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AMSE205 Thermodynamics I

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1. Calculate ΔH_{1600} and ΔS_{1600} for the reaction $Zr(\beta) + O_2 = ZrO_2(\beta)$.
   (Utilize the Tables in the APPENDIX of the textbook.)

2. Calculate the value of ΔG for the reaction

   $$Si_3N_4 + 3\ O_2 = 3\ SiO_2\ (\alpha\text{-quartz}) + 2\ N_2$$

   at 800 K. What percentage error occurs if it is assumed that ΔC_p for the reaction is zero?

3. 모든 결정은 원자가 일정한 격자 자리에 위치하고 있다. 원자가 있어야 할 격자 자리가 비어 있는 경우 원자공공 (vacancy)이 발생했다고 한다. Vacancy formation energy 는 vacancy 가 하나 생겼을 때 증가하는 system 의 에너지를 말하며 ΔH_v 로 표시한다. N 개의 격자 자리로 이루어진 순수 결정에서 평형 vacancy 수 (n) 또는 vacancy 와 총 격자 자리 개수 비율 (n/N)의 표현 식을, 통계열역학적 접근 방식과 고전열역학적 접근 방식을 사용하여 각각 유도하시오.

20200865 정세희

Problem Set #3.

책에는 298K 기준 나옴. 298K 기준으로 찾자.

1. Calculate ΔH_{1600} and ΔS_{1600} for the reaction $Zr(\beta) + O_2 = ZrO_2(\beta)$. (Utilize the Tables in the APPENDIX of the textbook.)

1136K에서 transition

a) ΔH_{1600}: $Zr(\beta) + O_2 = ZrO_2(\beta)$

1478 K 에서 transition 발생 ($\alpha \to \beta$)

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

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

$$= -1100800 + 5900 + \int_{298}^{1478} 69.62 + 7.53\times10^{-3}T - \frac{14.06\times10^5}{T^2}\, dT + \int_{1478}^{1600} 74.48\, dT$$

$$= -1100800 + 5900 + \left[69.62T + 3.765\times10^{-3}T^2 + 14.06\times10^5\cdot\frac{1}{T}\right]_{298}^{1478} + 74.48(1600-1478)$$

$$= -1094900 + (112517.63 - 25888.63) + 9086.56 = -999538\,(J)$$

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

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

$$= 3900 + \left[21.97T + 5.815\times10^{-3}T^2\right]_{298}^{1136} + \left[23.22T + 2.32\times10^{-3}T^2\right]_{1136}^{1600}$$

$$= 43018\,(J)$$

$$\Delta H_{O_2,1600} = \int_{298}^{1600} C_p\, dT$$

$$= \int_{298}^{1600} 29.96 + 4.18\times10^{-3}T - 1.67\times10^5\cdot\frac{1}{T^2}\, dT$$

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

$$= 53390.78 - 9674.08 = 43716.7\,(J)$$

$$\therefore \Delta H_{1600} = -999539 - (43018 + 43717) = -1.086\times10^{6}\,(J)$$

b) ΔS_{1600}

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

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

$$= 50.4 + \int_{298}^{1478} \frac{69.62}{T} + 7.53\times10^{-3} - \frac{14.06\times10^{5}}{T^{3}}\,dT + \Delta S_{\alpha\to\beta}$$

$$+ \int_{1478}^{1600} \frac{74.48}{T}\,dT$$

$$= 50.4 + \left[69.62\ln T + 7.53\times10^{-3}T + \frac{1}{2}\cdot\frac{14.06\times10^{5}}{T^{2}}\right]_{298}^{1478} + 74.48\ln\frac{1600}{1478} + \frac{5900}{1478}$$

$$= 173.08\,(J/K)$$

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

$$= 39 + \int_{298}^{1136} \frac{21.97}{T} + 11.63\times10^{-3}\,dT$$

$$+ \int_{1136}^{1600} \frac{23.22}{T} + 4.64\times10^{-3}\,dT + \frac{3900}{1136}$$

