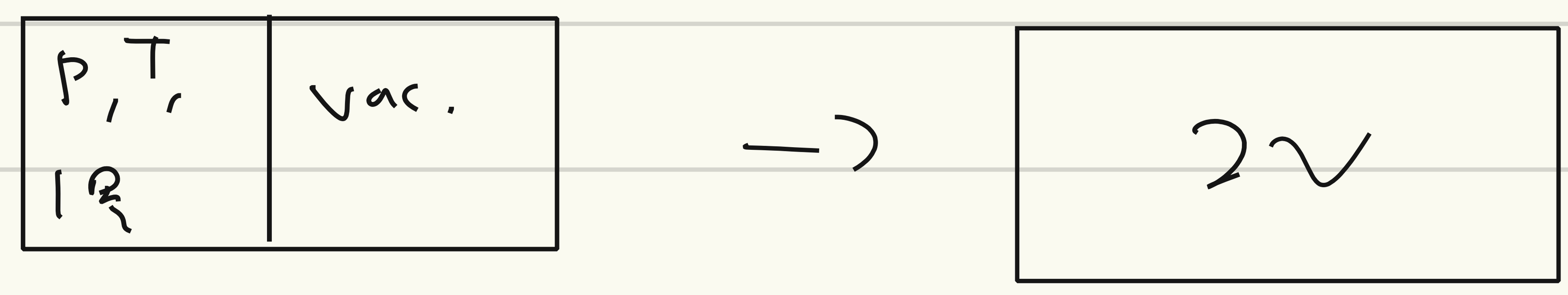
1. Determine the values of ΔU, ΔH, ΔS, ΔF and ΔG for the following processes. [In (b), (c), (d), show that the absolute value of the entropy is required.]

(a) One mole of ideal gas at the pressure P and temperature T expands into a vacuum to double its volume.
(b) The reversible adiabatic expansion of 1 mole of an ideal gas from P_1, T_1 to P_2, T_2.
(c) A constant-pressure expansion of 1 mole of an ideal gas from V_1, T_1 to V_2, T_2.
(d) A constant-volume change of state of 1 mole of an ideal gas from P_1, T_1 to P_2, T_2.

(a)



$\Delta U = 0$, $\Delta H = 0$. $\Delta U = q - w$

$\rightarrow$ $w = \int p\,dV = nRT \ln 2 = q$

$\Delta S = \dfrac{q_{rev}}{T} = \dfrac{nRT\ln 2}{T} = nR \ln 2 = R \ln 2.$

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

$\Delta F = \Delta U - \Delta S T = 0 - RT \ln 2 = -RT\ln 2.$

(b) $q = 0$, $P \rightarrow P'$, $T \rightarrow T'$, $n = 1$.

$\Delta U = n C_v \Delta T$, $\Delta H = n C_p \Delta T$.

$q = 0 \rightarrow \Delta S = \int \frac{dq}{T} = 0$

$dG = dH - T\,\overset{0}{dS} - S\,dT$

$\rightarrow \Delta G = \int dG = \Delta H - S\int dT$
$= \Delta H - S\Delta T$
$= \Delta T\,(C_p - S) = (T' - T)(C_p - S)$

(c) $V \rightarrow V'$, $T \rightarrow T'$

$\Delta U = nC_v\Delta T$. $\Delta H = nC_p\Delta T$

$\delta q = dU + p\,dV = C_v\,dT + p\,dV$

$\Delta S = \int \frac{dq_{rev}}{T} = C_v \int \frac{dT}{T} + \int \frac{p}{T}\,dV$

$= C_v \ln\left(\frac{T'}{T}\right) + nR \ln\left(\frac{V'}{V}\right)$

[const p) $\frac{T'}{T} = \frac{V'}{V}$] $= (C_v + R)\ln \frac{T'}{T}$

$= C_p \ln \frac{T'}{T}$

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

$= \Delta H - T'(S + \Delta S) - TS$

$= \Delta H - S\Delta T + T'\Delta S$

$= \Delta H - S\Delta T + T' \cdot C_p \ln \frac{T'}{T}$

(d) $p \to p'$, $T \to T'$, const V.

$\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$, $q = C_v \Delta T$.

$$\Delta S = \int \frac{\delta q_{rev}}{T} = \int \frac{C_v\, dT}{T} = C_v \ln \frac{T'}{T}$$

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

$$= \Delta H - S\Delta T - T' C_v \ln \frac{T'}{T}$$

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

$$= \Delta U - S\Delta T + T' C_v \ln \frac{T_2}{T_1}$$

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? (Utilize the Tables in the APPENDIX of the textbook.)

$$\Delta H^\circ_{298} = 3\Delta H^\circ_{SiO_2} - \Delta H^\circ_{Si_3N_4} = -1.9439 \times 10^6\ J/mol$$

$$\Delta S^\circ_{298} = 3S^\circ_{SiO_2} + 2S^\circ_{N_2} - S^\circ_{Si_3N_4} - 3S^\circ_{O_2} = -22.8\ J/mol\cdot K$$

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

$$= -1.8 \times 10^6\ J$$

at $\Delta C_p = 0$ $\Rightarrow \Delta G^{\circ\prime} = \Delta H^\circ_{298} + 800 \times \Delta S^\circ_{298}$

