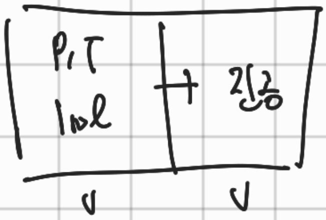
1.

(a)

부피 2배가 되는 자유팽창.



$w=0$, $\Delta U=0$, $\Delta H=0$

ΔS는 등온팽창 과정의 ΔS와 같은 값을 가짐.

$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = 1\times R\ln\times\left(\frac{2V}{V}\right) = R\ln 2$

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

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

(b) reversible 단열 팽창 $(P_1, T_1 \to P_2, T_2)$ $q=0$

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

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

$\Delta S = \int \frac{dq_{rev}}{T} = 0.$ → 처음과 나중 같아 엔트로피 변화 0

$\Delta S = S - S = 0.$

$$dG = dH - d(TS) = dH - SdT + T\cancel{dS} = 0.$$

$$= dH - SdT$$

$$\Delta G = \int dH - \int S dT$$

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

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

$$dF = dU - d(TS) = dU - SdT + T\cancel{dS} = 0.$$

$$= dU - SdT$$

$$\Delta F = \int dU - \int S dT$$

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

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

(c) 등압 팽창 ($V_1, T_1 \to V_2, T_2$)

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

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

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_p}{T} dT = C_p \ln\left(\frac{T_2}{T_1}\right)$$

$$S(T) = S(T_0) + C_p \ln \frac{T}{T_0}$$

$$dG = V\,dP^{0} - S\,dT = -S\,dT$$

$$\Delta G = \int dG = -\int_{T_1}^{T_2} S\,dT = -\int_{T_1}^{T_2} \left(S(T_0) + C_p \ln \frac{T}{T_0} \right) dT,$$

$$= -\int_{T_1}^{T_2} \left(S(T_0) + C_p \ln T - C_p \ln T_0 \right) dT$$

$$= -\Big(S(T_0)(T_2 - T_1) - C_p \ln T_0 \,(T_2 - T_1)$$

$$+ C_p \ln\left(\frac{T_2}{T_1}\right) \Big)$$

$$= -\left((T_2 - T_1)\big(\underbrace{S(T_0)}_{\text{absolute entropy needed}} - C_p \ln T_0 \big) + C_p \ln \frac{T_2}{T_1} \right),$$

또는

$$\Delta G = \Delta H - \Delta(TS)$$

$$= \Delta H - T_2 S_2 + T_1 S_1 = \Delta H - T_2\left(S_1 + C_p \ln\left(\frac{T_2}{T_1}\right) \right) + T_1 S_1$$

$$= \Delta H - S_1 (T_2 - T_1) - T_2 C_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta F = \Delta U - \Delta(TS)$$

$$= \Delta U - T_2 S_2 + T_1 S_1 = \Delta U - T_2\left(S_1 + C_p \ln\left(\frac{T_2}{T_1}\right) \right) + T_1 S_1$$

$$= \Delta U - S_1 (T_2 - T_1) - T_2 C_p \ln\left(\frac{T_2}{T_1}\right)$$

absolute entropy needed

(d) 등적과정

$$\Delta U = n C_v \Delta T = C_v (T_2 - T_1)$$

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

$$\Delta S = \int_{T_2}^{T_1} \frac{n C_v}{T} dT = C_v \ln \left(\frac{T_1}{T_2} \right)$$

$$\Delta G = \Delta H - \Delta (TS)$$

$$= \Delta H - T_2 S_2 + T_1 S_1 = \Delta H - T_2 \left(S_1 + C_v \ln \left(\frac{T_2}{T_1} \right) \right) + T_1 S_1$$

$$= \Delta H - S_1 (T_2 - T_1) - T_2 C_v \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta F = \Delta U - \Delta (TS)$$

$$= \Delta U - T_2 S_2 + T_1 S_1 = \Delta U - T_2 \left(S_1 + C_v \ln \left(\frac{T_2}{T_1} \right) \right) + T_1 S_1$$

$$= \Delta U - S_1 (T_2 - T_1) - T_2 C_v \ln \left(\frac{T_2}{T_1} \right)$$

absolute entropy needed

2. $\Delta G^\circ_{T800} = \Delta H^\circ_{298} - 800K\, \Delta S^\circ_{298}$

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

$\Delta H^\circ_{298} = 3\,\Delta H^\circ_{SiO_2} - \Delta H_{Si_3N_4} = -1987900\ J/mol.$

