HW 3

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

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

Sol)

우선, 주어진 Appendix에서 $Zr(\alpha) + O_2 = ZrO_2(\alpha)$ 의

$\Delta H^\circ_{298} = -1100800\,J$, $\Delta S^\circ_{298} = 50.4\,J/K$

Zr의 molar entropy $= 39.0\,J/K$

$ZrO_2(\alpha)$: $C_p = 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2}\ J/mole\cdot K$ (in the range of $298 \sim 1478\,K$)

$ZrO_2(\beta)$: $C_p = 74.48\ J/mole\cdot K$ (in the range of $1478 \sim 2950\,K$)

$Zr(\alpha)$: $C_p = 21.97 + 11.63\times10^{-3}T\ J/mole\cdot K$ ($298 \sim 1136\,K$)

$Zr(\beta)$: $C_p = 23.22 + 4.64\times10^{-3}T\ J/mole\cdot K$ ($1136 \sim 2128\,K$)

Molar heats of transformation
- $Zr(\alpha) \rightarrow Zr(\beta)$: $\Delta H = 3900\,J$, $T_{trans} = 1136\,K$
- $ZrO_2(\alpha) \rightarrow ZrO_2(\beta)$: $\Delta H = 5900\,J$, $T_{trans} = 1478\,K$

O_2 : $C_p = 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2}\ J/K$

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

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

$\Delta H_{1600} = H_{ZrO_2(\alpha)} + \int_{298}^{1136}(C_p\,ZrO_2(\alpha) - C_p\,Zr(\alpha) - C_p\,O_2)\,dT$

$- \Delta H_{Zr(\alpha)\rightarrow(\beta)} + \int_{1136}^{1478}(C_p\,ZrO_2(\alpha) - C_p\,Zr(\beta) - C_p\,O_2)\,dT$

1136 K에서 transition

$+ \Delta H_{ZrO_2(\alpha)\rightarrow(\beta)} + \int_{1478}^{1600}(C_p\,ZrO_2(\beta) - C_p\,Zr(\beta) - C_p\,O_2)\,dT$

$= -1100800 + \int_{298}^{1136}\Big((69.62 - 21.97 - 29.96) + (7.53 - 11.63 - 4.18)\times10^{-3}T - (-14.06 + 1.67)10^{5}\Big)dT - 3900 +$

(17.69, −8.28, −12.39)

$\int_{1136}^{1478}\Big((69.62 - 23.22 - 29.96) - 1.29\times10^{-3}T + 12.39\times10^{5}T^{-2}\Big)dT$

(15.44)

$+ 5900 + \int_{1478}^{1600}(21.3 - (4.64 + 4.18)\times10^{-3}T - 1.67\times10^{5}T^{-2})\,dT$

$= -1086\,kJ$

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

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

From Appendix,

$$\begin{cases} \Delta S_{Zr\,(\alpha)\rightarrow(\beta)} = \dfrac{3900}{1136} \\ \Delta S_{ZrO_2\,(\alpha)\rightarrow(\beta)} = \dfrac{5900}{1478} \end{cases} \qquad \Delta S_{ZrO_2,298} : 50.4\ J/K$$

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

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

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

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

$$\therefore \Delta S_{1600} = -108\ J/K$$

#2 Calculate the value of ΔG for the reaction

$$Si_3N_4 + 3O_2 = 3SiO_2\ (\alpha\text{-quartz}) + 2N_2 \quad at\ 800K.$$

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

1) 298 K 에서

$\Delta H_{298} = 3H_{SiO_2} - H_{Si_3N_4} = -1987900$ J/K

$\Delta S_{298} = 3S_{SiO_2} + 2S_{N_2} - S_{Si_3N_4} - 3S_{O_2} = -220.8$ J/K

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

2) $\Delta C_p = 2C_pN_2 + 3C_pSiO_2 - C_pSi_3N_4 - 3C_pO_2$

3) 800 K 에서 $\Delta G = \Delta H - T\Delta S$

$= -1987900 + \int_{298}^{800} \Delta C_p\, dT - 800 \cdot \Delta S_{800}$

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

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

$= -1804187$ J

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

$= -1811260$ J

Error 를 % 로 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 System의 에너지 증가에 기여하는 정도.

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

1) 통계열역학적 접근

분배 함수 $Z = \sum_i \exp\left(-\frac{\varepsilon_i}{kT}\right) = \underbrace{\exp\left(-\frac{0}{kT}\right)}_{\text{no defect (atom)}} + \underbrace{\exp\left(-\frac{\Delta H_v}{kT}\right)}_{\text{vacancy}}$

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

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

lattice에 존재하는 atomic site가 vacancy일 확률이 p_i라고 하면

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

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

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

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

2) 고전열역학적 접근

헬름홀츠 자유에너지의 변화량이 평형상태에서 0이라고 하면

$\Delta F = \Delta U - T\Delta S = 0$. Vacancy 와 atom 위치가 무질서한 분할으로 정해진다면

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

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

$\simeq 0$

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

$$\Delta S_{config} = k\Big((N+n)\ln(N+n) - (N+n) - N\ln N + N - n\ln n + n \Big)$$

$$= k\big((N+n)\ln(N+n) - N\ln N - n\ln n \big)$$

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

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

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

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

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