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) 1mol, $P_1 = P$, $T_1 = T$, $V_1 = V$

↓ by $PV = nRT$

$P_2 = \frac{P}{2}$, $T_2 = T$, $V_2 = 2V$

$\Delta U = \Delta H = 0$, $Q = W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\frac{V_2}{V_1} = RT\ln 2$, $\Delta S = \frac{Q}{T} = R\ln 2$

$F = U - TS$, $\Delta F = -RT\ln 2$

$G = H - TS$, $\Delta G = -RT\ln 2$

b) 1mol, P_1, T_1

↓ adiabatic

P_2, T_2

$Q = 0$, $\Delta U = C_V(T_2 - T_1)$, $\Delta H = C_P(T_2 - T_1)$, $\Delta S = \frac{Q}{T} = 0$

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

$\Delta G = \Delta H - S(T_2 - T_1) = (C_P - S)(T_2 - T_1)$

c) 1mol, V_1, T_1

↓ isobaric

V_2, T_2

$\Delta U = C_V(T_2 - T_1)$, $\Delta H = C_P(T_2 - T_1)$,

$Q = nC_P dT = C_P dT$, $\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT = C_P \ln\frac{T_2}{T_1}$

$\Delta F = \Delta U - (T_2 - T_1)S_1 - T_2\Delta S = (T_2 - T_1)(C_V - S_1) - T_2 C_P \ln\frac{T_2}{T_1}$

$\Delta G = \Delta H - (T_2 - T_1)S_1 - T_2\Delta S = (T_2 - T_1)(C_P - S_1) - T_2 C_P \ln\frac{T_2}{T_1}$

d) 1mol, P_1, T_1

↓ isochoric

P_2, T_2

$\Delta U = C_V(T_2 - T_1)$, $\Delta H = C_P(T_2 - T_1)$

$W = 0$, $\Delta U = Q = nC_V dT$, $\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \ln\frac{T_2}{T_1}$

$\Delta F = \Delta U - (T_2 - T_1)S_1 - T_2\Delta S = (T_2 - T_1)(C_V - S_1) - T_2 C_P \ln\frac{T_2}{T_1}$

$\Delta G = \Delta H - (T_2 - T_1)S_1 - T_2\Delta S = (T_2 - T_1)(C_P - S_1) - T_2 C_P \ln\frac{T_2}{T_1}$

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.)

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

i) $\Delta H = \sum n H_{생성물} - \sum n H_{반응물}$

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

$H_{800,\ SiO_2(\alpha)} = H_{298,\ SiO_2(\alpha)} + \int_{298}^{800} C_{p,\ SiO_2}\, dT$

$= -910900 + \left[43.89(800-298) + \frac{100\cdot10^{-3}}{2}(800^2-298^2) + 6.02\cdot10^5\left(\frac{1}{800}-\frac{1}{298}\right)\right]$

$= -889859\ J$

$H_{800,\ N_2} = \underbrace{H_{298,\ N_2}}_{=0} + \int_{298}^{800} C_{p,\ N_2}\, dT$

$= \left[27.87(800-298) + \frac{4.27\cdot10^{-3}}{2}(800^2-298^2)\right]$

$= 15167.5\ J$

$H_{800,\ Si_3N_4} = H_{298,\ Si_3N_4} + \int_{298}^{800} C_{p,\ Si_3N_4}\, dT$

$= -744800 + \left[170.54(800-298) + \frac{98.74\cdot10^{-3}}{2}(800^2-298^2)\right]$

$= -682176\ J$

$H_{800,\ O_2} = \underbrace{H_{298,\ O_2}}_{=0} + \int_{298}^{800} C_{p,\ O_2}\, dT$

$= \left[29.96(800-298) + \frac{4.18\cdot10^{-3}}{2}(800^2-298^2) + 1.67\cdot10^5\left(\frac{1}{800}-\frac{1}{298}\right)\right]$

$= 15840.3\ J$

$\therefore \Delta H_{800} = -2004587\ J$

ii) $\Delta S = \sum n S_{생성물} - \sum n S_{반응물}$

$\Delta S_{800} = 3S_{800,\ SiO_2} + 2S_{800,\ N_2} - S_{800,\ Si_3N_4} - 3S_{800,\ O_2}$

$S_{800,\ SiO_2} = S_{298,\ SiO_2} + \int_{298}^{800} \frac{C_{p,\ SiO_2}}{T}\, dT$

$= 41.5 + \left[43.85\ln\frac{800}{298} + 10^{-3}(800-298) + \frac{6.02\cdot10^5}{2}\left(\frac{1}{800^2}-\frac{1}{298^2}\right)\right]$

