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.)

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

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

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

$$+5900 + \int_{1478}^{1600} 74.48\,dT$$

$$= -1100800 + 69.62(1478-298) + 3.765\times10^{-3}(1478^2-298^2) + 14.06\times10^{5}\left(\frac{1}{1478}-\frac{1}{298}\right)$$

$$+5900 + 74.48(1600-1478)$$

$$= -99.95\times10^{4}\ J$$

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

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

$$= 21.97(1136-298) + 5.815\times10^{-3}(1136^2-298^2) + 3900 + 23.22(1600-1136) + 2.32\times10^{-3}(1600^2-1136^2)$$

$$= 4.302\times10^{4}\ J$$

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

$$= 29.96(1600-298) + 2.09\times10^{-3}(1600^2-298^2) + 1.67\times10^{5}\left(\frac{1}{1600}-\frac{1}{298}\right)$$

$$= 4.396\times10^{4}\ J$$

$$\therefore \Delta H_{1600} = -99.95\times10^{4} - 4.302\times10^{4} - 4.396\times10^{4} = -1.086\times10^{6}\ J$$

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

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

$$= 50.4 + 69.62\ln\left(\frac{1478}{298}\right) + 7.53\times10^{-3}(1478-298) + 7.03\times10^{5}\left(\frac{1}{1478^2}-\frac{1}{298^2}\right)$$

$$+ \frac{5900}{1478} + 74.48\ln\left(\frac{1600}{1478}\right)$$

$$= 173.1\ J/K$$

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

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

$$= 91.7\ J/K$$

$$\Delta S_{1600,\,O_2} = \Delta S_{298,\,O_2} + \int_{298}^{1600} \frac{C_p}{T}\,dT$$

$$= 205.1 + 29.96\ln\left(\frac{1600}{298}\right) + 4.18\times10^{-3}(1600-298) + 0.835\times10^{5}\left(\frac{1}{1600^2}-\frac{1}{298^2}\right) = 260.0\ J/K$$

$$\therefore \Delta S_{1600} = 173.1 - 91.7 - 260.0 = -178.6\ J/K$$

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?

$\Delta H_{298} = 3\times(-910900) - (-744800) = -1987900$ J

$\Delta S_{298} = 3(41.5) + 2(191.5) - 113 - 3(205.1) = -220.8$ J/K

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

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

$= -1987900 + 26.99(800-298) - 49.87\times10^{-3}(800^2-298^2) + 13.05\times10^{5}\left(\frac{1}{800} - \frac{1}{298}\right)$

$= -2.005\times10^{6}$ J

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

$= -220.8 + 26.99\ln\left(\frac{800}{298}\right) - 99.74\times10^{-3}(800-298) + 6.525\times10^{5}\left(\frac{1}{800^2} - \frac{1}{298^2}\right)$

$= -250.5$ J/K

$\Rightarrow \Delta G_{800} = \Delta H - T\Delta S = -2005000 - 800\times(-250.5) = -1.805\times10^{6}$ J

If $\Delta C_p = 0$, $\Delta G_{800} = -1987900 - 800\times(-220.8) = -1.811\times10^{6}$ J

$\text{Error} = \left|\frac{(-1.811\times10^{6}) - (-1.805\times10^{6})}{(-1.805\times10^{6})}\right| = 0.003\ (0.3\%)$

$\therefore$ $\Delta G_{800} = -1.805\times10^{6}$ J

If $C_p = 0$, $\Delta G_{800} = -1.811\times10^{6}$ J

Error = 0.3%

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 고전열역학적 방식

Let $n = \#\,\text{vacancy}$, $N = \#\,\text{all atom}$

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

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

$$\Delta F = \Delta U - T\Delta S = n\cdot\Delta H_v - Tk\left((N-n)\ln\frac{N}{N-n} + n\ln\frac{N}{n}\right)$$

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

$$= \Delta H_v - Tk\left(\ln\frac{N-n}{n}\right) = 0 \text{ 일때 평형}$$

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

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

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

② 통계 열역학적 방식

$$\text{particle function},\ Z = \sum_j e^{-\varepsilon_j/kT} = \overset{\text{atom이 채워진자리}}{e^{-0/kT}} + \overset{\text{vacancy 자리}}{e^{-\Delta H_v/kT}} = 1+e^{-\Delta H_v/kT}$$

$$n = \frac{Ne^{-\Delta H_v/kT}}{Z}$$

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

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