소재열역학 HW3 20200984 김성수

ΔH_{1600}, ΔS_{1600} $Zr(\beta) + O_2 = ZrO_2(\beta)$.

① ΔH_{1600}

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

1478 K 일때 $\alpha \to \beta$로 phase가 변한다.

$\Delta H_{1600}(ZrO_2(\beta)) = \Delta H^{298}_{0\,(ZrO_2)} + \int_{298}^{1478} C_{p\alpha}\, dT + \Delta H_{trans} + \int_{1478}^{1600} C_{p\beta}\, dT$

$\Delta H^{298}_{0\,(ZrO_2)} = \underline{-1,100,800\, J}$

$C_{p\alpha} = 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}\, T^{-2}$ J/mole·K.

$\int_{298}^{1478} 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}\, T^{-2}\, dT$

$= \left(69.62T + 3.765\times10^{-3}T^2 + 14.06\times10^{5}\,T^{-1}\right)_{298}^{1478} = 112074.2278 - 25799.22787$

$= \underline{86275\, J}$.

$C_{p\beta} = 74.48$ J/mole·K

$\int_{1478}^{1600} 74.48\, dT = (74.48T)_{1478}^{1600} = \underline{9123J}$, $\Delta H_{trans} = \underline{5900\, J}$.

$\therefore \Delta H_{1600}(ZrO_2(\beta)) = -1,100,800 + 86275 + 5900 + 9123 = -999502\, J$

$\Delta H_{1600}(O_2) = \int_{298}^{1600} C_p\, dT \leftarrow C_p = 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}\, T^{-2}$ J/mole·K.

$\Delta H_0^{298} = 0$,

$\int_{298}^{1600} C_p\, dT = \left[29.96T + 2.09\times10^{-3}T^2 + 1.67\times10^{5}\, T^{-1}\right]_{298}^{1600}$

$= \left(29.96(1600-298) + 2.09\times10^{-3}(1600^2 - 298^2) + 1.67\times10^{5}\left(\frac{1}{1600} - \frac{1}{298}\right)\right)$

$= 43716.7\, J.$

$\Delta H_{1600}(Zr)$

$= \Delta H_0^{298} + \int_{298}^{1136} C_{P(\alpha)}\, dT + \Delta H_{trans} + \int_{1136}^{1600} C_{P(\beta)}\, dT$

$\Delta H_0^{298}(Zr) = 0.$

$\int_{298}^{1136} C_{P(\alpha)}\, dT = \int_{298}^{1136} 21.97 + 11.63\times10^{-3}T\, dT = \left[21.97T + 5.815\times10^{-3}T^2\right]_{298}^{1136}$

$= 21.97(1136-298) + 11.63\times10^{-3}(1136^2-298^2) = \underline{24641.63J}.$

$\Delta H_{trans} = \underline{3900J}.$

$\int_{1136}^{1600} C_{P(\beta)}\, dT = \int_{1136}^{1600} 23.22 + 4.64\times10^{-3}T\, dT = \left[23.22T + 2.32\times10^{-3}T^2\right]_{1136}^{1600}$

$= 23.22(1600-1136) + 2.32\times10^{-3}(1600^2-1136^2) = \underline{13719.33J}.$

$\Delta H_{1600}(Zr) = 24641.63 + 3900 + 13719.33 = \boxed{42261J}$

$\therefore \Delta H_{1600} = -999502 - 43717 - 42261 = -1085480J$

$\boxed{\Delta H_{1600} = -1085480J}$

$\Delta S_{1600} = ?$

$\Delta S_{1600} = \Delta S_{1600}(ZrO_2(\beta)) - \Delta S_{1600}(O_2) - \Delta S_{1600}(Zr(\beta))$

$\Delta S_{1600} = \Delta S_0^{298} + \int_{298}^{1478} \frac{C_{P(\alpha)}}{T}\, dT + \Delta S_{trans} + \int_{1478}^{1600} \frac{C_{P(\beta)}}{T}\, dT.$

$\Delta S_0^{298} = \underline{50.4J/k}.$

$\int_{298}^{1478} \frac{C_{P(\alpha)}}{T}\, dT = \int_{298}^{1478} \frac{69.62}{T} + 7.53\times10^{-3} - 14.06\times10^5 T^{-3}\, dT$

