

Thermodynamics HW #3

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1. Calculate ΔH_{1600} and ΔS_{1600} for the reaction $\text{Zr}(\beta) + \text{O}_2 = \text{ZrO}_2(\beta)$.

(Utilize the Tables in the APPENDIX of the textbook.)

Table A.2 The Constant-Pressure Molar Heat Capacities of Various Substances ($c_p = a + bT + cT^{-2}$ J/mole·K)

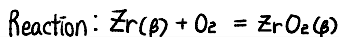
Substance	a	$b \times 10^3$	$c \times 10^{-5}$	Range, K	Remarks
$\text{O}_{2(g)}$	29.96	4.18	-1.67	298-3000	
$\text{Zr}_{(\alpha)}$	21.97	11.63	—	298-1136	
$\text{Zr}_{(\beta)}$	23.22	4.64	—	1136-2128	
$\text{ZrO}_{2(\alpha)}$	69.62	7.53	-14.06	298-1478	
$\text{ZrO}_{2(\beta)}$	74.48	—	—	1478-2950(T_m)	

Table A.3 The Standard Molar Heats of Formation and Molar Entropies of Various Substances at 298 K

Substance	ΔH_{298}° , J	S_{298}° , J/K
O_2	—	205.1
Zr	—	39.0
ZrO_2	-1,100,800	50.4

Table A.5 Molar Heats of Melting and Transformation

Substance	Trans.	ΔH_{trans} , J	T_{trans} , K
Zr	$\alpha \rightarrow \beta$	3,900	1,136
ZrO_2	$\alpha \rightarrow \beta$	5,900	1,478



$$1) \Delta H_T = \Delta H_{298} + \int_{298}^T c_p dT \rightarrow \Delta H_{1600} = \Delta H_{298} + \int_{298}^{1600} c_p dT$$

$$\begin{aligned} \Delta H_{1600}(\text{ZrO}_2) &= \Delta H_{298}^\circ + \int_{298}^{1478} c_p dT + \Delta H(\text{ZrO}_2(\alpha) \rightarrow (\beta)) + \int_{1478}^{1600} c_p dT \\ &= -1100800 + \int_{298}^{1478} (69.62 + 7.53 \times 10^{-3}T - 14.06 \times 10^{-5}T^{-2}) dT + 5900 + \int_{1478}^{1600} 74.48 dT \\ &= -1100800 + [69.62T + 3.765 \times 10^{-3}T^2 + 14.06 \times 10^{-5}T^{-1}]_{298}^{1478} + 5900 + [74.48T]_{1478}^{1600} \\ &= -1100800 + 86275 + 5900 + 9086.56 = -999538.44 \text{ J} = -999.54 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H_{1600}(\text{Zr}) &= \Delta H_{298}^\circ + \int_{298}^{1136} c_p dT + \Delta H(\text{Zr}(\alpha) \rightarrow (\beta)) + \int_{1136}^{1600} c_p dT \\ &= 0 + \int_{298}^{1136} (21.97 + 11.63 \times 10^{-3}T) dT + 3900 + \int_{1136}^{1600} (23.22 + 4.64 \times 10^{-3}T) dT \\ &= 0 + 25398.7 + 3900 + 13719.3 = 43018 \text{ J} = 43.02 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H_{1600}(\text{O}_2) &= \Delta H_{298}^\circ + \int_{298}^{1600} c_p dT \\ &= 0 + \int_{298}^{1600} (29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{-5}T^{-2}) dT \\ &= 0 + [29.96T + 2.09 \times 10^{-3}T^2 + 1.67 \times 10^{-5}T^{-1}]_{298}^{1600} = 43716.7 \text{ J} = 43.72 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \therefore \Delta H_{1600} &= \sum \Delta H_{1600, \text{product}} - \sum \Delta H_{1600, \text{reactant}} \\ &= \Delta H_{1600}(\text{ZrO}_2) - \{\Delta H_{1600}(\text{Zr}) + \Delta H_{1600}(\text{O}_2)\} \\ &= -999.54 - (43.02 + 43.72) = -1086.28 \text{ kJ} \end{aligned}$$

$$2) dS = dQ/T \rightarrow \Delta S = \int_{T_1}^{T_2} \frac{c_p}{T} dT$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^T \frac{c_p}{T} dT \rightarrow \Delta H_{1600} = \Delta H_{298}^\circ + \int_{298}^{1600} c_p dT$$

