

AMSE205 Thermodynamics I

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Problem Set #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.)

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?

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.

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

Substance	$\Delta H_{298}^\circ, \text{J}$	$S_{298}^\circ, \text{J/K}$
Al ₂ O ₃	-1,675,700	50.9
Ba	—	62.4
BaO	-548,100	72.1
BaTiO ₃	-1,653,100	107.9
C _(graphite)	—	5.73
C _(diamond)	1,900	2.43
CH ₄	-74,800	186.3
CO	-110,500	197.5
CO ₂	-393,500	213.7
Ca	—	41.6
CaO	-634,900	38.1
CaTiO ₃	-1,660,600	93.7
3CaO·Al ₂ O ₃ ·3SiO ₂	-6,646,300	241.4
CaO·Al ₂ O ₃ ·SiO ₂	-3,293,200	144.8
CaO·Al ₂ O ₃ ·2SiO ₂	-4,223,700	202.5
2CaO·Al ₂ O ₃ ·SiO ₂	-3,989,400	198.3
Cr ₂ O ₃	-1,134,700	81.2
H ₂ O _(g)	-241,800	232.9
N ₂	—	191.5
O ₂	—	205.1
SiO _{2,(α-quartz)}	-910,900	41.5
Si ₃ N ₄	-744,800	113.0
Ti	—	30.7
TiO	-543,000	34.7
Ti ₂ O ₃	-1,521,000	77.2
Ti ₃ O ₅	-2,459,000	129.4
TiO ₂	-944,000	50.6
Zr	—	39.0
ZrO ₂	-1,100,800	50.4

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
Ag	21.30	8.54	1.51	298–1234 (T_m)	
Ag _(l)	30.50	—	—	1234–1600	
Al _(s)	20.67	12.38	—	298–933 (T_m)	
Al _(l)	31.76	—	—	933–1600	
Al ₂ O ₃	106.6	17.78	-28.53	298–2325 (T_m)	
Ba _(α)	-473.2	1587.0	128.2	298–648	
Ba _(β)	-5.69	80.33	—	648–1003	
BaO	53.30	4.35	-8.30	298–2286 (T_m)	
BaTiO ₃	121.46	8.54	-19.16	298–1800	
C _(graphite)	0.11	38.94	-1.48	298–1100	-17.38 × 10 ⁻⁶ T ²
C _(graphite)	24.43	0.44	-31.63	1100–4000	
C _(diamond)	9.12	13.22	-6.19	298–1200	
CO	28.41	4.10	-0.46	298–2500	
CO ₂	44.14	9.04	-8.54	298–2500	
Ca _(α)	25.37	-7.26	—	298–716	23.72 × 10 ⁻⁶ T ²
Ca _(β)	-0.36	41.25	—	716–1115	
CaO	49.62	4.51	-6.95	298–1177	
CaTiO ₃	127.49	5.69	-27.99	298–1530	
Cr _(s)	24.43	9.87	-3.68	298–2130 (T_m)	
Cr ₂ O ₃	119.37	9.30	-15.65	298–1800	
Cu _(s)	22.64	6.28	—	298–1356 (T_m)	
Fe _(α/δ)	37.12	6.17	—	298–1183/1664–1809	
Fe _(γ)	24.47	8.45	—	1187–1664	
Fe _(l)	41.8	—	—	1809–1873	
H ₂ O _(g)	30.00	10.71	0.33	298–2500	
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	
Ti	22.09	10.46	—	298–1155	
TiO _{2(rutile)}	75.19	1.17	-18.20	298–1800	
Zr _(α)	21.97	11.63	—	298–1136	
Zr _(β)	23.22	4.64	—	1136–2128	
ZrO _{2(α)}	69.62	7.53	-14.06	298–1478	
ZrO _{2(β)}	74.48	—	—	1478–2950 (T_m)	

