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.)

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

Substance	a	$b\times10^3$	$c\times10^{-5}$	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_2O_3	106.6	17.78	−28.53	298–2325(T_m)	
$Ba_{(\alpha)}$	−473.2	1587.0	128.2	298–648	
$Ba_{(\beta)}$	−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	$-17.38\times10^{-6}T^2$
$C_{(graphite)}$	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	
$Ca_{(\alpha)}$	25.37	−7.26	—	298–716	$23.72\times10^{-6}T^2$
$Ca_{(\beta)}$	−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_2O_3	119.37	9.30	−15.65	298–1800	
$Cu_{(s)}$	22.64	6.28	—	298–1356(T_m)	
$Fe_{(\alpha/\delta)}$	37.12	6.17	—	298–1183/1664–1809	
$Fe_{(\gamma)}$	24.47	8.45	—	1187–1664	
$Fe_{(l)}$	41.8	—	—	1809–1873	
$H_2O_{(g)}$	30.00	10.71	0.33	298–2500	
$O_{2(g)}$	29.96	4.18	−1.67	298–3000	
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	626.34	91.21	−200.83	298–1738(T_m)	
N_2	27.87	4.27	—	298–2500	
Si_3N_4	70.54	98.74	—	298–900	
$SiO_{2(\alpha\text{-quartz})}$	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	
$Zr_{(\alpha)}$	21.97	11.63	—	298–1136	
$Zr_{(\beta)}$	23.22	4.64	—	1136–2128	
$ZrO_{2(\alpha)}$	69.62	7.53	−14.06	298–1478	
$ZrO_{2(\beta)}$	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
Al_2O_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
$3CaO{\cdot}Al_2O_3{\cdot}3SiO_2$	−6,646,300	241.4
$CaO{\cdot}Al_2O_3{\cdot}SiO_2$	−3,293,200	144.8
$CaO{\cdot}Al_3O_3{\cdot}2SiO_2$	−4,223,700	202.5
$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$	−3,989,400	198.3
Cr_2O_3	−1,134,700	81.2
$H_2O_{(g)}$	−241,800	232.9
N_2	—	191.5
O_2	—	205.1
$SiO_{2,(\alpha\text{-quartz})}$	−910,900	41.5
Si_3N_4	−744,800	113.0
Ti	—	30.7
TiO	−543,000	34.7
Ti_2O_3	−1,521,000	77.2
Ti_3O_5	−2,459,000	129.4
TiO_2	−944,000	50.6
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
Ag	$s \rightarrow l$	11,090	1,234
Al	$s \rightarrow l$	10,700	934
Al_2O_3	$s \rightarrow l$	107,500	2,324
Au	$s \rightarrow l$	12,600	1,338
Ba	$\alpha \rightarrow \beta$	630	648
Ba	$\beta \rightarrow l$	7,650	1,003
Cu	$s \rightarrow l$	12,970	1,356
Ca	$\alpha \rightarrow \beta$	900	716
CaF_2	$s \rightarrow l$	31,200	1,691
Fe	$\alpha \rightarrow \gamma$	670	1,187
Fe	$\gamma \rightarrow \delta$	840	1,664
Fe	$\delta \rightarrow l$	13,770	1,809
H_2O	$s \rightarrow l$	6,008	273
$K_2O{\cdot}B_2O_3$	$s \rightarrow l$	62,800	1,220
MgF_3	$s \rightarrow l$	58,160	1,563
$Na_2O{\cdot}B_2O3$	$s \rightarrow l$	67,000	1,240
Pb	$s \rightarrow l$	4,810	600
PbO	$s \rightarrow l$	27,480	1,158
Si	$s \rightarrow l$	50,200	1,685
V	$s \rightarrow l$	22,840	2,193
Zr	$\alpha \rightarrow \beta$	3,900	1,136
ZrO_2	$\alpha \rightarrow \beta$	5,900	1,478

$$C_p = a + bT + cT^{-2}$$

$$\int C_p\,dT = aT + \frac{1}{2}bT^2 - cT^{-1} + K_1$$

$$\int \frac{C_p}{T}dT = a\ln T + bT - \frac{1}{2}cT^{-2} + K_2$$

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

1. $\Delta H_{ZrO_2(\beta),1600} = \Delta H^\circ_{ZrO_2} + \int_{298}^{1478} C_p(ZrO_{2(\alpha)})\,dT + \Delta H_{trans}(ZrO_2(\alpha\rightarrow\beta)) + \int_{1478}^{1600} C_p(ZrO_{2(\beta)})\,dT$

$= -1100800 + 69.62(1478-298) + \frac{1}{2}\cdot 7.53\times10^{-3}\left(1478^2-298^2\right) - 14.06\times10^5\left(1478^{-1}-298^{-1}\right) + 5900$

$+ 74.48(1600-1478) = -199538$ (J)

2. $\Delta H_{Zr(\beta),1600} = \Delta H^{\circ}_{Zr} + \int_{298}^{1136} C_p(Zr(\alpha))\,dT + \Delta H_{trans}(Zr(\alpha\to\beta)) + \int_{1136}^{1600} C_p(Zr(\beta))\,dT$

$= 21.97[1136-298) + \frac{1}{2}\cdot 11.63\times10^{-3}(1136^2-298^2) + 3900 + 23.22(1600-1136) + 4.64\times10^{-3}(1600^2-1136^2)$

$= 43018[J]$

3. $\Delta H_{O_2,1600} = \Delta H^{\circ}_{O_2} + \int_{298}^{1600} C_p(O_2)\,dT = 29.96(1600-298) + 4.18\times10^{-3}(1600^2-298^2) + (-1.67)\times10^{5}(1600^{-1}-298^{-1})$