$$= 39 + \left[21.97\ln T + 11.63\times10^{-3}T\right]_{298}^{1136}$$

$$+ \left[23.22\ln T + 4.64\times10^{-3}T\right]_{1136}^{1600} + \frac{3900}{1136}$$

$$= 91.684$$

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

$$= 205.1 + \left[29.96\ln T + 4.18\times10^{-3}T + 0.835\times10^{5}\frac{1}{T^{2}}\right]_{298}^{1600}$$

$$= 259.99$$

$$\Rightarrow \Delta S_{1600} = -178.6\,J/K$$

2. Calculate the value of ΔG for the reaction

$$Si_3N_4 + 3\,O_2 = 3\,SiO_2\ (\alpha\text{-quartz}) + 2\,N_2$$

at 800 K. What percentage error occurs if it is assumed that ΔC_p for the reaction is zero?

① 800K 에서 ΔG

$$\Delta G_{800} = \Delta H_{800} - T\Delta S_{800} = \Delta H_{800} - 800\Delta S_{800}$$

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

$$\Delta H_{SiO_2(\alpha\text{-quartz}),800} = \Delta H_{SiO_2,298} + \int_{298}^{800} \Delta C_p dT$$

$$= -910900 + \int_{298}^{800} 43.89 + 10^{-3}T - \frac{6.02\times10^5}{T^2} dT$$

$$= -910900 + \left[43.89T + \frac{1}{2}\times10^{-3}T^2 + 6.02\times10^5\times\frac{1}{T}\right]_{298}^{800}$$

$$= -889859.26$$

$$\Delta H_{N_2} = \Delta H_{N_2,298} + \int_{298}^{800} \Delta C_p dT$$

$$= \int_{298}^{800} 27.87 + 4.27\times10^{-3}T\, dT$$

$$= \left[27.87T + 2.135\times10^{-3}T^2\right]_{298}^{800} = 15167.5$$

$$\Delta H_{Si_3N_4} = \Delta H_{Si_3N_4,298} + \int_{298}^{800} \Delta C_p dT$$

$$= -744800 + \int_{298}^{800} 70.54 + 98.74\times10^{-3}\times T\, dT$$

$$= -744800 + \left[70.54T + 49.37\times10^{-3}\times T^2\right]_{298}^{800}$$

$$= -682176.4$$

$$\Delta H_{O_2,800} = \Delta H_{O_2,298} + \int_{298}^{800} \Delta C_p dT$$

$$= \int_{298}^{800} 29.96 + 4.18\times10^{-3}T - 1.67\times10^5\times\frac{1}{T^2} dT$$

$$= \left[29.96T + 2.09\times10^{-3}T^2 + 1.67\times10^5\times\frac{1}{T}\right]_{298}^{800}$$

$$= 15840.27$$

$$\therefore \Delta H_{800} = -2004587.2\,(J)$$

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

$$S_{SiO_2,800} = S_{SiO_2,298} + \int_{298}^{800} \Delta C_p\, dT$$

$$= 41.5 + \int_{298}^{800} \frac{43.89}{T} + 10^{-3} - 6.02\times10^{5}\times\frac{1}{T^3}\, dT$$

$$= 41.5 + \left[43.89\ln T + \underset{10^{-3}}{\wedge} T + 3.01\times10^{5}\times\frac{1}{T^2}\right]_{298}^{800}$$

$$= 82.425$$

$$S_{N_2,800} = S_{N_2,298} + \int_{298}^{800} \Delta C_p\, dT$$

$$= 191.5 + \int_{298}^{800} \frac{27.87}{T} + 4.27\times10^{-3}\, dT$$

$$= 191.5 + \left[27.87\ln T + 4.27\times10^{-3}\,T\right]_{298}^{800} = 221.17$$