$= \left[69.62\ln T + 7.53\times10^{-3}T + 7.03\times10^5 T^{-2}\right]_{298}^{1478}$

$= 69.62\ln\left(\frac{1478}{298}\right) + 7.53\times10^{-3}(1478-298) + 7.03\times10^5\left(\frac{1}{1478^2} - \frac{1}{298^2}\right)$

$= \underline{112.78\ J/k}.$

CamScanner로 스캔하기

$$\Delta S_{trans} = \frac{5900}{1478} = 3.99\,J/K$$

$$\int_{1478}^{1600} \frac{C_{p(\beta)}}{T} dT = \int_{1478}^{1600} \frac{74.48}{T} dT = 74.48 \ln\left(\frac{1600}{1478}\right) = 5.9\,J/K$$

$$\Delta S_{1600}(ZrO_2(\beta)) = 50.4 + 112.78 + 3.99 + 5.9 = \boxed{173\,J/K}$$

$$\Delta S_{1600}(O_2) = ?$$

$$\Delta S_{1600}(O_2) = \Delta S^\circ_{298} + \int_{298}^{1600} \frac{C_{p(O_2)}}{T} dT \rightarrow \Delta S^\circ_{298}(O_2) = 205.1\,J/K$$

$$\int_{298}^{1600} \frac{C_p}{T} dT = \int_{298}^{1600} \frac{29.96}{T} + 4.18\times10^{-3} - 1.67\times10^{5}\,T^{-3}\, dT$$

$$= \left[29.96 \ln T + 4.18\times10^{-3}\,T + 0.835\times10^{5}\,T^{-2}\right]_{298}^{1600}$$

$$= 29.96 \ln\left(\frac{1600}{298}\right) + 4.18\times10^{-3}(1600-298) + 0.835\times10^{5}\left(\frac{1}{1600^2} - \frac{1}{298^2}\right) = 54.89\,J/K$$

$$\Delta S_{1600}(O_2) = 205.1 + 54.89 = \boxed{260\,J/K}$$

$$\Delta S_{1600}(Zr(\beta)) = ?$$

$$\Delta S_{1600}(Zr(\beta)) = \Delta S^\circ_{298} + \int_{298}^{1136} \frac{C_{p(\alpha)}}{T} dT + \Delta S_{trans} + \int_{1136}^{1600} \frac{C_{p(\beta)}}{T} dT$$

$$\Delta S^\circ_{298} = 39.0\,J/K$$

$$\int_{298}^{1136} \frac{C_{p(\alpha)}}{T} dT = \int_{298}^{1136} \frac{21.97}{T} + 11.63\times10^{-3}\, dT = 21.97 \ln\left(\frac{1136}{298}\right) + 11.63\times10^{-3}(1136-298)$$

$$= 39.15\,J/K$$

$$\Delta S_{trans} = \frac{3900}{1136} = 3.43\,J/K$$

$$\int_{1136}^{1600} \frac{C_{p(\beta)}}{T} dT = \int_{1136}^{1600} \frac{23.22}{T} + 4.64\times10^{-3}\, dT = 23.22 \ln\left(\frac{1600}{1136}\right) + 4.64\times10^{-3}(1600-1136)$$

$$= 10.1\,J/K$$

$$\therefore \Delta S_{1600}(Zr(\beta)) = 39.0 + 39.15 + 3.43 + 10.1 = \boxed{91.7\,J/K}$$

$$\therefore \Delta S_{1600} = 173 - 260 - 91.7 = \boxed{-178.7\,J/K}$$

$$\therefore \Delta S_{1600} = -178.7\,J/K$$

total: $\Delta H_{1600} = -1085480\,J,\ \Delta S_{1600} = -178.7\,J/K$

2.

