,800J$$

298K→1136K) $Zr(\alpha) \rightarrow Zr(\beta)$, $O_2(g) \rightarrow O_2(g)$, $ZrO_2(\alpha) \rightarrow ZrO_2(\alpha)$

$$\Delta H_1 = \int_{298}^{1136} (C_{p,ZrO_2(\alpha)} - (C_{p,Zr(\alpha)} + C_{p,O_2(g)}))\,dT$$
$$= \int_{298}^{1136} (69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2} - (21.97 + 11.63\times10^{-3}T + 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}))\,dT$$
$$= \int_{298}^{1136} (17.69 - 8.28\times10^{-3}T - 12.39\times10^{5}T^{-2})\,dT$$
$$= 6782.17 J$$

$$\Delta H_{trans,Zr} = 3,900J$$

1136K→1478K)

$Zr(\beta) \rightarrow Zr(\beta)$, $O_2(g) \rightarrow O_2(g)$, $ZrO_2(\alpha) \rightarrow ZrO_2(\beta)$

$$\Delta H_{trans,ZrO_2} = 5,900J$$

$$\Delta H_2 = \int_{1136}^{1478} \left(C_{p,ZrO_2(\alpha)} - \left(C_{p,Zr(\beta)} + C_{p,O_2(g)}\right)\right) dT$$

$$= \int_{1136}^{1478} \left(69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2} - \left(23.22 + 4.64\times10^{-3}T + 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}\right)\right) dT$$

$$= \int_{1136}^{1478} \left(16.44 - 1.29\times10^{-3}T - 12.39\times10^{5}T^{-2}\right) dT$$

$$= 4793.48\,J$$

1478K → 1600K)

$Zr(\beta) \to Zr(\beta)$, $O_2(g) \to O_2(g)$, $ZrO_2(\beta) \to ZrO_2(\beta)$

$$\Delta H_3 = \int_{1478}^{1600} \left(C_{p,ZrO_2(\beta)} - \left(C_{p,Zr(\beta)} + C_{p,O_2(g)}\right)\right) dT$$

$$= \int_{1478}^{1600} \left(74.48 - \left(23.22 + 4.64\times10^{-3}T + 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}\right)\right) dT$$

$$= \int_{1478}^{1600} \left(21.3 - 8.82\times10^{-3}T + 1.67\times10^{5}T^{-2}\right) dT$$

$$= 951.19\,J$$

$$\therefore \Delta H_{1600} = \Delta H_{298} + \Delta H_1 - \Delta H_{trans,Zr} + \Delta H_2 + \Delta H_{trans,ZrO_2} + \Delta H_3$$

$$= -1,100,800J + 6782.17J - 3900J + 4793.48J + 5900J + 951.19J = -1.086\times10^{6}\,J$$

ii) ΔS_{1600}

$$\Delta S_{298} = S^{\circ}_{298,ZrO_2} - \left(S^{\circ}_{298,Zr} + S^{\circ}_{298,O_2}\right)$$

$$= 50.4\,J/K - \left(39.0\,J/K + 205.1\,J/K\right) = -193.7\,J/K$$

$$\frac{\Delta H_{trans,Zr}}{T_{trans,Zr}} = \frac{3900J}{1136K} = 3.433\,J/K, \quad \frac{\Delta H_{trans,ZrO_2}}{T_{trans,ZrO_2}} = \frac{5900J}{1478K} = 3.992\,J/K$$

298K→1136K) $Zr(\alpha) \rightarrow Zr(\beta)$, $O_2(g) \rightarrow O_2(g)$, $ZrO_2(\alpha) \rightarrow ZrO_2(\alpha)$

$$\Delta S_1 = \int_{298}^{1136} \frac{C_{p,ZrO_2(\alpha)} - (C_{p,Zr(\alpha)} + C_{p,O_2(g)})}{T} \, dT$$

$$= \int_{298}^{1136} (17.69T^{-1} - 8.28\times10^{-3} - 12.39\times10^{5}\,T^{-3})\,dT$$ (ΔH_1의 계산 이용)

$$= 10.2377 \text{ J/K}$$

1136K→1478K) $Zr(\beta) \rightarrow Zr(\beta)$, $O_2(g) \rightarrow O_2(g)$, $ZrO_2(\alpha) \rightarrow ZrO_2(\beta)$

