1. (a) 자유팽창 $\Delta T = w = 0 \rightarrow \Delta U = 0,\ \Delta H = 0$

등온 과정이라 생각하고 ΔS 구하기

$$\Delta S = \frac{\Delta q}{T} = \frac{\Delta w}{T} = \frac{\int p\,dV}{T} = \frac{nRT\ln\frac{V_2}{V_1}}{T} = R\ln 2$$ → 상태함수이므로 자유팽창의 $\Delta S = R\ln 2$

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

(b) 가역 단열 팽창 $q = 0$.

$\Delta U = nC_v\Delta T = C_v(T_2 - T_1)$, $\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$\Delta S = \int \frac{1}{T}\,dq_{rev} = 0$ $(\because q = 0)$

$G = H - TS \rightarrow dG = dH - TdS - SdT = dH - SdT$

$$\Delta G = \Delta H - S\int_{T_1}^{T_2} dT = \Delta H - S(T_2 - T_1) = C_p(T_2 - T_1) - S(T_2 - T_1) = (C_p - S)(T_2 - T_1)$$

$F = U - TS \rightarrow dF = dU - TdS - SdT = dU - SdT$

$$\Delta F = \Delta U - S(T_2 - T_1) = C_v(T_2 - T_1) - S(T_2 - T_1) = (C_v - S)(T_2 - T_1)$$

$\therefore$ ΔG, ΔF를 구하기 위해 S 값을 알아야 한다

(c) 등압 팽창. $\Delta P = 0$

$\Delta U = nC_v\Delta T = C_v(T_2 - T_1)$, $\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$$\Delta S = \int \frac{1}{T}\,dq_{rev} = \int \frac{1}{T}(C_v\,dT + P\,dV) = C_v\ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} = (C_v + R)\ln\frac{T_2}{T_1} = C_p\ln\frac{T_2}{T_1}$$

$P_1 = P_2$ $\therefore \frac{T_2}{T_1} = \frac{V_2}{V_1}$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2S_2 - T_1S_1) = \Delta H - (T_2(S_1 + \Delta S) - T_1S_1)$$
$$= \Delta H - S(T_2 - T_1) - T_2\Delta S$$
$$= (C_p - S_1)(T_2 - T_1) - C_p \cdot T_2 \cdot \ln\frac{T_2}{T_1}$$

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - S_1(T_2 - T_1) - T_2\Delta S = (C_v - S_1)(T_2 - T_1) - C_pT_2\ln\frac{T_2}{T_1}$$

$\therefore$ ΔG, ΔF를 구하기 위해 S 값을 알아야한다.

(d) 등적 과정 $\Delta V = 0$

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

$$\Delta S = \int \frac{\delta q_{rev}}{T} = \int \frac{\delta q_v}{T} = \int_{T_1}^{T_2} \frac{1}{T} C_v\,dT = C_v\ln\frac{T_2}{T_1}$$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2S_2 - T_1S_1) = \Delta H - (T_2(S_1 + \Delta S) - T_1S_1)$$
$$= \Delta H - S_1(T_2 - T_1) - T_2\Delta S = (C_p - S_1)(T_2 - T_1) - C_v \cdot T_2\ln\frac{T_2}{T_1}$$

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - S_1(T_2 - T_1) - T_2 \cdot \Delta S = (C_v - S_1)(T_2 - T_1) - C_v \cdot T_2\ln\frac{T_2}{T_1}$$

$\therefore$ ΔG, ΔF를 구하기 위해 S 값을 알아야 한다

2. $\Delta H^\circ_{298} = 3\Delta H^\circ_{SiO_2} - \Delta H'_{Si_3N_4} = -198790$ J/mol

$\Delta S^\circ_{298} = 3S^\circ_{SiO_2} + 2S^\circ_{N_2} - (S^\circ_{Si_3N_4} + 3S^\circ_{O_2}) = -220.8$ J/mol·K

$\Delta C_p = 3C_{p,SiO_2} + 2C_{p,N_2} - (C_{p,Si_3N_4} + 3C_{p,O_2}) = 26.991 - 99.14\times10^{-3}T - 13.05\times10^5 T^{-2}$

