1. (a) 진공 $\Rightarrow \Delta U = \Delta H = 0$

(∵ 진공에서 팽창해도 T 변화 없는데, $\Delta U$와 $\Delta H$ depends on $\Delta T$)

$n=1,\ V_2 = 2V_1$

$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = R\ln 2$

$\Delta F = \Delta U - T\Delta S - S\Delta T = -T\Delta S = -RT\ln 2$

$\Delta G = \Delta H - T\Delta S - S\Delta T = -T\Delta S = -RT\ln 2$

$\therefore \Delta U = 0, \Delta H = 0, \Delta S = R\ln 2, \Delta F = -RT\ln 2, \Delta G = -RT\ln 2$

(b) adiabatic $\Rightarrow q = 0$ , $n=1$ , $(P_1, T_1) \rightarrow (P_2, T_2)$

$\Delta U = q - W = -W = nC_V\Delta T = C_V(T_2 - T_1)$

$\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$\Delta S = \frac{q_{rev}}{T} = 0$

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

$= C_V(T_2 - T_1) - S(T_2 - T_1)$

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

$= C_p(T_2 - T_1) - S(T_2 - T_1)$

$\therefore \Delta U = C_V(T_2 - T_1),\ \Delta H = C_p(T_2 - T_1),\ \Delta S = 0,$

$\Delta F = (C_V - S)(T_2 - T_1),\ \Delta G = (C_p - S)(T_2 - T_1)$

$\Rightarrow$ absolute value of S is needed

(c) $\Delta P = 0$, $n=1$ , $(V_1, T_1) \rightarrow (V_2, T_2)$

$\Delta U = nC_V\Delta T = C_V(T_2 - T_1)$

$\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$\Delta S = C_p\ln\left(\frac{T_2}{T_1}\right)$ $\left(\because dS = \frac{C_p}{T}dT\right)$

$\Delta F = \Delta U - T\Delta S - S\Delta T = C_V(T_2 - T_1) - T_2\Delta S - S_1(T_2 - T_1)$

$\Delta G = \Delta H - T\Delta S - S\Delta T = C_p(T_2 - T_1) - T_2\Delta S - S_1(T_2 - T_1)$

$\therefore \Delta U = C_V(T_2 - T_1),\ \Delta H = C_p(T_2 - T_1),\ \Delta S = C_p\ln\left(\frac{T_2}{T_1}\right),$

$\Delta F = (C_V - S_1)(T_2 - T_1) - T_2\Delta S,\ \Delta G = (C_p - S_1)(T_2 - T_1) - T_2\Delta S$

$\Rightarrow$ absolute value of $S_1$ is needed

(d) $\Delta V = 0$, $n=1$ , $(P_1, T_1) \rightarrow (P_2, T_2)$

$\Delta U = nC_V\Delta T = C_V(T_2 - T_1)$

$\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$\Delta S = C_V\ln\left(\frac{T_2}{T_1}\right)$ $\left(\because dS = \frac{C_V}{T}dT\right)$

$\Delta F = \Delta U - T\Delta S - S\Delta T = C_V(T_2 - T_1) - T_2\Delta S - S_1(T_2 - T_1)$

$\Delta G = \Delta H - T\Delta S - S\Delta T = C_p(T_2 - T_1) - T_2\Delta S - S_1(T_2 - T_1)$

$\therefore \Delta U = C_V(T_2 - T_1),\ \Delta H = C_p(T_2 - T_1),\ \Delta S = C_V\ln\left(\frac{T_2}{T_1}\right)$

$\Delta F = (C_V - S_1)(T_2 - T_1) - T_2\Delta S,\ \Delta G = (C_p - S_1)(T_2 - T_1) - T_2\Delta S$

$\Rightarrow$ absolute value of $S_1$ is needed

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

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

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

$\Delta H^\circ_{298} = -910900\ J$

$\int_{298}^{800} C_p dT = \int_{298}^{800} (43.89 + 1.00\times10^{-3}T - 6.02\times10^{5}T^{-2})dT$

$= \left[43.89T + 0.500\times10^{-3}T^2 + 6.02\times10^{5}T^{-1}\right]_{298}^{800}$