$$\Delta S_2 = \int_{1136}^{1478} \frac{C_{p,ZrO_2(\alpha)} - (C_{p,Zr(\beta)} + C_{p,O_2(g)})}{T} \, dT$$

$$= \int_{1136}^{1478} (16.44T^{-1} - 1.29\times10^{-3} - 12.39\times10^{5}\,T^{-3})\,dT$$

$$= 3.68898 \text{ J/K}$$

1478K→1600K) $Zr(\beta) \rightarrow Zr(\beta)$, $O_2(g) \rightarrow O_2(g)$, $ZrO_2(\beta) \rightarrow ZrO_2(\beta)$

$$\Delta S_3 = \int_{1478}^{1600} \frac{C_{p,ZrO_2(\beta)} - (C_{p,Zr(\beta)} + C_{p,O_2(g)})}{T} \, dT$$

$$= \int_{1478}^{1600} (21.3T^{-1} - 8.82\times10^{-3} + 1.67\times10^{5}\,T^{-3})\,dT$$

$$= 0.618951 \text{ J/K}$$

$$\therefore \Delta S_{1600} = \Delta S_{298} - \frac{\Delta H_{trans,Zr}}{T_{trans,Zr}} + \frac{\Delta H_{trans,ZrO_2}}{T_{trans,ZrO_2}} + \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= -193.7\ J/K - 3.433\ J/K + 3.992\ J/K + 10.2377\ J/K$$
$$+ 3.68898\ J/K + 0.618951\ J/K$$

$$= -178.5\ J/K$$

2.

$$Si_3N_4 + 3O_2 = 3SiO_2(\alpha\text{-quarts}) + 2N_2$$

i) ΔH_{800}

$$H_{800,N_2} = \Delta H^{\circ}_{298,N_2} + \int_{298}^{800} C_p\,dT$$

$$= 0 + \int_{298}^{800} (27.87 + 4.27\times10^{-3}T)\,dT$$

$$= 15167.5J$$

$$H_{800,SiO_2} = \Delta H^{\circ}_{298,SiO_2} + \int_{298}^{800} C_p\,dT$$

$$= -910,900J + \int_{298}^{800} (43.89 + 1\times10^{-3}T - 6.02\times10^{5}T^{-2})\,dT$$

$$= -889859J$$

$$H_{800,O_2} = \Delta H^{\circ}_{298,O_2} + \int_{298}^{800} C_p\,dT$$

$$= 0 + \int_{298}^{800} (29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2})\,dT$$

$$= 15840.3J$$

$$H_{800,Si_3N_4} = \Delta H^{\circ}_{298,Si_3N_4} + \int_{298}^{800} C_p\,dT$$

$$= -744,800 + \int_{298}^{800} (70.54 + 98.74\times10^{-3}T)\,dT$$

$$= -682176.4J$$

$$\Rightarrow \Delta H_{800} = (3H_{800,SiO_2} + 2H_{800,N_2}) - (H_{800,Si_3N_4} + 3H_{800,O_2})$$

$$= -2004590J$$

ii) ΔS_{800}

$$S_{800,N_2} = S^{\circ}_{298,N_2} + \int_{298}^{800} \frac{C_p}{T}\,dT$$

$$= 191.5J/K + \int_{298}^{800} (27.87 + 4.27\times10^{-3}T)T^{-1}\,dT$$

$$= 221.166J/K$$

$$S_{800,SiO_2} = S^{\circ}_{298,SiO_2} + \int_{298}^{800} \frac{C_p}{T} dT$$
$$= 41.5 J/K + \int_{298}^{800} (43.89 + 1\times10^{-3}T - 6.02\times10^{5}T^{-2})T^{-1} dT$$
$$= 82.425 J/K$$

$$S_{800,O_2} = S^{\circ}_{298,O_2} + \int_{298}^{800} \frac{C_p}{T} dT$$
$$= 205.1 J/K + \int_{298}^{800} (29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2})T^{-1} dT$$
$$= 235.995 J/K$$

$$S_{800,Si_3N_4} = S^{\circ}_{298,Si_3N_4} + \int_{298}^{800} \frac{C_p}{T} dT$$
$$= 113 J/K + \int_{298}^{800} (70.54 + 98.74\times10^{-3}T)T^{-1} dT$$
$$= 232.227 J/K$$

$$\Rightarrow \Delta S_{800} = (3S_{800,SiO_2} + 2S_{800,N_2}) - (S_{800,Si_3N_4} + 3S_{800,O_2})$$
$$= -250.545 J/K$$

$$\therefore \Delta G_{800} = \Delta H_{800} - T\Delta S_{800}$$
$$= -1804154 J$$