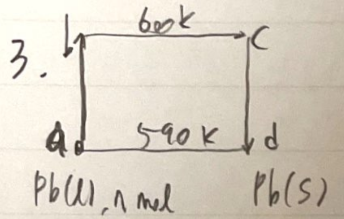
$$\Delta G_{800} = \Delta H^\circ_{298} - 800\,\Delta S^\circ_{298} + \int_{298}^{800} \Delta C_p\, dT - 800\cdot\int_{298}^{800} \frac{\Delta C_p}{T}\, dT$$

$$= -1.804\times10^6\ \text{J}$$

if $\Delta C_p = 0$, $\Delta G'_{800} = -1.811\times10^6$ J

$\therefore$ 오차 $= \dfrac{\Delta G_{800} - \Delta G'_{800}}{\Delta G_{800}} = 0.4\%$

3.



(1) $\Delta S_{(a\to d)} = \Delta S_{(a\to b)} + \Delta S_{(b\to c)} + \Delta S_{(c\to d)}$ ($\because$ ΔS은 상태함수)

$$= \int_{590}^{600} \frac{nC_p(l)}{T}\,dT + \frac{q}{T} + \int_{600}^{590} \frac{nC_p(s)}{T}\,dT = -7.997n\ \text{J/K}$$

$$\Delta S_{surr} = \frac{q}{T} = \frac{-\Delta H_{(a\to d)}}{T} = -\frac{1}{T}\left(\Delta H_{(a\to b)} + \Delta H_{(b\to c)} + \Delta H_{(c\to d)}\right)$$

$$= -\frac{1}{T}\left(\int_{590}^{600} nC_p(l)\,dT + (-\Delta H_{melting})\times n + \int_{600}^{590} nC_p(s)\cdot dT\right) = 8.132n\ \text{J/K}$$

$\therefore \Delta S_{irr} = \Delta S_{(a\to d)} + \Delta S_{surr} = 0.316n$ J/K > 0 → 자발적.

(2) $\Delta G = \Delta H_{(a\to d)} - T\Delta S_{(a\to d)}$

$= -4798n - 590\cdot(-7.997\cdot n) = -79.77n$ J < 0 → 자발적

(3) 550K에서 $\Delta S'_{(a\to d)}$ 와 $\Delta S'_{surr}$ 를 구하고

$\Delta S'_{(a\to d)} = \Delta S'_{(a\to b)} + \Delta S'_{(b\to c)} + \Delta S'_{(c\to d)}$

$$= \int_{550}^{600} \frac{nC_p(l)}{T}\,dT + \frac{q}{T} + \int_{600}^{550} \frac{nC_p(s)}{T}\cdot dT = -7.894n\ \text{J/K}$$

$$\Delta S'_{surr} = -\frac{1}{T}\left(\Delta H'_{(a\to b)} + \Delta H'_{(b\to c)} + \Delta H'_{(c\to d)}\right)$$

$$= -\frac{1}{T}\left(\int_{550}^{600} nC_p(l)\,dT + (-\Delta H_{melting})\cdot n + \int_{600}^{550} n\cdot C_p(s)\,dT\right) = 8.616n\ \text{J/K}$$

$\therefore \Delta S'_{irr} = \Delta S'_{(a\to d)} + \Delta S_{surr} = 0.722n$ J/K　$\Delta S'_{irr} > \Delta S_{irr}$ 이므로 more irreversible

(4) Entropy Criterion은 계 만이 아닌 우주 전체의 엔트로피 변화계산을 통해 자발성을 확인할 수 있다. Gibbs Energy Criterion은 계의 엔탈피 변화와 엔트로피 변화로 자발성을 확인할 수 있다.

4. 3개의 과냉된 철분이 자발적인 과정을 응고가 일어나고 이때 일어나는 발열로 인해 액상은 함께 존재하는 것이다. 정확한 비율을 구해보면

→ n몰 중 x몰이 응고

$$\Delta H_{(a\to c)} = \Delta H_{(a\to b)} + \Delta H_{(b\to c)} = 0 \quad (\because q=0)$$

$$= \int_{500}^{600} nC_p(l)\,dT - 4810\times n\times x = 306n - 4810nx = 0$$

$$\therefore x = 0.064$$