$= 82.4\ J/K\cdot mol$

$S_{800,\ N_2} = S_{298,\ N_2} + \int_{298}^{800} \frac{C_{p,\ N_2}}{T}\, dT$

$= 191.5 + \left[27.87\ln\frac{800}{298} + 4.27\cdot10^{-3}(800-298)\right]$

$= 221.16\ J/K\cdot mol$

$S_{800,\ Si_3N_4} = S_{298,\ Si_3N_4} + \int_{298}^{800} \frac{C_{p,\ Si_3N_4}}{T}\, dT$

$= 113.0 + \left[170.54\ln\frac{800}{298} + 98.74\cdot10^{-3}(800-298)\right]$

$= 232\ J/K\cdot mol$

$S_{800,\ O_2} = S_{298,\ O_2} + \int_{298}^{800} \frac{C_{p,\ O_2}}{T}\, dT$

$= 205.1 + \left[29.96\ln\frac{800}{298} + 4.18\cdot10^{-3}(800-298) - \frac{1.67\cdot10^5}{2}\left(\frac{1}{800^2}-\frac{1}{298^2}\right)\right]$

$= 236.2\ J/K\cdot mol$

$\therefore \Delta S_{800} = -250.2\ J/K$

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.)

$$\begin{cases} \Delta H_{800} = -2004587\ J \\ \Delta S_{800} = -250.2\ J/K \end{cases}$$

$$\therefore \Delta G_{800} = \Delta H_{800} - 800 \cdot \Delta S_{800}$$

$$= -18044.29\ J$$

$$C_{p,total} = 3C_{p,SiO_2} + 2C_{p,N_2} - C_{p,Si_3N_4} - 3C_{p,O_2}$$

$$= 3\left(42.89 + 1.00\cdot10^{-3}T - 6.02\cdot10^{5}T^{-2}\right) + 2\left(27.87 + 4.27\cdot10^{-3}T\right) - \left(90.54 + 98.74\cdot10^{-3}T\right)$$

$$-3\left(29.96 + 4.18\cdot10^{-3}T - 1.67\cdot10^{5}T^{-2}\right)$$

$$= 26.99 - 49.87\cdot10^{-3}T + 13.05\cdot10^{5}T^{-2}$$

$$\Delta G_{800} = H_{298} + \int_{298}^{800} C_{p,total}\,dT - 800\cdot\left(S_{298} + \int_{298}^{800}\frac{C_{p,total}}{T}\,dT\right)$$

$$= -1.863\cdot10^{6}\ J$$

$$\Delta G_{800,C_p=0} = H_{298} - 800\,S_{298} \quad (\Delta C_p = 0)$$

$$= -1.8126\cdot10^{6}\ J$$

$$\therefore \text{Error} = \left|\frac{\Delta G_{800} - \Delta G_{800,C_p=0}}{\Delta G_{800}}\right|$$

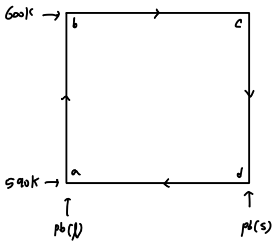
$$= 0.002774879$$

$$\approx 0.003$$

3.1 1기압 하 Pb의 melting point는 600K이다. 1기압 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?



a → b : 과냉각된 액체 Pb, 납이 1atm, 590K에서 600K으로 가역적으로 가열됨
b → c : 액체 납이 600K에서 가역적으로 응고
c → d : 고체 납이 1atm, 600K에서 590K으로 가역적으로 냉각됨

(처음 액상 1몰가 n몰 있었다고 가정
일정한 온도 590K로 유지되는 열저장체)

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

$\Delta S_{(a\to b)} = \int_{590K}^{600K} \frac{nC_{p,Pb(l)}}{T} dT = n\int_{590K}^{600K} \left(\frac{32.4}{T} - 3.1\cdot10^{-3}\right) dT$

$= n\left(32.4 \ln\frac{600}{590} - 3.1\cdot10^{-3}(600-590)\right)$

$= n\cdot 0.514\ J/K$

$\Delta S_{(b\to c)} = \frac{q_p}{T} = -n\cdot\frac{4810}{600} = -n\cdot 8.017\ J/K$

$\Delta S_{(c\to d)} = \int_{600K}^{590K} \frac{nC_{p,Pb(s)}dT}{T} = n\int_{600K}^{590K} \left(\frac{23.6}{T} + 9.75\cdot10^{-3}\right) dT$

$= n\cdot\left(23.6\cdot\ln\frac{590}{600} + 9.75\cdot10^{-3}(590-600)\right)$

$= -n\cdot 0.494\ J/K$

$\therefore \Delta S_{(a\to d)} = -n\cdot 7.997\ J/K$

· 열저장체에 대해서

$\Delta H_{(a\to d)} = \Delta H_{(a\to b)} + \Delta H_{(b\to c)} + \Delta H_{(c\to d)}$

$\Delta H_{(a\to b)} = \int_{590K}^{600K} nC_{p,Pb(l)}\, dT = n\int_{590K}^{600K} (32.4 - 3.1\cdot10^{-3}T)\, dT$