Table A.5 Molar Heats of Melting and Transformation

Substance	Trans.	$\Delta H_{\text{trans}}, \text{J}$	$T_{\text{trans}}, \text{K}$
Ag	s → l	11,090	1,234
Al	s → l	10,700	934
Al ₂ O ₃	s → l	107,500	2,324
Au	s → l	12,600	1,338
Ba	α → β	630	648
Ba	β → l	7,650	1,003
Cu	s → l	12,970	1,356
Ca	α → β	900	716
CaF ₂	s → l	31,200	1,691
Fe	α → γ	670	1,187
Fe	γ → δ	840	1,664
Fe	δ → l	13,770	1,809
H ₂ O	s → l	6,008	273
K ₂ O·B ₂ O ₃	s → l	62,800	1,220
MgF ₃	s → l	58,160	1,563
Na ₂ O·B ₂ O ₃	s → l	67,000	1,240
Pb	s → l	4,810	600
PbO	s → l	27,480	1,158
Si	s → l	50,200	1,685
V	s → l	22,840	2,193
Zr	α → β	3,900	1,136
ZrO ₂	α → β	5,900	1,478

$$\left\langle \Delta H_{1600} = \Delta H_{298} - \Delta H_{\text{trans } \text{Zr}(qs)} + \Delta H_{\text{trans } \text{ZrO}_2(qs)} + x + y + z \right\rangle \quad \begin{matrix} (\text{Zr}(qs) \rightarrow \text{reactant}) \\ (\text{ZrO}_2(qs) \rightarrow \text{product}) \end{matrix}$$

$$\textcircled{1} \Delta H_{298} = \Delta H_{298}^{\circ} \text{ZrO}_2 - (\Delta H_{298}^{\circ} \text{Zr} + \Delta H_{298}^{\circ} \text{O}_2) = -1100800 \text{ J}$$

$$\textcircled{1} x = \int_{298}^{1136} C_{p \text{ZrO}_2(\alpha)} - (C_{p \text{Zr}(\alpha)} + C_{p \text{O}_2(g)}) dT$$

$$\textcircled{2} T = 1136 \text{ K mK} \quad \text{Zr}(\alpha) \rightarrow \text{Zr}(qs), \quad -\Delta H_{\text{trans } \text{Zr}(qs)} = -3900 \text{ J}$$

$$\textcircled{2} y = \int_{1136}^{1418} C_{p \text{ZrO}_2(\alpha)} - (C_{p \text{Zr}(qs)} + C_{p \text{O}_2(g)}) dT$$

$$\textcircled{4} T = 1418 \text{ K mK} \quad \text{ZrO}_2(\alpha) \rightarrow \text{ZrO}_2(\beta), \quad +\Delta H_{\text{trans } \text{ZrO}_2(qs)} = +5900 \text{ J}$$

$$\textcircled{3} z = \int_{1418}^{1600} C_{p \text{ZrO}_2(\beta)} - (C_{p \text{Zr}(qs)} + C_{p \text{O}_2(g)}) dT$$

$$x = \int_{298}^{1136} C_{p \text{ZrO}_2(\alpha)} - (C_{p \text{Zr}(\alpha)} + C_{p \text{O}_2(g)}) dT$$

$$= \int_{298}^{1136} (69.62 - 21.97 - 29.96) + (7.53 - 11.63 - 4.18) \times 10^{-3} T$$

$$+ (-14.06 - 0 - (-1.67)) \times 10^5 \cdot T^{-2} dT$$

$$= 6782.17 \text{ (J)}$$

$$y = \int_{1136}^{1418} C_{p, \text{ZrO}_2(s)} - (C_{p, \text{Zr}(g)} + C_{p, \text{O}_2(g)}) dT$$

$$= \int_{1136}^{1418} (69.62 - 23.22 - 29.96) + (7.53 - 4.64 - 4.18) \times 10^{-3} T \\ + (-14.06 - 0 - (-1.67)) \times 10^5 \cdot T^{-2} dT$$

$$= 4793.48 \text{ (J)}$$

$$z = \int_{1418}^{1600} C_{p, \text{ZrO}_2(l)} - (C_{p, \text{Zr}(g)} + C_{p, \text{O}_2(g)}) dT$$