$$S_{Si_3N_4,800} = S_{Si_3N_4,298} + \int_{298}^{800} \Delta C_p\, dT$$

$$= 113 + \int_{298}^{800} \frac{70.54}{T} + 98.74\times10^{-3}\, dT$$

$$= 113 + \left[70.54\ln T + 98.74\times10^{-3}\,T\right]_{298}^{800}$$

$$= 232.23\ (J/K)$$

$$S_{O_2,800} = S_{O_2,298} + \int_{298}^{800} \Delta C_p\, dT$$

$$= 205.1 + \int_{298}^{800} 29.96\times\frac{1}{T} + 4.18\times10^{-3} - 1.67\times10^{5}\times\frac{1}{T^3}\, dT$$

$$= 205.1 + \left[29.96\ln T + 4.18\times10^{-3}\,T + 0.835\times10^{5}\times\frac{1}{T^2}\right]_{298}^{800}$$

$$= 235.9746$$

$$\therefore \Delta S_{800} = 3\times82.425 + 2\times221.17 - 232.23 - 3\times235.9746$$

$$= -250.5388$$

$$\therefore \Delta G_{800} = \Delta H_{800} - 800\,\Delta S_{800} = -2004587.2 + 800\times250.5388$$

$$= \boxed{-1804156\ (J)}$$

$\Delta C_p = 0$이라 가정하면,

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = -910900 \times 3 + 744800 = -1987900$$

$$\Delta S = 3 \times 41.5 + 2 \times 191.5 - 113 - 3 \times 205.1$$
$$= -220.8$$

$$\Delta G = -1987900 + 800 \times 220.8 = -1811260$$

$$\therefore \text{error} = \frac{1811260 - 1804156}{1804156} \times 100(\%) \simeq 0.394(\%)$$

$$\Delta G = -1804156J, \ \text{error} = 0.394\%$$

3. 모든 결정은 원자가 일정한 격자 자리에 위치하고 있다. 원자가 있어야 할 격자 자리가 비어 있는 경우 원자공공 (vacancy)이 발생했다고 한다. Vacancy formation energy 는 vacancy 가 하나 생겼을 때 증가하는 system 의 에너지를 말하며 ΔH_v 로 표시한다. N 개의 격자 자리로 이루어진 순수 결정에서 평형 vacancy 수 (n) 또는 vacancy 와 총 격자 자리 개수 비율 (n/N)의 표현 식을, 통계열역학적 접근 방식과 고전열역학적 접근 방식을 사용하여 각각 유도하시오.

vacancy formation energy : vacancy 하나 생길 때 증가하는 system의 E. ΔH_v

① 통계열역학적 접근방식

N개의 격자자리

vacancy

$$Z = \sum_i \exp\left(-\frac{E_i}{kT}\right) = 1 + e^{-\frac{\Delta H}{kT}}$$

atom 채워짐 : $e^0 = 1$

$$\therefore p = \frac{e^{-\frac{\Delta H}{kT}}}{1 + e^{-\frac{\Delta H}{kT}}} = \frac{1}{e^{\frac{\Delta H}{kT}} + 1}$$

② 고전열역학적 방식

$$\Delta S = k \ln \frac{N!}{(N-n)!} = k(\ln N! - \ln(N-n)!)$$

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

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

$$= k(N-n)\ln\frac{N}{N-n} + kn\ln\frac{n}{N}$$

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

$$= n_v \Delta H_v - Tk(N-n)\ln\frac{n}{N-n} - Tkn\ln\frac{n}{N}$$

$$\frac{dF}{dn} = \Delta H_v - T_k\left(\cancel{-\ln N} + \ln(N-n)\cancel{+1} + \cancel{\ln\frac{n}{N}+1}\right)$$

$$\cancel{\ln N - \ln n}$$

$$= \Delta H_v - T_k \ln\frac{N-n}{n} = 0$$

$$T_k \ln\frac{N-n}{n} = \Delta H_v \qquad \ln\frac{N-n}{n} = \frac{\Delta H_v}{T_k}$$

$$\frac{N-n}{n} = e^{\frac{\Delta H_v}{T_k}} \rightarrow \frac{N}{n} = e^{\frac{\Delta H_v}{T_k}} + 1$$

$$\therefore \frac{n}{N} = \frac{1}{1+e^{\frac{\Delta H_v}{T_k}}}$$