$= n\cdot\left\{32.4(600-590) - \frac{3.1\cdot10^{-3}}{2}(600^2 - 590^2)\right\}$

$= n\cdot 306\ J$

$\Delta H_{(b\to c)} = -n\cdot 4810\ J$

$\Delta H_{(c\to d)} = \int_{600K}^{590K} nC_{p,Pb(s)}\, dT = n\int_{600K}^{590K} (23.6 + 9.75\cdot10^{-3}T)\, dT$

$= n\cdot\left\{23.6(590-600) + \frac{9.75\cdot10^{-3}}{2}(590^2 - 600^2)\right\}$

$= -n\cdot 294\ J$

$\therefore \Delta H_{(a\to d)} = -n\cdot 4799\ J$ (열저장체가 흡수)

$\Delta S_{열저장체} = n\cdot\frac{4799}{590} = n\cdot 8.314\ J/K$

$\Rightarrow \Delta S_{irr} = n\cdot 0.317\ J/K > 0$ (자발적인 반응)

2) 과냉각된 납에 대해서

$\Delta S_{(a\to d)} = -n\cdot 7.997\ J/K$

$\Delta H_{(a\to d)} = -n\cdot 4799\ J$

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

$= -n\cdot 4799 - 590\cdot(-n\cdot 7.997)$

$= -n\cdot 80.77 < 0$ (자발적인 반응)

3) 590K → 550K

동일하게 $\Delta S_{(a\to d)}$, $\Delta S_{열저장체}$를 구하자

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

$= n\cdot 2.664 - n\cdot 8.017 - n\cdot 2.541$

$= -n\cdot 7.894\ J/K$

$\Delta H_{(a\to d)} = \Delta H_{(a\to b)} + \Delta H_{(b\to c)} + \Delta H_{(c\to d)}$

$= n\cdot 1531\ J - n\cdot 4810\ J - n\cdot 1460\ J$

$= -n\cdot 4739\ J$

$\Delta S_{열저장체} = n\cdot\frac{4739}{550} = n\cdot 8.616\ J/K$

$\Delta S_{irr,550K} = n\cdot 0.722\ J/K > \Delta S_{irr,590K}$

4) 엔트로피 기준의 경우 계와 주위에 대해서 둘의 합을 이용해 자발, 비자발을 판단

깁스 자유 에너지 기준의 경우 계의 엔탈피, 엔트로피만으로 자발, 비자발의 판단 가능

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

단열된 계의 평형상태는 자발적으로 응고된 고체와 나머지 액체가 600에서 공존해 있는 것이다.
1몰의 Pb, 납에 대해 생각하고 몰분율 x로 응고되어 있다고 생각하자
(a → b → c or a → d → c)

i) a → b → c

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

$$\therefore \Delta H_{(a\to b)} = -\Delta H_{(b\to c)}$$

$$\Delta H_{(a\to b)} = \int_{590K}^{600K} C_{p,Pb(l)}\,dT = \int_{590K}^{600K} (32.4 - 3.1\cdot 10^{-3}T)\,dT$$

$$= \left\{ 32.4(600-590) - \frac{3.1\cdot 10^{-3}}{2}(600^2 - 590^2) \right\}$$

$$= 306\ J$$

$$\Delta H_{(b\to c)} = -4810\cdot x\ J$$

$$\therefore 306 = 4810\cdot x, \quad x = 306/4810 = 0.064$$

ii) a → d → c

$$\Delta H_{(a\to d)} = -x\left(\Delta H_{m(600K)} + \int_{600K}^{590K} \Delta C_{p(s\to l)}\,dT\right)$$

$$= -x\left(4810 + \int_{600K}^{590K}(8.8 - 12.85\cdot 10^{-3}T)\,dT\right)$$

$$= -x\left(4810 + 8.8(590-600) - 12.85\cdot 10^{-3}(590^2 - 600^2)\right)$$

$$= -x\cdot 4875\ J$$

$$\Delta H_{(d\to c)} = x\int_{590K}^{600K} C_{p,Pb(s)}\,dT + (1-x)\int_{590K}^{600K} C_{p,Pb(l)}\,dT$$

$$= x\int_{590K}^{600K}(23.6 + 9.75\cdot 10^{-3}T)\,dT + (1-x)\int_{590K}^{600K}(32.4 - 3.1\cdot 10^{-3}T)\,dT$$

$$= x\left\{23.6(600-590) + \frac{9.75\cdot 10^{-3}}{2}(600^2 - 590^2)\right\} + (1-x)\left\{32.4(600-590) - \frac{3.1\cdot 10^{-3}}{2}(600^2-590^2)\right\}$$

$$= x\cdot 294 + (1-x)\cdot 306$$

$$= 306 - 12x$$

$$\therefore 306 - 12x = 4875x, \quad 306 = 4887x, \quad x = 306/4887 \approx 0.064$$