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) P_0, T_0, V_0

$V_1 = 2V_0$, $P_1 = \frac{P_0}{2}$, $T_1 = T_0$ (free)

$\Delta U = \Delta H = 0$

$\Delta S = \int \frac{P}{T} dV = \int_{V_0}^{2V_0} \frac{R}{V} dV = R \ln 2$

$\Delta F = -\int P dV = -\int_{V_0}^{2V_0} \frac{RT}{V} dV = -RT \ln 2$

$\Delta G = \int V dP = \int_{P_0}^{\frac{1}{2}P_0} \frac{RT}{P} dV = -RT \ln 2$

(b) $V_1 = \frac{RT_1}{P_1}$, $V_2 = \frac{RT_2}{P_2}$

$\Delta U = \int_{T_1}^{T_2} C_V dT$, $\Delta H = \int_{T_1}^{T_2} C_p dT$ $\Delta S = 0$

reversible adiabatic $\Delta F = \Delta G = 0$

(c) $\Delta U = \int_{T_1}^{T_2} C_V dT$, $\Delta H = \int_{T_1}^{T_2} C_p dT$

$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT + \int_{V_1}^{V_2} \frac{R}{V} dV = C_p \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$

$\Delta F = P(V_2 - V_1) - C_V (T_2 \ln T_2 - T_1 \ln T_1 + (S_0 - 1)(T_2 - T_1))$

$\Delta G = \Delta H - T_2 \Delta S$

$= \int_{T_1}^{T_2} C_p dT - T_2 \left(C_p \ln T + R \ln\left(\frac{V_2}{V_1}\right)\right)$

(d) $\Delta U = \int_{T_1}^{T_2} C_V dT$, $\Delta H = \int_{T_1}^{T_2} C_p dT$

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

$$\Delta F = -C_V \ln(T_2 \ln T_2 - T_1 \ln T_1) + (S_0 - 1)(T_2 - T_1))$$

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

$$= \int_{T_1}^{T_2} C_p dT - T_2 C_V \ln\left(\frac{T_2}{T_1}\right)$$

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.)

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

엔탈피 $\Rightarrow$ $\Delta H_{tot} = 3\Delta H_{SiO_2} + 2\Delta H_{N_2} - \Delta H_{Si_3N_4} - 3\Delta H_{O_2}$

* $H_{SiO_2(800)} = H^\circ_{SiO_2(298)} + \int_{298}^{800} C_{p\,N_2}\,dT$ $\quad (H^\circ_{SiO_2(800)} = -910900J)$

$$= -910900 + \int_{298}^{800} \left(43.89 + \frac{10^{-3}}{2}T + 6.02\times(10^5 T^{-2})\right) dT$$

$$= -910900 + 43.89(800-298) + \frac{10^{-3}}{2}(800^2 - 298^2)$$

$$+6.02\times10^5\left(\frac{1}{800} - \frac{1}{298}\right) = -889859J$$

$$3\,\Delta H_{SiO_2(800)} = -2669577J$$

* $H_{N_2(800)} = H^\circ_{N_2(298)} + \int_{298}^{800} C_p\,dT$ $\quad (H^\circ_{N_2(298)} = 0J)$

$$= 0 + \int_{298}^{800} (27.87 + 4.27\times(10^{-3}T))\,dT$$

$$= 27.87(800-298) + 4.27\times10^{-3}(800^2 - 298^2)$$

$$= 15168J$$

$$2\times H_{N_2(800)} = 30335J$$

* $H_{Si_3N_4(800)} = H^\circ_{Si_3N_4(298)} + \int_{298}^{800} C_p dT$ $\quad (H^\circ_{Si_3N_4(298)} = -744800J)$

$$= -744800 + \int_{298}^{800} (70.94 + 98.74\times10^{-3}T)\,dT$$

$$= -744800 + 70.94(800-298) + 98.74\times10^{-3}(800^2 - 298^2)$$

$$= -682176J$$

$$*H_{O_2(800)} = H^\circ_{O_2(298)} + \int_{298}^{800} C_p dT \quad (H^\circ_{O_2,298} = 0\,J)$$