ΔC_p가 0이면 $\Delta H_{800}' = -1984900 J$, $\Delta S_{800}' = -220.8 J/K$

$$\Rightarrow \Delta G_{800}' = \Delta H_{800}' - T\Delta S_{800}'$$
$$= -1811260 J$$

따라서 error를 구해보면

$$(\text{error}) = \frac{\Delta G_{800} - \Delta G_{800}'}{\Delta G_{800}} \times 100 = 0.3\%$$

3.

i) 통계열역학

$$Z = \sum_i e^{-\varepsilon_i/kT} = e^{0/kT} + e^{-\Delta H_v/kT} = 1 + e^{-\Delta H_v/kT}$$

(atom이 채워지면 energy가 0, 아니면 ΔH_v 라 하면)

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

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

ii) 고전열역학

N : 전체 경우의 수 ($N = n_a + n_v$)

n_v : vacancy 수, n_a : 차있는 atom의 수

$$\Delta F = \Delta U - T\Delta S$$
$$= \Delta H_v \cdot n_v - T\underbrace{\Delta S}_{\text{mixing entrophy}}$$

$$\Rightarrow \Delta S = k \ln \Omega = k \ln \frac{(n_a + n_b)!}{n_a! \cdot n_v!} = k \ln \frac{N!}{n_a! \cdot n_v!}$$

Stirling's approximation

$$= k\{\ln(N!) - \ln(n_a)! - \ln(n_v)!\}$$
$$= k\{N\ln(N) - N - n_a\ln(n_a) + n_a - n_v\ln(n_v) + n_v\}$$
$$= k\{N\ln(N) - n_a\ln(n_a) - n_v\ln(n_v)\}$$
$$= k\{N\ln(N) - (N - n_v)\ln(N - n_v) - n_v\ln(n_v)\}$$
$$= k\{N\ln(N) - N\ln(N - n_v) + n_v\ln(N - n_v) - n_v\ln(n_v)\}$$
$$= k\{N\ln\frac{N}{N - n_v} + n_v\ln\frac{N - n_v}{n_v}\}$$

$$\Rightarrow \Delta F = \Delta U - T\Delta S$$

$$= \Delta H_v \cdot n_v - Tk \left\{ N \ln \frac{N}{N-n_v} + n_v \ln \frac{N-n_v}{n_v} \right\}$$

평형점(극값)을 찾기 위해 n_v에 대해 미분해 주면

$$\frac{d}{dn_v}\Delta F = \frac{d}{dn_v}(\Delta H_v \cdot n_v) - \frac{d}{dn_v}\left(Tk\left(N \ln \frac{N}{N-n_v} + n_v \ln \frac{N-n_v}{n_v}\right)\right)$$

$$= \Delta H_v - Tk \cdot \frac{d}{dn_v}\left(N\ln N - N\ln(N-n_v) + n_v \ln(N-n_v) - n_v \ln n_v\right)$$

$$= \Delta H_v - Tk\left(-N\frac{-1}{N-n_v} + \ln(N-n_v) + n_v\frac{-1}{N-n_v} - \ln n_v - n_v\frac{1}{n_v}\right)$$

$$= \Delta H_v - Tk\left(\ln(N-n_v) - \ln n_v\right)$$

$$= \Delta H_v - Tk \ln \frac{N-n_v}{n_v}$$

$\Delta H_v - Tk \ln \frac{N-n_v}{n_v} = 0$ 일 때 평형이므로

$$\Rightarrow \Delta H_v = kT \ln \frac{N-n_v}{n_v} \Rightarrow \frac{\Delta H_v}{kT} = \ln \frac{N-n_v}{n_v} \Rightarrow e^{\Delta H_v/kT} = \frac{N-n_v}{n_v}$$

$$\Rightarrow e^{\Delta H_v/kT} = \frac{N}{n_v} - 1 \Rightarrow \frac{n}{N} = \frac{1}{1+e^{\Delta H_v/kT}} \quad (n_v = n)$$