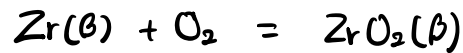


Hwl

20200809 宋正魁

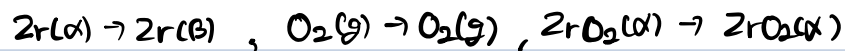
1.



i) ΔH_{1600}

$$\begin{aligned}\Delta H_{298} &= \Delta H_{298, \text{ZrO}_2}^\circ - (\Delta H_{298, \text{Zr}}^\circ + \Delta H_{298, \text{O}_2}^\circ) \\ &= -1,100,800 \text{ J}\end{aligned}$$

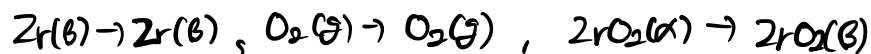
298K → 1136K



$$\begin{aligned}\Delta H_1 &= \int_{298}^{1136} (C_{p, \text{ZrO}_2(\alpha)} - (C_{p, \text{Zr}(\alpha)} + C_{p, \text{O}_2(\text{g})})) dT \\ &= \int_{298}^{1136} (69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^5 T^{-2} - (21.97 + 11.63 \times 10^{-3} T + 29.96 \\ &\quad + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2})) dT \\ &= \int_{298}^{1136} (17.65 - 8.28 \times 10^{-3} T - 12.39 \times 10^5 T^{-2}) dT \\ &= 6782.17 \text{ J}\end{aligned}$$

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

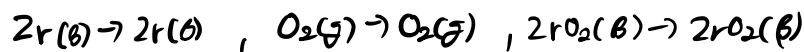
1136K → 1418K



$$\Delta H_{\text{trans, ZrO}_2} = 5,900 \text{ J}$$

$$\begin{aligned}
 \Delta H_2 &= \int_{1136}^{1418} (C_{p,2rO_2(g)} - (C_{p,2r(g)} + C_{p,O_2(g)})) dT \\
 &= \int_{1136}^{1418} (69.62 + 7.53 \times 10^{-3}T - 14.06 \times 10^{-5}T^2 - (23.22 + 4.64 \times 10^{-3}T \\
 &\quad + 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{-5}T^2)) dT \\
 &= \int_{1136}^{1418} (16.44 - 1.29 \times 10^{-3}T - 12.39 \times 10^{-5}T^2) dT \\
 &= 4193.48 \text{ J}
 \end{aligned}$$

1418K → 1600K



$$\begin{aligned}
 \Delta H_3 &= \int_{1418}^{1600} (C_{p,2rO_2(s)} - (C_{p,2r(l)} + C_{p,O_2(l)})) dT \\
 &= \int_{1418}^{1600} (74.48 - (23.22 + 4.64 \times 10^{-3}T + 29.96 + 4.18 \times 10^{-3}T \\
 &\quad - 1.67 \times 10^{-5}T^2)) dT \\
 &= \int_{1418}^{1600} (21.3 - 8.82 \times 10^{-3}T + 1.67 \times 10^{-5}T^2) dT \\
 &= 951.19 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \Delta H_{1600} &= \Delta H_{298} + \Delta H_1 - \Delta H_{\text{trans},2r} + \Delta H_2 + \Delta H_{\text{trans},2rO_2} + \Delta H_3 \\
 &= -1,100,800 \text{ J} + 6182.17 \text{ J} - 3900 \text{ J} + 4193.48 \text{ J} \\
 &\quad + 5900 \text{ J} + 951.19 \text{ J} = -1.086 \times 10^6 \text{ J}
 \end{aligned}$$

i) ΔS_{1600}

$$\begin{aligned}
 \Delta S_{298} &= S_{298,2rO_2}^{\circ} - (S_{298,2r}^{\circ} + S_{298,O_2}^{\circ}) \\
 &= 50.4 \text{ J/K} - (39.0 \text{ J/K} + 205.1 \text{ J/K}) = -193.7 \text{ J/K}
 \end{aligned}$$

$$\frac{\Delta H_{\text{trans},2r}}{T_{\text{trans},2r}} = \frac{3900 \text{ J}}{1136 \text{ K}} = 3.433 \text{ J/K}, \quad \frac{\Delta H_{\text{trans},2rO_2}}{T_{\text{trans},2rO_2}} = \frac{5900 \text{ J}}{1418 \text{ K}} = 3.992 \text{ J/K}$$