$$= 0 + \int_{298}^{800} (29.96 + 4.18\times10^{-3}T - 1.67\times10^{5}T^{-2})dT$$

$$= 29.96(800-298) + 418\times10^{-3}(800^2-298^2) + 1.67\times10^{5}\left(\frac{1}{800}-\frac{1}{298}\right)$$

$$= \underline{15840\,J}$$

$$3H_{O_2(800)} = \underline{47520\,J}$$

$$\Delta H_{tot(800)} = -2669977 + 303357 + 682176 - 47520\,(J)$$

$$= \underline{-2004586\,J}$$

엔트로피 $\Rightarrow$ $\Delta S_{tot(800)} = 3\Delta S_{STO_2(800)} + 2\Delta S_{N_2(800)} - \Delta S_{ST_3N_4(800)} - 3\Delta S_{O_2(800)}$

$$*\Delta S_{STO_2(800)} = \Delta S^\circ_{STO_2(298)} + \int_{298}^{800} \frac{C_p}{T} dT \quad (\Delta S^\circ_{STO_2(298)} = 41.5\,J/K)$$

$$= 41.5\,J/K + \int_{298}^{800} \left(\frac{43.89}{T} + 10^{-3} - 6.02\times10^{5}T^{-3}\right)dT$$

$$= 41.5\,J/K + 43.89\ln\left(\frac{800}{298}\right) + 10^{-3}(800-298) + 3.01\times10^{5}\times\left(\frac{1}{800^2}-\frac{1}{298^2}\right) = \underline{82.4\,J/K}$$

$$3\Delta S_{STO_3(800)} = 4\times82.4\,(J/K) = \underline{247.2\,J/K}$$

$$*\Delta S_{N_2(800)} = \Delta S^\circ_{N_2(298)} + \int_{298}^{800} \frac{C_p}{T} dT \quad (\Delta S^\circ_{N_2(298)} = 191.5\,J/K)$$

$$= 191.5\,J/K + \int_{298}^{800} \left(\frac{27.87}{T} + 4.27\times10^{-3}\right)dT$$

$$= 191.5\,J/K + 27.87\ln\left(\frac{800}{298}\right) + 4.27\times10^{-3}(800-298)$$

$$= 221.2\,J/K$$

$$2\Delta S_{N_2(800)} = 2\times221.2\,(J/K) = \underline{442.4\,J/K}$$

$$* \Delta S_{Si_3N_4(800)} = \Delta S^\circ_{Si_3N_4(298)} + \int_{298}^{800} \frac{C_p}{T} dT \quad (\Delta S^\circ_{Si_3N_4(298)} = 113 J/K)$$

$$= 113 J/K + \int_{298}^{800} \left(\frac{70.54}{T} + 98.74 \times 10^{-3}\right) dT$$

$$= 113 J/K + 70.54 \ln\left(\frac{800}{298}\right) + 98.74 \times 10^{-3} (800 - 298)$$

$$= 232.2 J/K$$

$$* \Delta S_{O_2(800)} = \Delta S^\circ_{O_2(298)} + \int_{298}^{800} \frac{C_p}{T} dT \quad (\Delta S^\circ_{O_2(298)} = 205.1 J/K)$$

$$= 205.1 J/K + \int_{298}^{800} \left(\frac{29.96}{T} + 4.18 \times 10^{-3} - 1.67 \times 10^5 T^{-2}\right) dT$$

$$= 205.1 J/K + 30.9 J/K = 236 J/K$$

$$3\Delta S_{O_2(800)} = 3 \times 236 = 708 J/K$$

$$\Delta S_{tot(800)} = 247.2 + 442.4 - 232.2 - 708 = -250 J/K$$

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

$$= -2004586 - 800(-250)$$

$$= -1804586 J$$

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?

과냉된 액상 Pb는 600K로 가열됨.
⇒ 가열된 액상 Pb는 응고됨.
⇒ 응고된 Pb는 액상 Pb로 과냉됨.

(1) $\Delta S_{tot} \geq 0$ 이면 자발적인 반응이다.