$Si_3N_4 + 3O_2 = 3SiO_2 + 2N_2$

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

$\Delta H_{800(SiO_2)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p\, dT \rightarrow \Delta H^\circ_{298} = -910900J$

$\int_{298}^{800} C_p\, dT = \int_{298}^{800} 43.89 + 1.00\times10^{-3}T - 6.02\times10^{5}T^{-2}\, dT$

$= \left(43.89T + 0.5\times10^{-3}T^2 + 6.02\times10^5 T^{-1}\right)_{298}^{800} = 21040.7J$

$3\Delta H_{800(SiO_2)} = 3(-910900 + 21040.7) = \boxed{-2669578J}$

$\Delta H_{800(N_2)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT = \int_{298}^{800} 27.87 + 4.27\times10^{-3}T = \left[27.87T + 2.135\times10^{-3}T^2\right]_{298}^{800}$

$\Delta H^\circ_{298} = 0$

$= 15167.5J$

$2\Delta H_{800(N_2)} = 2\times15167.5 = \boxed{30335J}$

$\Delta H_{800(Si_3N_4)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT \quad \Delta H^\circ_{298} = -744800J$

$\int_{298}^{800} C_p dT = \int_{298}^{800} 70.54 + 98.74\times10^{-3}T\, dT = \left[70.54T + 49.37\times10^{-3}T^2\right]_{298}^{800}$

$= 70.54(800-298) + 49.37\times10^{-3}(800^2 - 298^2) = 62623.6J$

$\Delta H_{800}(Si_3N_4) = -744800 + 62623.6 = \boxed{-682176J}$

$\Delta H_{800}(O_2) = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT = \int_{298}^{800} 29.96 + 4.18\times10^{-3}T - 1.67\times10^5 T^{-2}\, dT$

$\Delta H^\circ_{298} = 0$

$= \left(29.96T + 2.09\times10^{-3}T^2 + 1.67\times10^5 T^{-1}\right)_{298}^{800} = 15840J$

$3\Delta H_{800(O_2)} = 3\times15840 = \boxed{47520J}$

$\Delta H_{800} = -2669578 + 30335 + 682176 - 47520 = -2004587$

$\therefore \boxed{\Delta H_{800} = -2004587J}$

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

$$\Delta S_{800(SiO_2)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT \qquad \Delta S^\circ_{298} = 41.5 J/K$$

$$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \frac{43.89}{T} + 1.00\times10^{-3} - 6.02\times10^{5} T^{-3} dT = \left[43.89 \ln T + 1.00\times10^{-3} T + 3.01\times10^{5} T^{-2}\right]_{298}^{800}$$

$$= 43.89 \ln\left(\frac{800}{298}\right) + 1.00\times10^{-3}(800-298) + 3.01\times10^{5}\left(\frac{1}{800^2} - \frac{1}{298^2}\right) = \boxed{40.9 J/K}$$

$$3\Delta S_{800(SiO_2)} = 3(41.5 + 40.9) = \boxed{247.2 J/K}$$

$$\Delta S_{800(N_2)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT \qquad \Delta S^\circ_{298} = 191.5 J/K$$

$$\int_{298}^{800} \frac{27.87}{T} + 4.27\times10^{-3} dT = \left[27.87 \ln T + 4.27\times10^{-3} T\right]_{298}^{800} = 29.7 J/K$$

$$2\Delta S_{800(N_2)} = 2(191.5 + 29.7) = \boxed{442.4 J/K}$$

$$\Delta S_{800(Si_3N_4)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT \qquad \Delta S^\circ_{298} = 113.0 J/K$$

$$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \frac{70.54}{T} + 98.74\times10^{-3} dT = \left[70.54 \ln T + 98.74\times10^{-3} T\right]_{298}^{800}$$

$$= 119.2 J/K.$$

$$\Delta S_{800(Si_3N_4)} = 113.0 + 119.2 = \boxed{232.2 J/K}$$

$$\Delta S_{800(O_2)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT \qquad \Delta S^\circ_{298} = 205.1 J/K$$

$$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \frac{29.96}{T} + 4.18\times10^{-3} - 1.67\times10^{5} T^{-3} dT$$

$$= \left(29.96 \ln T + 4.18\times10^{-3} T + 0.835\times10^{5} T^{-2}\right)_{298}^{800} = 30.9 J/K$$