$$= \int_{1418}^{1600} (74.48 - 23.22 - 29.96) + (0 - 4.64 - 4.18) \times 10^{-3} T \\ + (0 - 0 - (-1.67)) \times 10^5 \cdot T^{-2} dT$$

$$= 951.19 \text{ J}$$

$$\therefore \Delta H_{1600} = \Delta H_{298} - \Delta H_{\text{trans Zr}(g)} + \Delta H_{\text{trans ZrO}_2(g)} + x + y + z$$

$$= -1100800 \text{ J} - 3900 \text{ J} + 5700 \text{ J} + 6782.17 \text{ J}$$

$$+ 4793.48 \text{ J} + 951.19 \text{ J} = -1.086 \times 10^6 \text{ (J)}$$

$$\Delta S_{1600} = \Delta S_{298} - \frac{\Delta H_{\text{trans Zr(s)}}}{T_{\text{trans Zr(s)}}} + \frac{\Delta H_{\text{trans ZrO}_2(\text{s})}}{T_{\text{trans ZrO}_2(\text{s})}} \quad \left(\begin{array}{l} \text{Zr(s)} \rightarrow \text{reactant} \\ \text{ZrO}_2(\text{s}) \rightarrow \text{product} \end{array} \right)$$

$$+ \int_{298}^{1136} \frac{C_{p, \text{ZrO}_2(\text{s})} - (C_{p, \text{Zr(s)}} + C_{p, \text{O}_2(\text{g})})}{T} dT$$

$$+ \int_{1136}^{1418} \frac{C_{p, \text{ZrO}_2(\text{s})} - (C_{p, \text{Zr(l)}} + C_{p, \text{O}_2(\text{g})})}{T} dT$$

$$+ \int_{1418}^{1600} \frac{C_{p, \text{ZrO}_2(\text{l})} - (C_{p, \text{Zr(l)}} + C_{p, \text{O}_2(\text{g})})}{T} dT$$

$$\Delta S_{298} = S_{298}^{\circ} \text{ZrO}_2 - (S_{298}^{\circ} \text{Zr} + S_{298}^{\circ} \text{O}_2)$$

$$= 50.4 - (39.0 + 205.1)$$

$$= -193.7 \text{ (J/K)}$$

$$- \frac{\Delta H_{\text{trans Zr(s)}}}{T_{\text{trans Zr(s)}}} + \frac{\Delta H_{\text{trans ZrO}_2(\text{s})}}{T_{\text{trans ZrO}_2(\text{s})}} = - \frac{3900}{1136} + \frac{5900}{1418}$$

$$= 0.559 \text{ J/K}$$

$$\bullet \int_{298}^{1136} \frac{C_{p_{ZrO_2(s)}} - (C_{p_{Zr(s)}} + C_{p_{O_2(g)}})}{T} dT$$

$$= \int_{298}^{1136} \frac{(69.62 - 21.97 - 29.96) + (7.53 - 11.63 - 4.18) \times 10^{-3} T + (-14.06 - 0 - (-1.67)) \times 10^5 \cdot T^{-2}}{T} dT$$

$$= 10.2377 \text{ (J/K)}$$

$$\bullet \int_{1136}^{1418} \frac{C_{p_{ZrO_2(s)}} - (C_{p_{Zr(l)}} + C_{p_{O_2(g)}})}{T} dT$$

$$\int_{1136}^{1418} \frac{(69.62 - 23.22 - 29.96) + (7.53 - 4.64 - 4.18) \times 10^{-3} T + (-14.06 - 0 - (-1.67)) \times 10^5 \cdot T^{-2}}{T} dT$$

$$= 3.68898 \text{ (J/K)}$$

$$\bullet \int_{1418}^{1600} \frac{C_{p_{ZrO_2(l)}} - (C_{p_{Zr(l)}} + C_{p_{O_2(g)}})}{T} dT$$

