1.

(a)

$\Delta T = 0 \rightarrow \Delta U = \Delta H = 0.$

$\Delta S = R \ln \frac{V_2}{V_1} = R \ln 2 . \quad \Delta G = \Delta H - \Delta(TS) = -T\Delta S = -RT\ln 2, \quad \Delta F = \Delta U - \Delta(TS) = -T\Delta S = -RT\ln 2.$

(b)

$\Delta U = C_V \Delta T = C_V \cdot (T_2 - T_1), \quad \Delta H = C_p \Delta T = C_p (T_2 - T_1).$

$q = 0 \rightarrow \Delta S = 0.$

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

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

) ⇒ need absolute value of the entropy.

(c)

$\Delta U = C_V \Delta T = C_V \cdot (T_2 - T_1), \quad \Delta H = C_p \Delta T = C_p (T_2 - T_1).$

$\Delta S = \int \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1},$

$\Delta F = \Delta U - T\Delta S - S\Delta T = (C_V - S)(T_2 - T_1) - T_2 C_p \ln \frac{T_2}{T_1}$

$\Delta G = \Delta H - T\Delta S - S\Delta T = (C_p - S)(T_2 - T_1) - T_2 C_p \ln \frac{T_2}{T_1}$

(d)

$\Delta U = C_V \Delta T = C_V \cdot (T_2 - T_1), \quad \Delta H = C_p \Delta T = C_p (T_2 - T_1).$

$\Delta S = \int \frac{C_V}{T} dT = C_V \ln \frac{T_2}{T_1},$

$\Delta F = \Delta U - T\Delta S - S\Delta T = (C_V - S)(T_2 - T_1) - T_2 C_V \ln \frac{T_2}{T_1}$

$\Delta G = \Delta H - T\Delta S - S\Delta T = (C_p - S)(T_2 - T_1) - T_2 C_V \ln \frac{T_2}{T_1}$

2.

$Si_3N_4 + 3O_2 \longrightarrow 3\,SiO_2(\alpha) + 2N_2$

$\Delta H^\circ_{298} = 3\Delta H^\circ_{SiO_2} + 2\Delta H^\circ_{N_2} - \Delta H^\circ_{Si_3N_4} - 3\Delta H^\circ_{O_2}$ 표준상태 엔탈피

$= 3\Delta H^\circ_{SiO_2} - \Delta H^\circ_{Si_3N_4}$

$= 3 \times -910.9 - -744.8 = -1988$ kJ/mol.

$\Delta S^\circ_{298} = 3\Delta S^\circ_{SiO_2} + 2\Delta S^\circ_{N_2} - \Delta S^\circ_{Si_3N_4} - 3\Delta S^\circ_{O_2}$

$= 3 \times 41.5 + 2 \times 191.1 - 113 - 3 \times 205 \simeq -220.8$ (J/mol·K)

$\Delta C_p = \sum n C_p = 3C_p(SiO_2) + 2C_p(N_2) - C_p(Si_3N_4) - 3C_p(O_2)$

$\simeq 26.99 + 99.74 \times 10^{-3}\,T - 13.05 \times 10^{5}\,T^{-2}$ (J/mol·K)

$\Delta H^\circ(800K) = \Delta H^\circ_{298} + \int_{298}^{800} \Delta C_p \cdot dT$

$= -1988 \times 10^3 + \int_{298}^{800} 26.99 + 99.74 \times 10^{-3}\,T - 13.05 \times 10^{5}\,T^{-2}\,dT$ $\quad T^{-1}$

$= -1988 \times 10^3 + 26.99 \cdot (502) + \frac{99.74}{2} \times 10^{-3}(800^2 - 298^2) + 13.05 \times 10^5 \left(\frac{1}{800} - \frac{1}{298}\right)$

$= -2005 \times 10^3$ (J)

$$\Delta S^0(800K) = \Delta S^0(298K) + \int_{298}^{800} \frac{\Delta C_p}{T}\, dT$$

T^{-4}

$$= -220.8 + \int_{298}^{800} \left(\frac{26.99}{T} + 99.74\times10^{-3} - 13.05\times10^5 T^{-3} \right) dT$$

$$= -220.8 + 26.99 \ln\frac{800}{298} + 99.74\times10^{-3}(800-298) + \frac{13.05\times10^5}{2}\left(\frac{1}{800^2} - \frac{1}{298^2}\right)$$

$$= -250 \ (J/K).$$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ 이므로

$$= -2005\times10^3 - 800\cdot -250 = -1805\times10^3 \ (J/mol)$$

$C_p = 0$ 일때 $\Delta S'^0 = -220.8$ 이다.

