Homework 3

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1. $C_p = \left(\frac{\partial H}{\partial T}\right)_p \rightarrow dH = C_p dT \rightarrow \Delta H = \int_{T_1}^{T_2} C_p dT$

$ZrO_2(\alpha)$: 1136K ~ 1478K / $ZrO_2(\beta)$: 1478K ~ 1600K

$Zr(\alpha)$: 298K ~ 1136K / $Zr(\beta)$: 1136K ~ 1600K

$O_2(g)$: 298K ~ 1600K

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

$$H_{ZrO_2(\beta),1600} = \Delta H^\circ_{ZrO_2(\alpha),298} + \int_{298}^{1478} Cp_{ZrO_2(\alpha)} dT + \Delta H_{ZrO_2(\alpha)\rightarrow(\beta)} + \int_{1478}^{1600} Cp_{ZrO_2(\beta)} dT$$

$$= -1100800 + \int_{298}^{1478} 69.62 + 7.53\times10^{-3}T - 14.06\times10^{5}T^{-2} dT$$

$$+ 5900 + \int_{1478}^{1600} 74.48 dT = -99.95\times10^4 J$$

$$H_{Zr(\beta),1600} = \int_{298}^{1136} Cp_{Zr(\alpha)} dT + \Delta H_{Zr(\alpha)\rightarrow(\beta)} + \int_{1136}^{1600} Cp_{Zr(\beta)} dT$$

$$= \int_{298}^{1136} 21.97 + 11.63\times10^{-3}T\, dT + 3900 + \int_{1136}^{1600} 23.22 + 4.64\times10^{-3}T dT$$

$$= 4.30\times10^4 J$$

$$H_{O_2,1600} = \int_{298}^{1600} Cp_{O_2} dT = \int_{298}^{1600} 29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2} dT$$

$$= 4.37\times10^4 J$$

$$\Delta H_{1600} = -108.62 MJ$$

$$dS = \frac{\delta q}{T} \rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT$$

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

$$S_{ZrO_2(\beta),1600} = S^{\circ}_{ZrO_2(\alpha),298} + \int_{298}^{1478} \frac{C_{p_{ZrO_2(\alpha)}}}{T}\, dT + \Delta S_{ZrO_2(\alpha)\rightarrow(\beta)} + \int_{1478}^{1600} \frac{C_{p_{ZrO_2(\beta)}}}{T}\, dT$$

$$= 50.4 + \int_{298}^{1478} 69.62\, T^{-1} + 7.53\times10^{-3} - 14.06\times10^{5}\, T^{-3}\, dT$$

$$+ \frac{5900}{1478} + \int_{1478}^{1600} 74.48\, T^{-1}\, dT = 172.7\ J/K$$

$$S_{Zr(\beta),1600} = S^{\circ}_{Zr(\alpha),298} + \int_{298}^{1136} \frac{C_{p_{Zr(\alpha)}}}{T} + \Delta S_{Zr(\alpha)\rightarrow(\beta)} + \int_{1136}^{1600} \frac{C_{p_{Zr(\beta)}}}{T}\, dT$$

$$= 39.0 + \int_{298}^{1136} 21.97\, T^{-1} + 11.63\, dT + \frac{3900}{1136}$$

$$+ \int_{1136}^{1600} 23.22\, T^{-1} + 4.64\, dT = 91.7\ J/K$$

$$S_{O_2,1600} = S^{\circ}_{O_2,298} + \int_{298}^{1600} \frac{C_{p_{O_2}}}{T} = 205.1 + 54.9 = 260.0$$

$$\Delta S_{1600} = -179.0\ J/K$$

2. $\Delta C_p = 3C_{p\,SiO_2(\alpha\text{-quartz})} + 2C_{p\,N_2} - C_{p\,Si_3N_4} - 3C_{p\,O_2}$

$= 26.99 - 99.74\times10^{-3}\,T - 13.05\times10^{5}\,T^{-2}$

$\Delta H_{800} = \underline{3\Delta H^{\circ}_{SiO_2(\alpha\text{-quartz}),298} - \Delta H^{\circ}_{Si_3N_4,298}} + \int_{298}^{800} \Delta C_p\, dT$

$= -1987900 - 16687 = -2004587\,J$

$\Delta S_{800} = \underline{3S^{\circ}_{SiO_2(\alpha\text{-quartz}),298} + 2S^{\circ}_{N_2,298} - S_{Si_3N_4} - 3S^{\circ}_{O_2}} + \int_{298}^{800} \frac{\Delta C_p}{T} dT$

$= -220.8 - 29.7 = -250.5\,J/K$

$\therefore \Delta G_{800} = \Delta H_{800} - T\Delta S_{800} = -2004587 - 800\times(-250.5) = -1.804\times10^{6}\,J$

$C_p = 0$ 일경우 ΔH_{800}, ΔS_{800} 에서 적분되는 term이 사라지므로

$\Delta G_{800} = -1987900 - 800\times(-220.8) = -1.811\times10^{6}\,J$

$error = \frac{(1.811 - 1.804)}{1.804} = 0.3880\,\%$

3. ① 고전 열역학적 방법.

$X_v = \frac{n}{N}$

$$\Delta S_{config} = k \ln \frac{N!}{n!(N-n)!} = k(N\ln N - n\ln n - (N-n)\ln(N-n))$$
$$= -kN(X_v \ln X_v + (1-X_v)\ln(1-X_v))$$

$$G = G_0 + N(X_v \Delta H_v + kT(X_v \ln X_v + (1-X_v)\ln(1-X_v)))$$

X_v는 매우 작기 때문에 생략되기도 함.

$$\frac{d\Delta G}{dX_v} = N(\Delta H_v + kT(\ln X_v + 1 - \ln(1-X_v) - 1))$$
$$= N\left(\Delta H_v + kT \ln \frac{X_v}{1-X_v}\right)$$

$$\left.\frac{d\Delta G}{dX_v}\right|_{X_v = X_v^e} = 0 \longrightarrow \Delta H_v = kT \ln \frac{1-X_v}{X_v} \Rightarrow X_v^e = \frac{1}{1+\exp\left(\frac{\Delta H_v}{kT}\right)}$$

thermal entropy 까지 고려하면 $\Delta H_v \rightarrow \Delta G_v$ $\approx \exp\left(-\frac{\Delta H_v}{kT}\right)$

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② 통계 열역학적 방법

ΔH_{atom} ($\because$ 원래 atom 위치니까)

$$Z = \sum_j \exp\left(-\frac{E_j}{kT}\right) = \exp\left(-\frac{0}{kT}\right) + \exp\left(-\frac{\Delta H_v}{kT}\right) = 1 + \exp\left(-\frac{\Delta H_v}{kT}\right)$$

$P_j = \frac{1}{Z}\exp\left(-\frac{E_j}{kT}\right)$ 이므로, vacancy가 존재할 확률 $P_v = \frac{1}{Z}\exp\left(-\frac{\Delta H_v}{kT}\right)$

$$= \frac{\exp\left(-\frac{\Delta H_v}{kT}\right)}{1+\exp\left(-\frac{\Delta H_v}{kT}\right)}$$

P_v는 통계적으로 X_v와 같기 때문에

$$X_v = \frac{\exp\left(-\frac{\Delta H_v}{kT}\right)}{1+\exp\left(-\frac{\Delta H_v}{kT}\right)} = \frac{1}{1+\exp\left(\frac{\Delta H_v}{kT}\right)}$$