$$= \int_{1418}^{1600} \frac{(74.48 - 23.22 - 29.96) + (0 - 4.64 - 4.18) \times 10^{-3} T + (0 - 0 - (-1.67)) \times 10^5 \cdot T^{-2}}{T} dT$$

$$= 0.0118951 \text{ (J/K)}$$

$$\begin{aligned}
 \Delta S_{1600} &= \Delta S_{298} - \frac{\Delta H_{\text{trans Zr}(q)}}{T_{\text{trans Zr}(q)}} + \frac{\Delta H_{\text{trans ZrO}_2(q)}}{T_{\text{trans ZrO}_2(p)}} \\
 &+ \int_{298}^{1136} \frac{C_{p, \text{ZrO}_2(s)} - (C_{p, \text{Zr}(s)} + C_{p, \text{O}_2(g)})}{T} dT \\
 &+ \int_{1136}^{1418} \frac{C_{p, \text{ZrO}_2(s)} - (C_{p, \text{Zr}(p)} + C_{p, \text{O}_2(g)})}{T} dT \\
 &+ \int_{1418}^{1600} \frac{C_{p, \text{ZrO}_2(p)} - (C_{p, \text{Zr}(p)} + C_{p, \text{O}_2(g)})}{T} dT
 \end{aligned}$$

$$= -193.7 \text{ (J/K)} + 0.559 \text{ (J/K)}$$

$$+ 10.2377 \text{ (J/K)} + 3.68898 \text{ (J/K)}$$

$$+ 0.0118951 \text{ (J/K)}$$

$$= -178.6 \text{ (J/K)}$$

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?

$$\Delta H_{800} = 2 \times H_{800, \text{N}_2} + 3 \times H_{800, \text{SiO}_2} - H_{800, \text{Si}_3\text{N}_4} - 3H_{800, \text{O}_2}$$

$$\textcircled{1} H_{800, \text{N}_2} = \Delta H_{298}^{\circ} \text{N}_2 + \int_{298}^{800} 27.87 + 4.27 \times 10^{-3} T \, dT$$

$$= \int_{298}^{800} 27.87 + 4.27 \times 10^{-3} T \, dT = 15167.5 \text{ J}$$

$$\textcircled{2} H_{800, \text{SiO}_2} = \Delta H_{298}^{\circ} \text{SiO}_2 + \int_{298}^{800} 43.89 + 10^{-3} T - \frac{6.02}{T^2} \times 10^5 \, dT$$

$$= -910,900 + 21040.7 = -889859.3 \text{ J}$$

$$\textcircled{3} H_{800, \text{Si}_3\text{N}_4} = \Delta H_{298}^{\circ} \text{Si}_3\text{N}_4 + \int_{298}^{800} 170.54 + 93.74 \times 10^{-3} T \, dT$$

$$= -1144,800 + 62623.6 = -682176.4 \text{ J}$$

$$\textcircled{4} H_{800, \text{O}_2} = \Delta H_{298}^{\circ} \text{O}_2 + \int_{298}^{800} 29.96 + 4.18 \times 10^{-3} T - \frac{1.67 \times 10^5}{T^2} \, dT$$

$$= 15840.3$$

$$\therefore \Delta H_{800} = -2004587.4 \text{ (J)}$$

$$\Delta S_{800} = 2 \times S_{800, N_2} + 3 \times S_{800, O_2} - S_{800, N_2O_4} - 3 S_{800, O_2}$$

$$\begin{aligned} \textcircled{1} S_{800, N_2} &= S_{298, N_2}^\circ + \int_{298}^{800} \frac{27.87 + 4.27 \times 10^{-3} T}{T} dT \\ &= 191.5 + 29.6657 = 221.1657 \text{ (J/K)} \end{aligned}$$

$$\begin{aligned} \textcircled{2} S_{800, O_2} &= S_{298, O_2}^\circ + \int_{298}^{800} \frac{43.89 + 10^{-3} T - \frac{6.02}{T^2} \times 10^5}{T} dT \\ &= 41.5 + 40.925 = 82.425 \text{ (J/K)} \end{aligned}$$