$= 43011[J]$

$\therefore \Delta H_{1600} = -1086213J$

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

1. $\Delta S_{ZrO_2(\beta),1600} = \Delta S^{\circ}_{ZrO_2} + \int_{298}^{1478} C_p(ZrO_2(\alpha))/T\,dT + \Delta S_{trans}(ZrO_2(\alpha\to\beta)) + \int_{1478}^{1600} C_p(ZrO_2(\beta))/T\,dT$

$= 50.4 + 69.62\ln(1478/298) + 7.53\times10^{-3}(1478-298) - \frac{1}{2}\cdot 14.06\times10^{5}(1478^{-2}-298^{-2}) + 5900/1478$

$+ 74.48\ln(1600/1478) = 173.1[J/K\cdot mol]$

2. $\Delta S_{Zr(\beta),1600} = \Delta S^{\circ}_{Zr} + \int_{298}^{1136} C_p(Zr(\alpha))/T\,dT + \Delta S_{trans}(Zr(\alpha\to\beta)) + \int_{1136}^{1600} C_p(Zr(\beta))/T\,dT$

$= 39.0 + 21.97\ln(1136/298) + 11.63\times10^{-3}(1136-298) + 3900/1136 + 23.22\ln(1600/1136) + 4.64\times10^{-3}(1600-1136)$

$= 85.0[J/K\cdot mol]$

3. $\Delta S_{O_2,1600} = \Delta S^{\circ}_{O_2} + \int_{298}^{1600} C_p(O_2)/T\,dT = 200.1 + 29.96\ln(1600/298) + 4.18\times10^{-3}(1600-298) + \frac{1}{2}(-1.67)\times10^{5}(1600^{-2}-298^{-2})$

$= 160.0[J/K\cdot mol]$

$\therefore \Delta S_{1600} = -171.9\ J/K$

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?

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

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

$\Delta H_{SiO_2,800} = \Delta H^\circ_{SiO_2} + \int_{298}^{800} C_p(SiO_2)\,dT$

$= -910900 + 43.89(800-298) + \frac{1}{2}\cdot 1.00\times10^{-3}(800^2-298^2) + 6.02\times10^5\left(800^{-1}-298^{-1}\right)$

$= -889959\ (J)$

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

$= 27.87(800-298) + \frac{1}{2}\cdot 4.27\times10^{-3}(800^2-298^2)$

$= 15167.5\ (J)$

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

$= -744800 + 70.54(800-298) + \frac{1}{2}\cdot 98.74\times10^{-3}(800^2-298^2)$

$= -692170\ (J)$

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

$= 29.96(800-298) + \frac{1}{2}\cdot 4.18\times10^{-3}(800^2-298^2) + 1.67\times10^5(800^{-1}-298^{-1})$

$= 15840.3\ (J)$

$\therefore \Delta H_{800} = -200458\ J$

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

$\Delta S_{SiO_2,800} = \Delta S^\circ_{SiO_2} + \int_{298}^{800} C_p(SiO_2)/T\,dT$

$= 41.5 + 43.85\ln(800/298) + 1.00\times10^{-3}(800-298) + \frac{1}{2}\cdot 6.02\times10^5(800^{-2}-298^{-2})$

$= 82.4\ (J/K\cdot mol)$

$\Delta S_{N_2,800} = \Delta S^\circ_{N_2} + \int_{298}^{800} C_p(N_2)/T\,dT$

$= 191.5 + 27.87\ln(800/298) + 4.27\times10^{-3}(800-298)$

$= 221.16\ (J/K\cdot mol)$

$$\Delta S_{Si_3N_4,800} = \Delta S^\circ_{Si_3N_4} + \int_{298}^{800} C_p(Si_3N_4)/T\,dT$$

$$= (113.0 + 70.54 \ln(800/298) + 98.74\times10^{-3}(800-298)$$

$$= 232 \ (J/K\cdot mol)$$

$$\Delta S_{O_2,800} = \Delta S^\circ_{O_2} + \int_{298}^{800} C_p(O_2)/T\,dT$$

$$= 205.1 + 29.96 \ln(800/298) + 4.18\times10^{-3}(800-298) - \frac{1}{2}\cdot 1.67\times10^{5}\left(800^{-2}-298^{-2}\right)$$

$$= 230.2 \ (J/K\cdot mol)$$

$\therefore \Delta S_{800} = -250.2 \ J/K$

$\therefore \Delta G = -1.80\times10^{6} \ J$

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. 통계열역학적 접근

$$Z = \sum e^{-E_i/kT}$$

$$\therefore \frac{n}{N} = \sum e^{-\Delta H_v/kT} = \frac{e^{-\frac{\Delta H_v}{kT}}}{1 - e^{-\Delta H_v/kT}} = \frac{1}{1 + e^{\Delta H_v/kT}}$$

2. 고전열역학적 접근

$$F \equiv U - TS$$

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

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

$$\simeq k\{N \ln N - n \ln n - (N-n)\ln(N-n)\}$$

$$dF = dU - TdS \quad (\because dT = 0)$$

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

$$\frac{dF}{dn} = \Delta H_v - kT\{\ln n - 1 + \ln(N-n) + 1\}$$

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

$\frac{dF}{dn} = 0$ 일 때 equilibrium

$$\therefore \ln \frac{N-n}{n} = \frac{\Delta H_v}{kT}, \quad \frac{N}{n} - 1 = e^{\Delta H_v/kT}, \quad \frac{n}{N} = \frac{1}{1 + e^{\Delta H_v/kT}}$$