$$\begin{aligned} \Delta S_{1600}(\text{ZrO}_2) &= \Delta S_{298}^\circ + \int_{298}^{1478} \frac{c_p}{T} dT + \frac{\Delta H(\text{ZrO}_2(\alpha) \rightarrow (\beta))}{T_{\text{trans}}} + \int_{1478}^{1600} \frac{c_p}{T} dT \\ &= 50.4 + \int_{298}^{1478} (69.62T^{-1} + 7.53 \times 10^{-3} - 14.06 \times 10^{-5}T^{-3}) dT + \frac{5900}{1478} + \int_{1478}^{1600} 74.48T^{-1} dT \\ &= 50.4 + 112.777 + 3.992 + 5.907 = 173.076 \text{ J/K} \end{aligned}$$

$$\begin{aligned}\Delta S_{1600}(\text{Zr}) &= \Delta S_{298}^{\circ} + \int_{298}^{1136} \frac{C_p}{T} dT + \frac{\Delta H(\text{Zr}(\alpha) \rightarrow (\beta))}{T_{\text{trans}}} + \int_{1136}^{1600} \frac{C_p}{T} dT \\ &= 39.0 + \int_{298}^{1136} (21.97T^{-1} + 11.63 \times 10^{-3}) dT + \frac{3900}{1136} + \int_{1136}^{1600} (23.22T^{-1} + 4.64 \times 10^{-3}) dT \\ &= 39.0 + 39.146 + 3.433 + 10.106 = 91.685 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\Delta S_{1600}(\text{O}_2) &= \Delta S_{298}^{\circ} + \int_{298}^{1600} \frac{C_p}{T} dT \\ &= 205.1 + \int_{298}^{1600} (29.96T^{-1} + 4.18 \times 10^{-3} - 1.67 \times 10^{-5} T^{-3}) dT \\ &= 205.1 + 54.887 = 259.987 \text{ J/K}\end{aligned}$$

$$\begin{aligned}\therefore \Delta S_{1600} &= \sum \Delta S_{1600, \text{product}} - \sum \Delta S_{1600, \text{reactant}} \\ &= \Delta S_{1600}(\text{ZrO}_2) - \{\Delta S_{1600}(\text{Zr}) + \Delta S_{1600}(\text{O}_2)\} \\ &= 173.076 - (91.685 + 259.987) = -178.596 \text{ J/K}\end{aligned}$$

2. Calculate the value of ΔG for the reaction



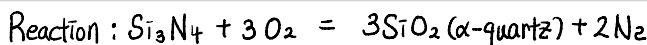
at 800 K. What percentage error occurs if it is assumed that ΔC_p for the reaction is zero?

Table A.2 The Constant-Pressure Molar Heat Capacities of Various Substances ($c_p = a + bT + cT^{-2}$ J/mole·K)

Substance	a	b × 10 ³	c × 10 ⁻⁵	Range, K	Remarks
O _{2(g)}	29.96	4.18	-1.67	298-3000	
2MgO·2Al ₂ O ₃ ·5SiO ₂	626.34	91.21	-200.83	298-1738(T _m)	
N ₂	27.87	4.27	—	298-2500	
Si ₃ N ₄	70.54	98.74	—	298-900	
SiO _{2(α-quartz)}	43.89	1.00	-6.02	298-847	

Table A.3 The Standard Molar Heats of Formation and Molar Entropies of Various Substances at 298 K

Substance	ΔH ₂₉₈ ^o , J	S ₂₉₈ ^o , J/K
N ₂	—	191.5
O ₂	—	205.1
SiO _{2(α-quartz)}	-910,900	41.5
Si ₃ N ₄	-744,800	113.0



$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT \rightarrow \Delta H_{800} = \Delta H_{298}^o + \int_{298}^{800} \Delta C_p dT$$

$$1) \Delta H_{298}^o = 3\Delta H_{298}^o(\text{SiO}_2(\alpha\text{-quartz})) - \Delta H_{298}^o(\text{Si}_3\text{N}_4)$$

$$= 3 \times (-910900) - (-744800) = -1987900 \text{ J}$$

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

$$= (3 \times 43.89 + 2 \times 27.87 - 70.54 - 3 \times 29.96)$$

$$+ (3 \times 1.00 + 2 \times 4.27 - 98.74 - 3 \times 4.18) \times 10^{-3} T$$

$$+ (3 \times (-6.02) - 3 \times (-1.67)) \times 10^{-5} T^{-2}$$

$$= 26.99 - 99.74 \times 10^{-3} T - 13.05 \times 10^{-5} T^{-2} \quad -16687 \text{ J}$$