$$\begin{aligned} \textcircled{3} S_{800, N_2O_4} &= S_{298, N_2O_4}^\circ + \int_{298}^{800} \frac{110.54 + 98.74 \times 10^{-3} T}{T} dT \\ &= 113.0 + 119.227 = 232.227 \end{aligned}$$

$$\begin{aligned} \textcircled{4} S_{800, O_2} &= S_{298, O_2}^\circ + \int_{298}^{800} \frac{29.96 + 4.18 \times 10^{-3} T - \frac{1.67 \times 10^5}{T^2}}{T} dT \\ &= 205.1 + 30.8746 = 235.9746 \end{aligned}$$

$$\therefore \Delta S_{800} = -250.544 \text{ (J/K)}$$

$$\begin{aligned} \frac{Z}{7} \Delta G_{800} &= \Delta H_{800} - T \Delta S_{800} \\ &= -2004587.4 - 800 \times (-250.544) \\ &= -1804152.2 \text{ J} \end{aligned}$$

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.

$$\text{Vacancy's } E_i = \Delta H_v$$

$$\text{자리가 차 있는 경우의 } E_i = 0$$

• 통계 열역학적 접근

$$\begin{aligned} \hookrightarrow Z &= \sum_i e^{-E_i/kT} \\ &= 1 + e^{-\Delta H_v/kT} \end{aligned}$$

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

(with vacancy partition)

• 고전 열역학적 접근

(N_A : 자리 차 있는 수)
 n_v : vacancy 수

$$N = N_A + n_v = \text{constant}$$

$$\hookrightarrow ds = k \ln \frac{(n_v + N_A)!}{n_v! N_A!}$$

$$= k \left((n_v + N_A) \ln (n_v + N_A) - n_v \ln n_v - N_A \ln N_A \right)$$

$$= k (n_v + N_A) \left\{ \ln (n_v + N_A) - \frac{n_v}{n_v + N_A} \ln n_v - \frac{N_A}{n_v + N_A} \ln N_A \right\}$$

$$= k (n_v + N_A) \left\{ \frac{n_v}{n_v + N_A} \ln \frac{n_v + N_A}{n_v} + \frac{N_A}{n_v + N_A} \ln \frac{n_v + N_A}{N_A} \right\}$$

$$F \equiv U - ST$$

$$\Delta F = dU - Tds - SdT$$

$$= dU - Tds \quad (dT=0)$$

$$= n_v \times \Delta H_v - TK(n_v + n_A) \left(\frac{n_v}{n_v + n_A} \ln \frac{n_v + n_A}{n_v} + \frac{n_A}{n_v + n_A} \ln \frac{n_v + n_A}{n_A} \right)$$

$$= n_v \times \Delta H_v - TK \left(n_v \ln \frac{N}{n_v} + n_A \ln \frac{N}{n_A} \right)$$

$$= n_v \Delta H_v - kT \left(n_v \ln N - n_v \ln n_v + (N - n_v) \ln N - (N - n_v) \ln (N - n_v) \right)$$

$$= n_v \Delta H_v - kT \left(-n_v \ln n_v + N \ln N - N \ln (N - n_v) + n_v \ln (N - n_v) \right)$$

$$\frac{\partial \Delta F}{\partial n_v} = \Delta H_v - kT \left(-\ln n_v - 1 + \frac{N}{N - n_v} + \ln (N - n_v) - \frac{n_v}{N - n_v} \right)$$

$$= \Delta H_v - kT \left(\ln \frac{N - n_v}{n_v} \right) = 0$$

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

$$\Rightarrow N - n_v = n_v e^{\frac{\Delta H_v}{kT}}$$

$$n_v = \frac{N}{1 + e^{\frac{\Delta H_v}{kT}}} \quad \therefore \frac{n_v}{N} = \frac{1}{1 + e^{\frac{\Delta H_v}{kT}}}$$