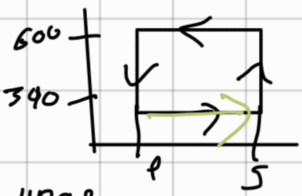
$$\Delta G'^0 = \Delta H^0 - T\Delta S'^0$$

$$= -2005\times10^3 - 800\cdot(-220.8) = -1828\times10^3 \ (J/mol)$$

$$\text{error}(\%) = \frac{\Delta G'^0 - \Delta G^0}{\Delta G^0} = \frac{-1828 + 1805}{-1828} = 0.013(\%)$$

3.

1) $\Delta H^{l\to s}(590K) = -\Delta H_m(600K) + \int_{600}^{590} C_p(s) - C_p(l)\, dT.$



$= -4810 + \int_{600}^{590} -8.8 + 12.85\times10^{-3}\, T\, dT$

$= -4810 + (-8.8 \times -10) + \frac{12.85\times10^{-3}}{2}(590^2 - 600^2) = -4798$

$\Delta S^{l\to s}(590K) = \int_{600}^{590} \frac{C_p(s) - C_p(l)}{T}\, dT + \frac{\Delta H^{l\to s}}{T}$

$\simeq \int_{600}^{590} \left(12.85\times10^{-3} - \frac{8.8}{T}\right) dT - \frac{4810}{600}$

$= 12.85\times10^{-3} \cdot -10 - 8.8 \ln\frac{59}{60} - 8.01$

$\simeq -8.00.$

이때 부피변화, 압력변화가 없으니까 ΔH가 열의 양과 같다고 볼수 있다.

$\Delta S_{외부}^{l\to s}(590K) = \frac{q}{T} = \frac{-\Delta H^{l\to s}(590K)}{T} = \frac{4798}{590} = 8.13\ (J)$

$\Delta S_{tot} = 0.13 > 0$ 로 자발적인 반응.

2)

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

$\Delta G^{l\to s}(590K) = \Delta H^{l\to s} - T\Delta S^{l\to s}$ at 590K.

$= -4798 + 8.00 \times 590 = -78 < 0$

$\Delta G > 0$ 으로 자발적 반응.

3)

$\Delta H^{l\to s}(550K) = -\Delta H_m(600K) + \int_{600}^{550} C_p(s) - C_p(l)\, dT$

$= -4810 + \int_{600}^{550} -8.8 + 12.85\times10^{-3}\, T\, dT$

$= -4810 + -8.8 \times -50 + \frac{12.85}{2}\times10^{-3}(550^2 - 600^2)$

$= -4739\ (J)$

$\Delta S^{l\to s}(550K) = \int_{600}^{550} \frac{C_p(s) - C_p(l)}{T}\, dT + \frac{\Delta H^{l\to s}(600K)}{T}$

$= \int_{600}^{550} \left(12.85\times10^{-3} - \frac{8.8}{T}\right) dT - \frac{4810}{600}$

$= 12.85\times10^{-3} \times -50 - 8.8 \ln\frac{55}{60} - 8.01$

$= -7.89\ (J)$

$\Delta S_{sur}^{l\to s}(550K) = \frac{+4739}{350} = 8.61\ (J)$

$\Delta S_{tot} = 0.73\ (J)$

$\Delta S_{tot}(550K) > \Delta S_{tot}(590K)$

즉 550k에서 더 irreversible 한 반응이 일어난다.

4)

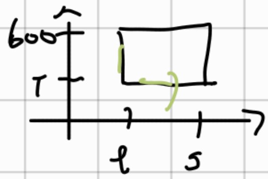
 ← ΔG 로 ΔG가 최솟값을 가지는 지점에서 평형이 일어난다.

ΔS는 ΔS를 통해서 과정이 가역적, 비가역적, 임을 알 수 있고

4.

단열된 용기에 있으면 $\Delta H^{l \to s}$로 발생한 열이 계 안에 존재한다.

따라서. 평형상태에서 liquid와 solid가 공존할 수 있다. 이때 l의 몰분율은 x라 두고.



상태방정식 ΔH 값을 이용해 비율을 구할 수 있다.