$\Delta S_{tot} = \Delta S_{l\to s} + \Delta S_{상태변화} + \Delta S_{s\to l}$

$*\Delta S_{l\to s} = \int_{590}^{600} \frac{C_{p(l)}}{T} dT = \int_{590}^{600} \left(\frac{32.4}{T} - 3.1\times10^{-3}\right) dT$

$= 32.4 \ln\left(\frac{600}{590}\right) - 3.1\times10^{-3}(10)$

$= 0.51\ J/K$

$*\Delta S_{상태변화} = \frac{\Delta H_m}{T} = -\frac{4810}{600} = -8.02\ J/K$

$*\Delta S_{s\to l} = \int_{600}^{590} \frac{C_{p(s)}}{T} dT = \int_{600}^{590} \left(\frac{23.6}{T} + 9.75\times10^{-3}\right) dT$

$= 23.6 \ln\left(\frac{590}{600}\right) + 9.75\times10^{-3}(-10)$

$= -0.49\ J/K$

$\Delta S_{sys,tot} = 0.51\ J/K - 8.02\ J/K - 0.49\ J/K = -8\ J/K$

* $\Delta S_{surr,tot}$

* $\Delta H_{l \to s} = \int_{590}^{600} (32.4 - 3.1 \times 10^{-3} T)\, dT$

$= 32.4(10) - 3.1 \times 10^{-3} (600^2 - 590^2) = 287\,J$

* $\Delta H_{상태변화} = -4810\,J$

* $\Delta H_{s \to l} = \int_{600}^{590} (23.6 + 9.75 \times 10^{-3} T)\, dT$

$= 23.6(-10) + 9.75 \times 10^{-3} (590^2 - 600^2)$

$= -352\,J$

* $\Delta H_{tot} = -4875\,J$

$\Delta S_{surr,tot} = \frac{4875(J)}{590(K)} = 8.26\,J/K$

$\Delta S_{sys,tot} + \Delta S_{surr,tot} = -8\,J/K + 8.26\,J/K$

$= 0.26\,J/K$

$\Delta S_{tot} > 0$ 이므로 자발적인 반응이다.

(2) $\Delta G < 0$ 이면 자발적인 반응이다.

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

$= -4875\,J - 590K \times (-8\,J/K) = -155\,J$

$\Rightarrow \Delta G < 0$ 이므로 자발적인 반응이다.

(3)

$\Delta S_{sys} = \Delta S_{l \to g} + \Delta S_{상변} + \Delta S_{g \to l}$

$* \Delta S_{l \to g} = \int_{590}^{600} \left(\frac{32.4}{T} - 3.1 \times 10^{-3}\right) dT = 2.66\,J/K$

$* \Delta S_{상태변화} = \frac{\Delta H_m}{T} = -\frac{4810}{600} = -8.02\,J/K$

$* \Delta S_{g \to l} = \int_{600}^{590} \left(\frac{23.6}{T} + 9.75 \times 10^{-3}\right) dT = -2.54\,J/K$

$\Delta S_{sys,tot} = -7.9\,J/K$

$* \Delta H_{s \to g} = \int_{590}^{600} (324 - 3.1 \times 10^{-3} T) dT = 1783\,J$

$* \Delta H = -4810\,J$

$* \Delta H_{g \to l} = \int_{600}^{590} (23.6 + 9.75 \times 10^{-3} T) dT = -1296\,J$

$\Delta S_{surr,tot} = \frac{4523}{590} = 8.22\,J/K$

$\Delta S_{sys,tot} + \Delta S_{surr,tot} = 0.32\,J/K$

590K 일때보다 ΔS_{tot}의 값이 더 크기때문에 더 자발적이다.

(4)

엔트로피로 자발성을 판단할 때에는 System과 surrounding에서의 엔트로피를 합한 값을 사용해 값의 양/음수로 판단한다.
반면, 깁스 자유 에너지로 자발성을 판단할 때에는 System에서의 엔탈피 값과 엔트로피값을 사용해 값의 양/음수로 판단한다.

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

고상 Pb와 액상 Pb가 평형상태로 존재할 것이다.
액상 Pb에서 자발적으로 응고되는 고상 Pb와
응고되지 못한 액상 Pb가 평형상태로 있을 것이다.