$= 22308\ J$

$\therefore 3\Delta H_{800(SiO_2)} = 3\times(-910900J + 22308J) = -2665176\ J$

ii) $\Delta H_{800(N_2)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT$, $\Delta H^\circ_{298} = 0\ J$,

$\int_{298}^{800} C_p dT = \int_{298}^{800} (27.89 + 4.27\times10^{-3}T)dT$

$= \left[27.87T + \frac{4.27\times10^{-3}}{2}T^2\right]_{298}^{800} = 15167\ J$

$\therefore 2\Delta H_{800(N_2)} = 2\times[0 + 15167\ J] = 30334\ J$

iii) $\Delta H_{800(Si_3N_4)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT$, $\Delta H^\circ_{298} = -744800\ J$,

$\int_{298}^{800} C_p dT = \int_{298}^{800} (70.54 + 98.74\times10^{-3}T)dT$

$= \left[70.54T + \frac{98.74\times10^{-3}}{2}T^2\right]_{298}^{800} = 61636\ J$

$\therefore \Delta H_{800(Si_3N_4)} = -744800\ J + 61636\ J = -682176\ J$

iv) $\Delta H_{800(O_2)} = \Delta H^\circ_{298} + \int_{298}^{800} C_p dT$, $\Delta H^\circ_{298} = 0\ J$

$\int_{298}^{800} C_p dT = \int_{298}^{800} (29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2})dT$

$= \left[29.96T + \frac{4.18\times10^{-3}}{2}T^2 + 1.67\times10^{5}T^{-1}\right]_{298}^{800} = 16491\ J$

$\therefore 3\Delta H_{800(O_2)} = 49573\ J$

$\therefore \Delta H = -2665176\ J + 30334\ J + 682176\ J - 49573\ J = \underline{-2001839\ J}$

$\Delta S_{800} = 3\Delta S_{800(Si_3O_6)} + 2\Delta S_{800(N_2)} - \Delta S_{800(Si_3N_4)} - 3\Delta S_{800(O_2)}$

i) $\Delta S_{800(Si_3O_6)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT$, $\Delta S^\circ_{298} = 41.5\ J/k$

$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \left(\frac{43.89}{T} + 1.00\times10^{-2} - 6.02\times10^{-5}T^{-3}\right)dT = 43.84\ J$

$\therefore 3\Delta S_{800(Si_3O_6)} = 256.02\ J/k$

ii) $\Delta S_{800(N_2)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT$, $\Delta S^\circ_{298} = 191.5\ J/k$

$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \left(\frac{29.87}{T} + 4.27\times10^{-3}\right)dT = 29.69\ J/k$

$\therefore 2\Delta S_{800(N_2)} = 442.3\ J/k$

iii) $\Delta S_{800(Si_3N_4)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT$, $\Delta S^\circ_{298} = 113.0\ J/k$

$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \left(\frac{770.54}{T} + 98.77\times10^{-3}\right)dT = 119.2\ J/k$

$\therefore \Delta S_{800(Si_3N_4)} = 232.2\ J/k$

iv) $\Delta S_{800(O_2)} = \Delta S^\circ_{298} + \int_{298}^{800} \frac{C_p}{T} dT$, $\Delta S^\circ_{298} = 205.1\ J/k$

$\int_{298}^{800} \frac{C_p}{T} dT = \int_{298}^{800} \left(\frac{29.96}{T} + 4.18\times10^{-3} - 1.67\times10^{-5}T^{-3}\right)dT$

$= 31.68\ J/k$

$3\Delta S_{800(O_2)} = 770.3\ J/k$

$\therefore \Delta S_{800} = 256.02\ J/k + 442.3\ J/k - 232.2\ J/k - 770.3\ J/k$

$= -244.2\ J/k$

$\therefore \Delta G_1 = \Delta H - T\Delta S = -2001839\ J - 800K(-244.2\ J/k)$

$= -1806479\ J$

$\Delta C_p = 0$ 이라면, $\Delta H_{800} = \Delta H^\circ_{298}$, $\Delta S_{800} = \Delta S^\circ_{298}$