298K → 1136K) $2r(\alpha) \rightarrow 2r(\beta)$, $O_2(g) \rightarrow O_2(g)$, $2rO_2(\alpha) \rightarrow 2rO_2(\alpha)$

$$\begin{aligned}\Delta S_1 &= \int_{298}^{1136} \frac{C_{p,2rO_2(\alpha)} - (C_{p,2r(\alpha)} + C_{p,O_2(g)})}{T} dT \\ &= \int_{298}^{1136} (17.69T^{-1} - 8.28 \times 10^{-3} - 12.39 \times 10^{-5} T^{-3}) dT \quad (\Delta H_1 \text{의 계산 사용}) \\ &= 10.2377 \text{ J/K}\end{aligned}$$

1136K → 1418K) $2r(\beta) \rightarrow 2r(\beta)$, $O_2(g) \rightarrow O_2(g)$, $2rO_2(\alpha) \rightarrow 2rO_2(\beta)$

$$\begin{aligned}\Delta S_2 &= \int_{1136}^{1418} \frac{C_{p,2rO_2(\beta)} - (C_{p,2r(\beta)} + C_{p,O_2(g)})}{T} dT \\ &= \int_{1136}^{1418} (16.44T^{-1} - 1.29 \times 10^{-3} - 12.39 \times 10^{-5} T^{-3}) dT \\ &= 3.68898 \text{ J/K}\end{aligned}$$

1418K → 1600K) $2r(\beta) \rightarrow 2r(\beta)$, $O_2(g) \rightarrow O_2(g)$, $2rO_2(\beta) \rightarrow 2rO_2(\beta)$

$$\begin{aligned}\Delta S_3 &= \int_{1418}^{1600} \frac{C_{p,2rO_2(\beta)} - (C_{p,2r(\beta)} + C_{p,O_2(g)})}{T} dT \\ &= \int_{1418}^{1600} (21.3T^{-1} - 8.82 \times 10^{-3} + 1.61 \times 10^{-5} T^{-3}) dT \\ &= 0.618951 \text{ J/K}\end{aligned}$$

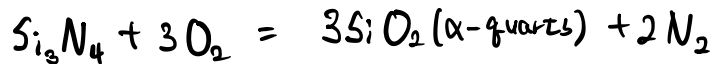
$$\therefore \Delta S_{600} = \Delta S_{298} - \frac{\Delta H_{\text{trans}, 2r}}{T_{\text{trans}, 2r}} + \frac{\Delta H_{\text{trans}, 2r_{\text{O}_2}}}{T_{\text{trans}, 2r_{\text{O}_2}}} + \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= -193.7 \text{ J/K} - 3.433 \text{ J/K} + 3.992 \text{ J/K} + 10.237 \text{ J/K}$$

$$+ 2.68878 \text{ J/K} + 0.61895 \text{ J/K}$$

$$= -178.5 \text{ J/K}$$

2.



i) ΔH_{800}

$$\begin{aligned} H_{800, \text{N}_2} &= \Delta H_{298, \text{N}_2}^{\circ} + \int_{298}^{800} C_p dT \\ &= 0 + \int_{298}^{800} (21.81 + 4.21 \times 10^{-3} T) dT \\ &= 15161.5 \text{ J} \end{aligned}$$

$$\begin{aligned} H_{800, \text{SiO}_2} &= \Delta H_{298, \text{SiO}_2}^{\circ} + \int_{298}^{800} C_p dT \\ &= -910,900 \text{ J} + \int_{298}^{800} (43.89 + 1 \times 10^{-3} T - 6.02 \times 10^{-5} T^2) dT \\ &= -889859 \text{ J} \end{aligned}$$

$$\begin{aligned} H_{800, \text{O}_2} &= \Delta H_{298, \text{O}_2}^{\circ} + \int_{298}^{800} C_p dT \\ &= 0 + \int_{298}^{800} (29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^2) dT \\ &= 15840.3 \text{ J} \end{aligned}$$

$$\begin{aligned} H_{800, \text{Si}_3\text{N}_4} &= \Delta H_{298, \text{Si}_3\text{N}_4}^{\circ} + \int_{298}^{800} C_p dT \\ &= -144,800 + \int_{298}^{800} (110.54 + 98.74 \times 10^{-3} T) dT \\ &= -682176.4 \text{ J} \end{aligned}$$

$$\begin{aligned} \Rightarrow \Delta H_{800} &= (3H_{800, \text{SiO}_2} + 2H_{800, \text{N}_2}) - (H_{800, \text{Si}_3\text{N}_4} + 3H_{800, \text{O}_2}) \\ &= -2004590 \text{ J} \end{aligned}$$