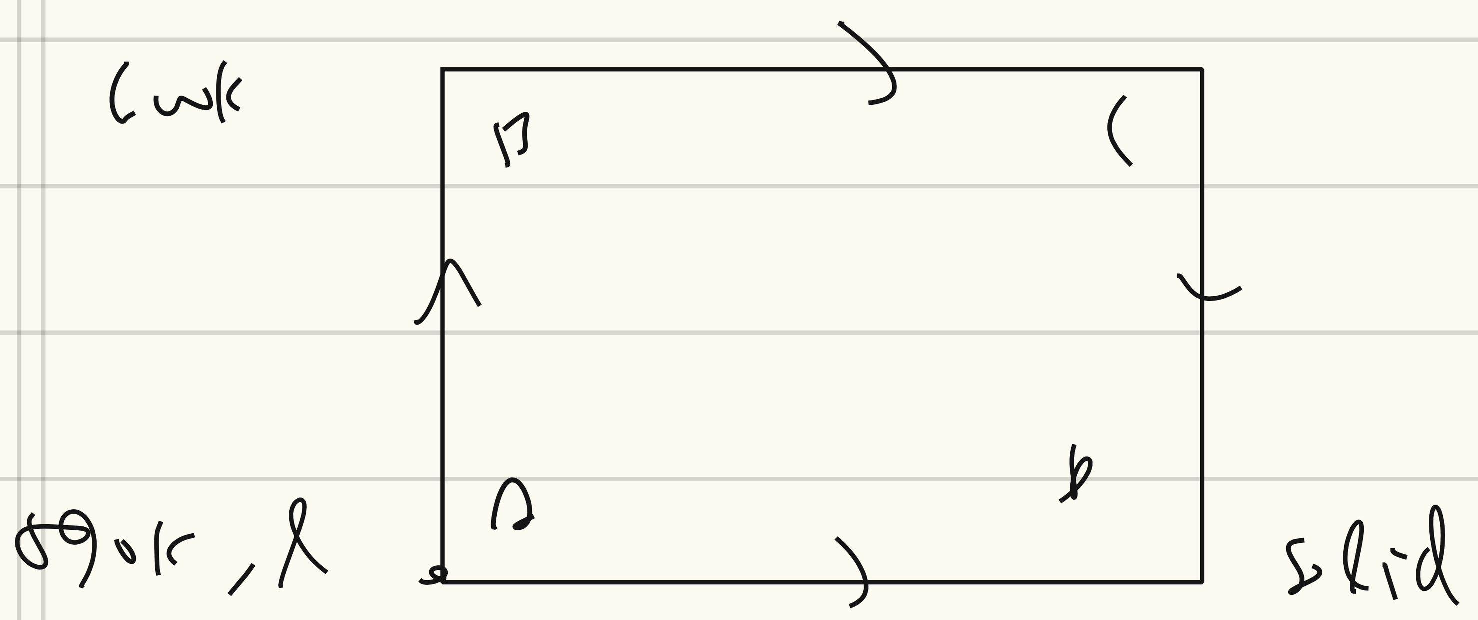
$$= -1.9112 \times 10^6$$

$$\rightarrow \frac{\Delta G' - \Delta G}{\Delta G} = 0.4\ \%$$

3. 1 기압 하 Pb의 melting point는 600K이다. 1 기압 하 590K로 과냉된 액상 Pb가 응고하는 것은 자발적인 반응이라는 것을 보이시오.

- $\Delta H_{melting} = 4810\ J/mole$
- $C_{p(l)} = 32.4 - 3.1\times10^{-3}T\ \ J/mol\cdot K$
- $C_{p(s)} = 23.6 + 9.75\times10^{-3}T\ \ J/mol\cdot K$

(1) Use the maximum entropy criterion
(2) Use the minimum Gibbs Energy criterion
(3) Show that the reaction becomes more irreversible at 550K.
(4) What is the difference between the entropy criterion and Gibbs energy criterion?



Cycle.

1기 n mol.

(1)

$\Delta S_{AB} = \int_{T_1}^{T_2} n C_{p,l} \frac{dT}{T} = 0.514 \times n$

$\Delta S_{BC} = \frac{q_p}{T} = \frac{\Delta H_m}{T} = -8.017 n$

$\Delta S_{CD} = \int_{T_2}^{T_1} n C_{p,s} \frac{dT}{T} = -0.494 n$

$\Rightarrow \Delta S = \Sigma \Delta S$

$= -8.00 n \quad \cdots \Delta S_{system}$

$\Delta S_{surr} = -\Sigma \Delta H / T_1$

$= \left(\int_{T_1}^{T_2} n C_{p,l}\, dT + (-4810) + \int_{T_2}^{T_1} n C_{p,s}\, dT \right) / (-T_1)$

$= -4798 n / T_1$

$= 8.132 \cdot n$

$\rightarrow \Delta S_{tot} = 0.135 n > 0$

(2) $\Delta G = \Delta H - T \Delta S_{sys}$

$= -79.77 n < 0$

(3) $T_1 = 55\sim K.$

같은 방법으로

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{nC_p}{T} dT + \frac{\Delta H_m}{T} + \int_{T_2}^{T_1} \frac{nC_p}{T} dT$$

$$= -7.894\, n$$

$$\Delta S_{surr} = \Delta H / (-T)$$

$$= \left(\int_{T_1}^{T_2} n C_p dT - 4810 n + \int_{T_2}^{T_1} n C_p dT \right)(-T)$$

$$= 8.616\, n$$

$\Rightarrow \Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 0.722 n > 0$ So

$\rightarrow$ it's irreversible

(4) we checked ΔS for system and surrounding to check reversibility, Gibbs energy is enough to check reversibility with only ΔH, ΔS of the system.

4. 위 문제에서 과냉된 액상 Pb 가 만약 단열된 용기에 보관되어 있었다면 용기 내부는 결국 어떠한 (평형)상태가 될 것인지 예측하시오.

Solid + liquid ($\leftarrow$ caused by latent heat)

$\Delta H_{total} = q_p = 0.$

$$= \int_{T_1}^{T_2} n C_{p,l} \, dT - 4810.7x = 0.$$

$\therefore x = 0.064$

$\Rightarrow$ 0.064 solid, others are liquid