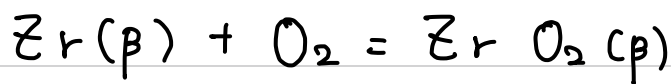


#1 Calculate ΔH_{1600} and ΔS_{1600} for the reaction



Sol)

우선, 주어진 Appendix에서 $\text{Zr}(a) + \text{O}_2 = \text{ZrO}_2(a)$ 의

$$\Delta H_{298}^\circ = -1100800 \text{ J}, \quad \Delta S_{298}^\circ = 50.4 \text{ J/K}$$

Zr의 molar entropy = 39.0 J/K

$$\text{ZrO}_2(a): C_p = 69.62 + 7.53 \times 10^{-3} T - 14.06 \times 10^{-5} T^{-2} \text{ J/mole} \cdot \text{K}$$

(in the range of 298 ~ 1478 K)

$$\text{ZrO}_2(p): C_p = 74.48 \text{ J/mole} \cdot \text{K} \text{ (in the range of 1478 ~ 2950 K)}$$

$$\text{Zr}(a): C_p = 21.97 + 11.63 \times 10^{-3} T \text{ J/mole} \cdot \text{K} \text{ (298 ~ 1136 K)}$$

$$\text{Zr}(p): C_p = 23.22 + 4.64 \times 10^{-3} T \text{ J/mole} \cdot \text{K} \text{ (1136 ~ 2128 K)}$$

Molar heats of transformation $\left[\begin{array}{l} \text{Zr}(a) \rightarrow \text{Zr}(p): \Delta H = 3900 \text{ J}, T_{\text{trans}} = 1136 \text{ K} \\ \text{ZrO}_2(a) \rightarrow \text{ZrO}_2(p): \Delta H = 5900 \text{ J}, T_{\text{trans}} = 1478 \text{ K} \end{array} \right.$

$$* C_p = \left(\frac{\partial H}{\partial T} \right)_p \rightarrow \Delta H = \int_T^{T'} C_p dT$$

$$\text{O}_2: C_p = 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^2 \text{ J/mole} \cdot \text{K}$$

$$\Delta H_{1600} = H_{\text{ZrO}_2(p), 1600} - H_{\text{Zr}(p), 1600} - H_{\text{O}_2, 1600}$$

$$\Delta H_{1600} = H_{\text{ZrO}_2(a)} + \int_{298}^{1136} (C_p \text{ZrO}_2(a) - C_p \text{Zr}(a) - C_p \text{O}_2) dT$$

$$- \Delta H_{\text{Zr}(a) \rightarrow (p)} + \int_{1136}^{1478} (C_p \text{ZrO}_2(a) - C_p \text{Zr}(p) - C_p \text{O}_2) dT$$

1136 K이하 transition

$$+ \Delta H_{\text{ZrO}_2(a) \rightarrow (p)} + \int_{1478}^{1600} (C_p \text{ZrO}_2(p) - C_p \text{Zr}(p) - C_p \text{O}_2) dT$$

$$= -1100800 + \int_{298}^{1136} \left((69.62 - 21.97 - 29.96) + (7.53 - 11.63 - 4.18) \times 10^{-3} T - (-14.06 + 1.67) \times 10^{-5} \right) dT - 3900 +$$

17.69, -8.28, -12.39

$$\int_{1136}^{1478} \left((69.62 - 23.22 - 29.96) - 1.29 \times 10^{-3} T + 12.39 \times 10^{-5} T^{-2} \right) dT$$

15.44

$$+ 5900 + \int_{1478}^{1600} (74.48 - (23.22 + 4.64 \times 10^{-3} T) - 1.67 \times 10^{-5} T^2) dT$$

$$= -1086 \text{ kJ}$$

$$\therefore \Delta H_{1600} = -1086 \text{ kJ}$$

$$dS = \frac{\delta q}{T} \rightarrow \Delta S = \int_T^{T'} \frac{C_p}{T} dT$$

From Appendix,

$$\begin{cases} \Delta S_{Zr(a) \rightarrow (p)} = \frac{3900}{1136} & \Delta S_{ZrO_2, 298} : 50.4 \text{ J/K} \\ \Delta S_{ZrO_2(a) \rightarrow (p)} = \frac{5900}{1478} \end{cases}$$

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

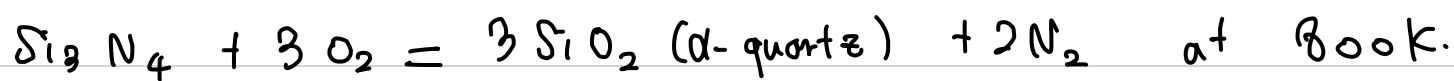
$$S_{ZrO_2(p), 1600} = S_{ZrO_2(a), 298} + \int_{298}^{1478} \frac{C_p ZrO_2(a)}{T} dT + \Delta S_{ZrO_2(a) \rightarrow (p)} + \int_{1478}^{1600} \frac{C_p ZrO_2(p)}{T} dT$$

$$S_{Zr(p), 1600} = S_{Zr(a), 298} + \int_{298}^{1136} \frac{C_p Zr(a)}{T} dT + \Delta S_{Zr(a) \rightarrow (p)} + \int_{1136}^{1600} \frac{C_p Zr(p)}{T} dT$$