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

$= -220.8\ J/mol \cdot K$

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

$= 26.99 - 99.74 \times 10^{-3}\,T - 13.05 \times 10^{5}\,\frac{1}{T^2}$

대입하면

$\Delta G^\circ_{T800} = -1987900\ J/mol - 800K \cdot (-220.8\ J/mol \cdot K)$

$- 16687\ J + 800 \times 29.7445\ J$

$= -1.804 \times 10^{6}\ J$

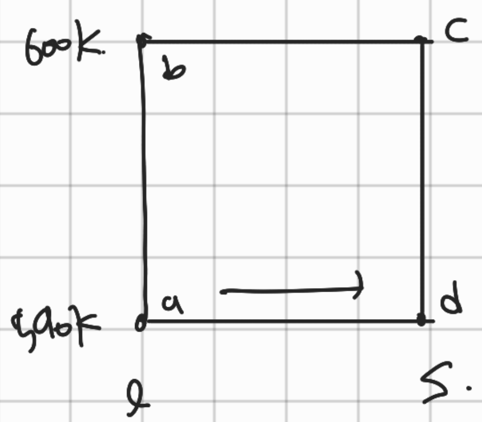
C_p 가 없다면 $\quad \Delta H^\circ_{298} = \Delta H^\circ_{800}$

$\Delta S^\circ_{298} = \Delta S^\circ_{800}$

$$\Delta G^\circ_{800} = \Delta H^\circ_{800} - 800\,\Delta S^\circ_{800} = -1.811 \times 10^{6}\ \mathrm{J}$$

$$\text{error} = \frac{\Delta G^\circ_{800} - \Delta G^{\circ\prime}_{800}}{\Delta G^\circ_{800}} = \text{약 } 0.3\%.$$

3.



Sn : 1몰로 가정

과냉된 액상 Pb가 응고하는 과정 A→D.

$$\Delta S(a\to d) = \Delta S(a\to b) + \Delta S(b\to c) + \Delta S(c\to d).$$

(1)

$$\Delta S = \Delta S_{sys} + \Delta S_{sur}$$

$$\Delta S_{sys} = \Delta S(a\to d) = \Delta S(a\to b) + \Delta S(b\to c) + \Delta S(c\to d$$

$$\Delta S(a\to b) = \int_{590}^{600} \frac{C_{p(l)}}{T}\,dT = \int_{590}^{600} \frac{32.4}{T} - 3.1\times10^{-3}\ dT$$

$$= 32.4 \ln\frac{600}{590} - 3.1\times10^{-3}(600-590) = 0.514\ \mathrm{J/K}$$

$$\Delta S(b\to c) = \frac{-\Delta H_{melt}}{T} = \frac{-4810J}{600K} = -8.017\ J/K$$

$$\Delta S(c\to d) = \int_{600}^{590} \frac{C_p(s)}{T}\,dT = \int_{600}^{590} \frac{22.6}{T} + 9.75\times10^{-3}\,dT$$

$$= 22.6 \ln\frac{600}{590} + 9.75\times10^{-3}(590-600) = -0.444\ J/k$$

$$\Delta S(a\to d) = -7.997$$

$$\Delta S_{surr} = \Delta S_{sur}(a\to d) = -\frac{\Delta H(a\to d)}{T} = -\frac{\Delta H(a\to d)}{590}$$

$$\Delta H(a\to d) = \Delta H(a\to b) + \Delta H(b\to c) + \Delta H(c\to d).$$

$$\Delta H(a\to b) = \int_{590}^{600} C_p(l)\,dT = \int_{590}^{600} 32.4 - 3.1\times10^{-3}T\,dT$$

$$= 32.4(600-590) - \frac{3.1\times10^{-3}}{2}\times(600^2-590^2) = 306\ J$$

$$\Delta H(b\to c) = -\Delta H_m = -4810J$$

$$\Delta H(c\to d) = \int_{600}^{590} C_p(s)\,dT = \int_{600}^{590} 23.6 + 9.75\times10^{-3}T\,dT$$

$$= 23.6(590-600) + \frac{9.75\times10^{-3}}{2}(590^2-600^2) = -294J$$

$$\Delta H(a\to d) = -4798\ J$$

$$\Delta S_{surr} = \frac{4798\,J}{590\,K} = 8.312\ J/K.$$

$$\Delta S = \Delta S_{sys} + \Delta S_{surr} = -7.99 + 8.312 = 0.315\ J/K > 0.$$