$\Rightarrow \Delta H = 3\Delta H^\circ_{298(Si_3O_6)} + 2\Delta H^\circ_{298(N_2)} - \Delta H^\circ_{298(Si_3N_4)} - 3\Delta H^\circ_{298(O_2)}$

$= -1989900\ J$

$\Delta S = 3\Delta S^\circ_{298(Si_3O_6)} + 2\Delta S^\circ_{298(N_2)} - \Delta S^\circ_{298(Si_3N_4)} - 3\Delta S^\circ_{298(O_2)}$

$= -220.8\ J/k$

$\Delta G_1 = \Delta H - T\Delta S = -1989900\ J - 800K(-220.8\ J/k) = -1811260\ J$

$error = \frac{1811260 - 1806479}{1806479} \times 100 = 0.265\ \%$

3.(1) $\Delta S_{sys} = \int_{590}^{600} \frac{C_{p(l)}}{T} dT + \frac{\Delta H_m}{T} + \int_{600}^{590} \frac{C_{p(s)}}{T} dT$

$= \int_{590}^{600} \left(\frac{32.4}{T} - 3.1\times10^{-3}\right)dT + \frac{-4810\ J/mole}{600K} + \int_{600}^{590} \left(\frac{23.6}{T} + 9.715\times10^{-3}\right)dT$

$= 32.4\ln\left(\frac{600}{590}\right) - 3.1\times10^{-2} - 8.02 + 23.6\ln\left(\frac{590}{600}\right) - 9.715\times10^{-2}$

$= -8.00\ J/$

$\Delta H = \int_{590}^{600} C_{p(l)} dT + \Delta H_m + \int_{600}^{590} C_{p(s)} dT$

$= \int_{590}^{600} (32.4 - 3.1\times10^{-3}T)dT - 4810 + \int_{600}^{590} (23.6 + 9.715\times10^{-3}T)dT$

$= 32.4\times10 - \frac{3.1\times10^{-3}}{2} \times (600^2 - 590^2) - 4810 + 23.6\times(-10)$

$+ \frac{9.715\times10^{-3}}{2}(590^2 - 600^2) = -4798\ J$

$\Delta S_{surrounding} = \frac{4798}{590} = 8.13\ (J/k)$

$\Delta S_{tot} = -8.00\ J/k + 8.13\ J/k = 0.13\ J/k > 0$

$\therefore$ 자발적

(2) $\Delta H = -4798\ J$, $\Delta S_{sys} = -8\ J/k$, $\Delta S_{tot} = 0.13\ J/k$

$\Delta G_{sys} = \Delta H - T\Delta S_{sys} = -4798 - 590(-8)$

$= -118\ J < 0$ $\therefore$ 자발적

(3) $\Delta S_{sys} = \int_{550}^{600} \frac{C_p}{T} dT + \frac{\Delta H}{T} + \int_{600}^{550} \frac{C_p}{T} dT$

$= 32.4\ln\left(\frac{600}{550}\right) - 3.1\times10^{-2} - 8.02 + 23.6\ln\left(\frac{550}{600}\right) - 9.715\times10^{-2}$

$= -11.38\ (J/k)$

$\Delta H = \int_{590}^{600} C_{p(l)} dT + \Delta H_m + \int_{600}^{590} C_{p(s)} dT$

$= 32.4\times10 - \frac{3.1\times10^{-3}}{2} \times (600^2 - 550^2) - 4810 + 23.6\times(-10)$

$+ \frac{9.715\times10^{-3}}{2}(550^2 - 600^2) = -4739\ J$

$\Delta S_{tot} = -11.38 + \frac{4739}{550} = 1.24\ (J/k)$

→ 590k일 때보다 550k일 때 $\Delta S_{tot}$이 더 크므로 더 자발적

(4) entropy criterion → system, surrounding을 모두 계산해서 자발성 판단.

Gibbs energy criterion → system만 고려

4. adiabatic → heat reservoir가 잠열을 모두 수용 불가, s→l로 상변화가 모두 이루어지지 않아 s/l 상이 평형을 이루며 공존