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

$$\therefore \Delta S_{1600} = -178 \text{ J/K}$$

#2 Calculate the value of ΔG for the reaction



What percentage error occurs if it is assumed that ΔC_p for rxn is zero

1) 298 K 일때

$$\Delta H_{298} = 3H_{\text{SiO}_2} - H_{\text{Si}_3\text{N}_4} = -1987900 \text{ J/K}$$

$$\Delta S_{298} = 3S_{\text{SiO}_2} + 2S_{\text{N}_2} - S_{\text{Si}_3\text{N}_4} - 3S_{\text{O}_2} = -220.8 \text{ J/K}$$

$$\Delta G = \Delta H - T\Delta S = -1987900 - 298(-220.8) = -1.922101 \times 10^6$$

$$2) \Delta C_p = 2C_{p\text{N}_2} + 3C_{p\text{SiO}_2} - C_{p\text{Si}_3\text{N}_4} - 3C_{p\text{O}_2}$$

$$3) 800\text{K 일때} \quad \Delta G = \Delta H - T\Delta S \\ = -1987900 + \int_{298}^{800} \Delta C_p dT - 800 \cdot \Delta S_{800}$$

$$4) \Delta S_{800} = \Delta S_{298} + \int_{298}^{800} \frac{\Delta C_p}{T} dT = -220.8 - 29.7 = -250.5 \text{ J/K}$$

$$\therefore \Delta G_{800} = -1987900 - 16687 + 800 \times 250.5 \\ = -1804187 \text{ J}$$

$$\text{Assume } \Delta C_p = 0, \Delta G_{800}' = -1987900 + 0 - 800(-220.8 + 0) \\ = -1811260 \text{ J}$$

$$\text{Error} \% \text{ 나타내면, } \left| \frac{100(\Delta G_{800}' - \Delta G_{800})}{\Delta G_{800}} \right| = \left| \frac{100(-1811260 + 1804187)}{1804187} \right|$$

$\therefore$ Error 는 0.39% 정도이다.

3

ΔH_v : Vacancy 1개당 System 의 에너지 증가에 기여하는 정표.

Find $\frac{n(\text{equilibrium number of vacancies})}{N(\text{total lattice \#})}$

1) 통계열역학적 접근

$$\begin{aligned} \text{분배 함수 } Z &= \sum_i \exp\left(-\frac{E_i}{kT}\right) = \underbrace{\exp\left(-\frac{0}{kT}\right)}_{\text{no defect (atom)}} + \underbrace{\exp\left(-\frac{\Delta H_v}{kT}\right)}_{\text{vacancy}} \\ &= 1 + e^{-\frac{\Delta H_v}{kT}} \end{aligned}$$

System이 어떤 microstate i 에 있을 확률 $p_i = \frac{1}{Z} e^{-\frac{E_i}{kT}}$ 이므로

lattice에 존재하는 atomic site 가 vacancy 일 확률이 p_i 라고 하면

$$n = N p_i, \quad \frac{n}{N} = p_i = \frac{e^{-\frac{\Delta H_v}{kT}}}{1 + e^{-\frac{\Delta H_v}{kT}}}$$

보통 crystal에서 $p_i \ll 1$, $1 + e^{-\frac{\Delta H_v}{kT}} \simeq 1$ 이므로

$$\frac{n}{N} = e^{-\frac{\Delta H_v}{kT}} \text{ 로 표현할 수 있다.}$$

$$c.f \quad F = -kT \ln Z$$

2) 고전 열역학적 접근

헬름홀츠 자유에너지의 변화량이 평형상태에서 0 이라고 하면

$\Delta F = \Delta U - T\Delta S = 0$. vacancy et atom 위치가 무질서한 혼합으로 정해진다면

$$\Delta U = n \cdot \Delta H_v, \quad \Delta S_{\text{config}} = k \ln \frac{(N+n)!}{N! n!}, \quad \Delta S_{\text{thermal}} = S_{\text{평형}} - S_{\text{초기}}$$

(N : atom, n : vacancy) = excess $E_{\text{vibrational}}$
 $\simeq 0$

Stirling 근사 $\ln N! \simeq N \ln N - N$ 활용

$$\begin{aligned} \Delta S_{\text{config}} &= k \left((N+n) \ln (N+n) - (N+n) - N \ln N + N - n \ln n + n \right) \\ &= k \left((N+n) \ln (N+n) - N \ln N - n \ln n \right) \end{aligned}$$

$$\therefore \Delta F = n \Delta H_v - kT \left((N+n) \ln (N+n) - N \ln N - n \ln n \right)$$

$$\frac{\partial F}{\partial n} = \Delta H_v - kT \left(\ln (N+n) - \ln n \right) = 0$$

$$\frac{\Delta H_v}{kT} = \ln \frac{N+n}{n} = - \ln \frac{n}{N+n}$$

$$\therefore \frac{n}{N+n} = e^{-\frac{\Delta H_v}{kT}}$$

$$\therefore \frac{n(\text{vacancy})}{N(\text{total})} = e^{-\frac{\Delta H_v}{kT}}$$