↳ 자발적

(2) $\Delta G = \Delta H - T\Delta S$

$$= \Delta H(a \to d) - 590\,(\Delta S(a \to d))$$

$$= -4798 - 590(-7.997) = -79.77 < 0$$

↳ 자발적

(3) (1)과 같은 방식으로 온도만 550K로 바꾸어서 풀면

$$\Delta S = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{sys} = \Delta S(a \to d) = \Delta S(a \to b) + \Delta S(b \to c) + \Delta S(c \to d$$

$$\Delta S(a \to b) = \int_{550}^{600} \frac{C_p(l)}{T}\,dT = \int_{550}^{600} \frac{32.4}{T} - 3.1\times10^{-3}\,dT$$

$$= 32.4 \ln\frac{600}{550} - 3.1\times10^{-3}(600 - 550) = 2.664\ J/K$$

$$\Delta S(b\to c) = \frac{-\Delta H_{melt}}{T} = \frac{-4810J}{600K} = -8.017\ J/K$$

$$\Delta S(c\to d) = \int_{600}^{550} \frac{C_p(s)}{T}\, dT = \int_{600}^{550} \frac{23.6}{T} + 9.75\times10^{-3}\ dT$$

$$= 23.6 \ln\frac{600}{550} + 9.75\times10^{-3}(550-600) = -2.514\ J/K$$

$$\Delta S(a\to d) = -7.994\ J/K$$

$$\Delta S_{sur} = \Delta S_{sur}(a\to d) = -\frac{\Delta H(a\to d)}{T} = -\frac{\Delta H(a\to d)}{590}$$

$$\Delta H(a\to d) = \Delta H(a\to b) + \Delta H(b\to c) + \Delta H(c\to d).$$

$$\Delta H(a\to b) = \int_{550}^{600} C_p(l)\, dT = \int_{550}^{600} 32.4 - 3.1\times10^{-3}\, T\ dT$$

$$= 32.4(600-550) - \frac{3.1\times10^{-3}}{2}\times(600^2 - 550^2) = 1531\ J$$

$$\Delta H(b\to c) = -\Delta H_m = -4810J$$

$$\Delta H(c\to d) = \int_{600}^{550} C_p(s)\, dT = \int_{600}^{550} 23.6 + 9.75\times10^{-3}\, T\ dT$$

$$= 23.6(550-600) + \frac{9.75\times10^{-3}}{2}(550^2 - 600^2) = -1460J$$

$$\Delta H(a\to d) = -4739\ J$$

$$\Delta S_{sur} = \frac{4739\,J}{550\,K} = 8.616\ J/K.$$

$$\Delta S = \Delta S_{sys} + \Delta S_{sur} = 0.722$$

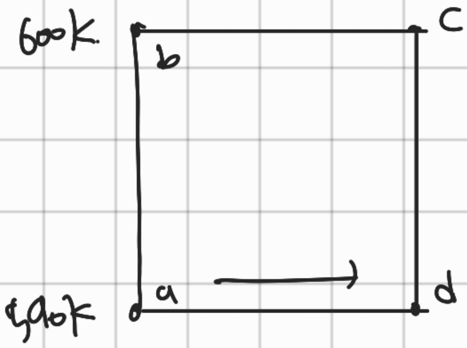
$$\Delta S\ (550K) > \Delta S\ (590K)$$

↳ 550K에서 더욱 irreversible

(4) Entropy criterion은 $\Delta S_{sys} + \Delta S_{sur}$ 을 통해 $\Delta S_{우주}$ 를 구하여 반응의 가역성을 확인하였다.

반면에 Gibbs energy criterion은 system의 값인 ΔH, ΔS, T 의 값으로 반응의 가역성을 확인하였다.

4. 단열용기에 보관되어 있는다면 일정한 양은 자발적으로 응고하기만 응고되기 위한 액상이 존재할 것이며 이를 사이의 평형이 이루어질 것이다.



Sn : 1몰로 가정

자발적으로 고상으로 변화하고 한다.

1 mol of l → (1-x) mol of l.

0 mol of S → x mol of S

$$\Delta H(a\to c) = \Delta H_c - \Delta H_a = 0 \quad (\text{단열})$$

$$\Delta H(a\to c) = \Delta H(a\to b) + \Delta H(b\to c) = 0$$

$$\Delta H(a\to b) = \int_{590}^{600} C_p(l)\,dT = \int_{590}^{600} 32.4 - 3.1\times10^{-3}\,T$$

$$= 306\text{J}$$

$$\Delta H(b\to c) = -\Delta H_m \cdot x = -4810x \cdot J$$

$$306 - 4810x = 0$$

$$x = 0.064$$

0.064의 분율만큼만 응고 되고 나머지는 액상으로 존재하며 평형을 이룬다.