$$3\Delta S_{800(O_2)} = 3(205.1 + 30.9) = \boxed{708 J/K}$$

$$\Delta S_{800} = 247.2 + 442.4 - 232.2 - 708 = -250 J$$

$$\Delta G = \Delta H - T\Delta S = -2004587 - 800(-250)$$

$$= -1804587 J$$

$$\therefore \boxed{\Delta G = -1804587 J}$$

If $\Delta C_p = 0 \rightarrow \Delta H_{800} = \Delta H^\circ_{298}$, $\Delta S_{800} = \Delta S^\circ_{298}$

$$\Delta H_{800} = 3\Delta H^\circ_{298(SiO_2)} + 2\Delta H^\circ_{298(N_2)} - \Delta H^\circ_{298(Si_3N_4)} - 3\Delta H^\circ_{298(O_2)}$$

$$= 3\cdot(-910900) - (-744800) = \underline{-1987900J}$$

$$\Delta S_{800} = 3\Delta S^\circ_{298(SiO_2)} + 2\Delta S^\circ_{298(N_2)} - \Delta S^\circ_{298(Si_3N_4)} - 3\Delta S^\circ_{298(O_2)}$$

$$= 3\cdot(41.5) + 2\cdot(191.5) - 113 - 3\cdot(205.1) = -220.8J/K$$

$$\Delta G_{800} = -1987900 - 800\cdot(-220.8) = \boxed{-1811260J}$$

$$\text{error} : \frac{|1804587 - 1811260|}{1804587} \times 100 \approx 0.3\%$$

3.

고전열역학적 접근 방식

ΔH_v: vacancy formation energy , $F = U - ST$, $\underset{전체}{N} = \underset{vacancy}{n_v} + \underset{atom}{N_a} \rightarrow N_a = N - n_v$

$$\Delta F = \Delta H_v \cdot n_v - \Delta S T \leftarrow \Delta S = \frac{N!}{(n_v)!(N-n_v)!}$$

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

$$\ln\left(\frac{N!}{(n_v)!(N-n_v)!}\right)$$

$$= N\ln N - N - (n_v \ln n_v - n_v + (N-n_v)\ln(N-n_v) - (N-n_v))$$

$$= N\ln N - n_v \ln n_v - (N-n_v)\ln(N-n_v)$$

$$\Delta F = \Delta H_v \cdot n_v - kT(N\ln N - n_v \ln n_v - (N-n_v)\ln(N-n_v))$$

$$\frac{\partial \Delta F}{\partial n_v} = \Delta H_v - kT(-\ln n_v - 1 + \ln(N-n_v) + 1) = 0$$

$$\rightarrow \Delta H_v - kT\ln\left(\frac{N-n_v}{n_v}\right) = 0$$

$$\rightarrow \Delta H_v + kT\ln\left(\frac{n_v}{N-n_v}\right) = 0$$

$$\ln\left(\frac{n_v}{N-n_v}\right) = -\frac{\Delta H_v}{kT} \rightarrow \frac{n_v}{N-n_v} = e^{-\frac{\Delta H_v}{kT}} \rightarrow \text{if } N \gg n_v \rightarrow \frac{n_v}{N} \approx e^{-\frac{\Delta H_v}{kT}}$$

$$\rightarrow n_v = (N-n_v)\, e^{-\frac{\Delta H_v}{kT}} \rightarrow n_v\left(1+e^{-\frac{\Delta H_v}{kT}}\right) = N e^{-\frac{\Delta H_v}{kT}}$$

$$\rightarrow \boxed{\frac{n_v}{N} = \frac{e^{-\frac{\Delta H_v}{kT}}}{1+e^{-\frac{\Delta H_v}{kT}}} = \frac{1}{1+e^{\frac{\Delta H_v}{kT}}}}$$

통계열역학적 접근 방식

N vacancy가 있을 때, $E = \Delta H_v \rightarrow e^{-\frac{\Delta H_v}{kT}}$

N atom이 있을 때, $E = 0 \rightarrow 1$

$\rightarrow$ partition function $Z = \sum_{\text{state}} e^{-\frac{E_i}{kT}}$

$$\therefore Z = 1 + e^{-\frac{\Delta H_v}{kT}}$$

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

$\therefore$ 고전열역학적 접근 방식으로 계산했을 때와 통계열역학적 접근 방식으로 계산했을 때의 $\frac{n_v}{N}$ 값은 $\frac{1}{1+e^{\frac{\Delta H_v}{kT}}}$로 같다.