$$\text{Then, } \int_{298}^{800} \Delta C_p dT = \int_{298}^{800} (26.99 - 99.74 \times 10^{-3} T - 13.05 \times 10^{-5} T^{-2}) dT = -16687.1 \text{ J}$$

$$\therefore \Delta H_{800} = -1987900 - 16687 = -2004587 \text{ J} \approx -2004.6 \text{ kJ}$$

$$\Delta S_T = \Delta S_{298} + \int_{298}^T \frac{\Delta C_p}{T} dT \rightarrow \Delta S_{800} = \Delta S_{298}^o + \int_{298}^{800} \frac{\Delta C_p}{T} dT$$

$$1) \Delta S_{298}^o = 3S_{298}^o(\text{SiO}_2(\alpha\text{-quartz})) + 2S_{298}^o(\text{N}_2) - S_{298}^o(\text{Si}_3\text{N}_4) - 3S_{298}^o(\text{O}_2)$$

$$= 3 \times 41.5 + 2 \times 191.5 - 113.0 - 3 \times 205.1 = -220.8 \text{ J/K}$$

$$2) \int_{298}^{800} \frac{\Delta C_p}{T} dT = \int_{298}^{800} (26.99 T^{-1} - 99.74 \times 10^{-3} - 13.05 \times 10^{-5} T^{-3}) dT = -29.7445 \text{ J/K} \approx -29.7 \text{ J/K}$$

$$\therefore \Delta S_{800} = -220.8 - 29.7 = -250.5 \text{ J/K}$$

$$\therefore \Delta G_{800} = \Delta H_{800} - T \Delta S_{800} = -2004587 \text{ J} - 800 \times (-250.5) = -1804187 \text{ J} = -1.804 \times 10^6 \text{ J}$$

if ΔC_p for the reaction is zero, then $\Delta H_{800} = -1987900 \text{ J}$, $\Delta S_{800} = -220.8 \text{ J/K}$

$$\Rightarrow \Delta G_{800} = -1987900 - 800 \times (-220.8) = -1811260 \text{ J} = -1.811 \times 10^6 \text{ J}$$

$$\therefore \text{error}(\%) = \frac{(-1.811 - (-1.804)) \times 10^6}{-1.804 \times 10^6} \times 100 = 0.388 \%$$

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 평균 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.

1) 통계 열역학적 방법

$$\begin{aligned} \cdot z &= \sum_i e^{-E_i/kT} = e^{-0/kT} + e^{-\Delta H_v/kT} = 1 + e^{-\Delta H_v/kT} \\ \cdot P_i &= \frac{1}{z} \cdot e^{-E_i/kT} \end{aligned} \Rightarrow \therefore P_v = X_v = \frac{e^{-\Delta H_v/kT}}{1 + e^{-\Delta H_v/kT}} = \frac{1}{e^{\Delta H_v/kT} + 1}$$

2) 고전 열역학적 방법

총 격자 자리수 : N, vacancy 수 : n

$$\begin{aligned} dS &= k \ln \frac{N!}{n!(N-n)!} = k \{ N \ln N - n \ln n - (N-n) \ln (N-n) \} \\ &= kN \left(\frac{n}{N} \ln \frac{N}{n} + \frac{N-n}{N} \ln \frac{N}{N-n} \right) \quad \downarrow \text{let } X_v = \frac{n}{N} \\ &= -kN \{ X_v \ln X_v + (1-X_v) \ln (1-X_v) \} \end{aligned}$$

$$\Delta G = n \cdot \Delta H_v + kT \cdot N \{ X_v \ln X_v + (1-X_v) \ln (1-X_v) \} \quad (\because n = N \cdot X_v)$$

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

$$= N \cdot \Delta H_v + kT \cdot N \cdot \ln \frac{X_v}{1-X_v}$$

$$\frac{d\Delta G}{dX_v} = 0 \text{ 이려면, } \Delta H_v = -kT \cdot \ln \frac{X_v}{1-X_v} = kT \cdot \ln \frac{1-X_v}{X_v}$$

$$\rightarrow e^{\Delta H_v/kT} = \frac{1-X_v}{X_v}$$

$$\rightarrow \frac{1}{X_v} = 1 + e^{\Delta H_v/kT}$$

$$\therefore X_v = \frac{1}{1 + e^{\Delta H_v/kT}}$$