ii) ΔS_{800}

$$\begin{aligned} S_{800, \text{N}_2} &= S_{298, \text{N}_2}^{\circ} + \int_{298}^{800} \frac{C_p}{T} dT \\ &= 191.5 \text{ J/K} + \int_{298}^{800} (21.81 + 4.21 \times 10^{-3} T) \frac{1}{T} dT \\ &= 221.166 \text{ J/K} \end{aligned}$$

$$\begin{aligned}
 S_{800, \text{SiO}_2} &= S_{298, \text{SiO}_2}^{\circ} + \int_{298}^{800} \frac{C_p}{T} dT \\
 &= 41.5 \text{ J/K} + \int_{298}^{800} (43.89 + 1 \times 10^{-3} T - 6.02 \times 10^{-5} T^2) T^{-1} dT \\
 &= 82.425 \text{ J/K}
 \end{aligned}$$

$$\begin{aligned}
 S_{800, \text{O}_2} &= S_{298, \text{O}_2}^{\circ} + \int_{298}^{800} \frac{C_p}{T} dT \\
 &= 205.1 \text{ J/K} + \int_{298}^{800} (29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^2) T^{-1} dT \\
 &= 235.975 \text{ J/K}
 \end{aligned}$$

$$\begin{aligned}
 S_{800, \text{Si}_2\text{M}_4} &= S_{298, \text{Si}_2\text{M}_4}^{\circ} + \int_{298}^{800} \frac{C_p}{T} dT \\
 &= 113 \text{ J/K} + \int_{298}^{800} (10.54 + 98.74 \times 10^{-3} T) T^{-1} dT \\
 &= 232.22 \text{ J/K}
 \end{aligned}$$

$$\begin{aligned}
 \Rightarrow \Delta S_{800} &= (3S_{800, \text{SiO}_2} + 2S_{800, \text{N}_2}) - (S_{800, \text{Si}_2\text{M}_4} + 3S_{800, \text{O}_2}) \\
 &= -259.545 \text{ J/K}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \Delta G_{800} &= \Delta H_{800} - T \Delta S_{800} \\
 &= -1804154 \text{ J}
 \end{aligned}$$

$$\begin{aligned}
 \Delta C_p \text{ 가 0 이면 } \Delta H_{800}' &= -1984900 \text{ J}, \Delta S_{800}' = -220.8 \text{ J/K} \\
 \Rightarrow \Delta G_{800}' &= \Delta H_{800}' - T \Delta S_{800}' \\
 &= -1811260 \text{ J}
 \end{aligned}$$

따라서 error % 구하면

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

3.

i) 통계열역학

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

(atom이 채워지면 energy가 0, 아니면 ΔH_v 가 나오면)

$$n = \frac{N e^{-\Delta H_v/kT}}{2}$$

$$\Rightarrow \frac{n}{N} = \frac{e^{-\Delta H_v/kT}}{2} = \frac{e^{-\Delta H_v/kT}}{1 + e^{-\Delta H_v/kT}} = \frac{1}{1 + e^{\Delta H_v/kT}}$$

ii) 고전열역학

N : 전체 경우의 수 ($N = n_a + n_v$)

n_v : vacant 수, n_a : 차있는 atom의 수

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

$$= \Delta H_v \cdot n_v - T \Delta S$$

mixing entropy

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

Stirling's approximation

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

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

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

$$= k \{ N \ln(N) - (N - n_v) \ln(N - n_v) - n_v \ln(n_v) \}$$

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

$$= k \left\{ N \ln \frac{N}{N - n_v} + n_v \ln \frac{N - n_v}{n_v} \right\}$$

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

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

평형점 (극값) 을 찾기 위해 n_v 에 대해 미분해 주면

$$\begin{aligned} \frac{d}{dn_v} \Delta F &= \frac{d}{dn_v} (\Delta H_v \cdot n_v) - \frac{d}{dn_v} \left(T k \left(N \ln \frac{N}{N-n_v} + n_v \ln \frac{N-n_v}{n_v} \right) \right) \\ &= \Delta H_v - T k \cdot \frac{d}{dn_v} \left(N \ln N - N \ln (N-n_v) + n_v \ln (N-n_v) - n_v \ln n_v \right) \\ &= \Delta H_v - T k \left(-N \frac{-1}{N-n_v} + \ln (N-n_v) + n_v \frac{-1}{N-n_v} - \ln n_v - n_v \frac{1}{n_v} \right) \\ &= \Delta H_v - T k \left(\ln (N-n_v) - \ln n_v \right) \\ &= \Delta H_v - T k \ln \frac{N-n_v}{n_v} \end{aligned}$$

$$\Delta H_v - T k \ln \frac{N-n_v}{n_v} = 0 \quad \text{일 때} \quad \text{평형 상태}$$

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

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