

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) 1 mole, P, T . $V = \frac{RT}{P} \rightarrow \frac{1}{2} P \cdot T \cdot \frac{2RT}{P}$

$$\Delta U = \Delta H = 0 \quad w = \int P dV = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{\Delta Q}{T} = nR \ln \frac{V_2}{V_1} = R \ln 2 = 5.76 \text{ J/K}$$

$$\Delta F = \Delta U - T \Delta S = -5.76 \text{ T J}$$

$$\Delta G = \Delta H - T \Delta S = -5.76 \text{ T J}$$

(b) 1 mole $P_1, T_1 \rightarrow P_2, T_2$

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

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

$$\Delta S = 0$$

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

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

(c) constant P 1 mole $V_1, T_1 \rightarrow V_2, T_2$

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

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

$$\Delta S = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1} = C_P \ln \frac{T_2}{T_1}$$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2 S_2 - T_1 S_1) = \Delta H - S_1(T_2 - T_1) - T_2 \Delta S = (C_P - S_1)(T_2 - T_1) - T_2 C_P \ln \frac{T_2}{T_1}$$

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - (T_2 S_2 - T_1 S_1) = \Delta U - S_1(T_2 - T_1) - T_2 \Delta S = (C_V - S_1)(T_2 - T_1) - T_2 C_P \ln \frac{T_2}{T_1}$$

(d) constant V 1 mole $P_1, T_1 \rightarrow P_2, T_2$

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

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

$$\Delta S = R \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1} = C_V \ln \frac{T_2}{T_1}$$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2 S_2 - T_1 S_1) = \Delta H - S_1(T_2 - T_1) - T_2 \Delta S = (C_P - S_1)(T_2 - T_1) - T_2 C_V \ln \frac{T_2}{T_1}$$

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - (T_2 S_2 - T_1 S_1) = \Delta U - S_1(T_2 - T_1) - T_2 \Delta S = (C_V - S_1)(T_2 - T_1) - T_2 C_V \ln \frac{T_2}{T_1}$$

2. Calculate the value of ΔG for the reaction



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.)

$$\Delta H_{298}^{\circ} = \sum \Delta H^{\circ}_{\text{products}} - \sum \Delta H^{\circ}_{\text{reactants}}$$

$$= [3(-910.9) + 2(0)] - [(-144.8) + 3(0)] \text{ kJ/mol}$$

$$= -1987.9 \text{ kJ/mol}$$

	$\Delta H^{\circ} (\text{J})$
SiO_2	-910900
Si_3N_4	-144800

	S°
SiO_2	41.5
Si_3N_4	113.0
N_2	191.5
O_2	205.1

$$\Delta S_{298}^{\circ} = \sum \Delta S^{\circ}_{\text{products}} - \sum \Delta S^{\circ}_{\text{reactants}}$$

$$= [3(41.5) + 2(191.5)] - [(113) + 3(205.1)] \text{ J/mol}\cdot\text{K}$$

$$= -220.8 \text{ J/mol}\cdot\text{K}$$

$$C_p \begin{cases} \text{Si}_3\text{N}_4: 10.54 + 98.74 \times 10^{-3} T \text{ J/mol}\cdot\text{K} \\ \text{O}_2: 29.66 + 4.18 \times 10^{-3} T - 1.67 \times 10^{-5} T^2 \text{ J/mol}\cdot\text{K} \\ \text{SiO}_2: 43.89 + 1.00 \times 10^{-3} T - 6.02 \times 10^{-5} T^2 \text{ J/mol}\cdot\text{K} \\ \text{N}_2: 27.87 + 4.27 \times 10^{-3} T \text{ J/mol}\cdot\text{K} \end{cases}$$

$$\text{total } C_p = 27.87 + 99.74 \times 10^{-3} T - 13.05 \times 10^{-5} T^2 \text{ J/mol}\cdot\text{K}$$

$$\Delta G_{800}^{\circ} = \Delta H_{298}^{\circ} - 800 \Delta S_{298}^{\circ} + \int_{298}^{800} \Delta C_p dT - 800 \int_{298}^{800} \frac{\Delta C_p}{T} dT$$

$$\int_{298}^{800} \Delta C_p dT = \int_{298}^{800} (27.87 + 99.74 \times 10^{-3} T - 13.05 \times 10^{-5} T^2) dT = -16681.1$$

$$\int_{298}^{800} \frac{\Delta C_p}{T} dT = \int_{298}^{800} \frac{(27.87 + 99.74 \times 10^{-3} T - 13.05 \times 10^{-5} T^2)}{T} dT = -29.1445$$

$$\Delta G_{800}^{\circ} = -1987900 - 800 \times (-220.8) - 16681.1 - 800 \times (-29.1445) = -1804 \text{ kJ}$$

$$\ast \Delta C_p = 0 \text{ or } T_{\text{avg}}^{\circ} \quad \Delta G_{800}^{\circ} = \Delta H_{298}^{\circ} - 800 \Delta S_{298}^{\circ} = -1811 \text{ kJ}$$

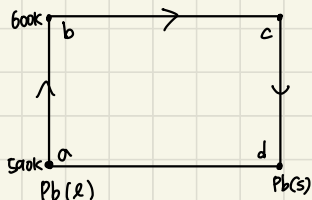
$$\text{error} = \frac{1811 - 1804}{1804} = 0.39\%$$

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

- $\Delta H_{\text{melting}} = 4810 \text{ J/mole}$
- $C_{p(l)} = 32.4 - 3.1 \times 10^{-3} T \text{ J/mol} \cdot K$
- $C_{p(s)} = 23.6 + 9.75 \times 10^{-3} T \text{ J/mol} \cdot K$

- (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?

(1)



(n=1 mol)

$$\begin{aligned} \Delta S_{a \rightarrow b} &= \int_{590}^{600} \frac{n C_{p(l)}}{T} dT = \int_{590}^{600} \left(\frac{32.4}{T} - 3.1 \times 10^{-3} \right) dT = 0.51 \text{ J/K} \\ \Delta S_{b \rightarrow c} &= \frac{\Delta Q}{T} = \frac{-4810}{600} = -8.02 \text{ J/K} \\ \Delta S_{c \rightarrow d} &= \int_{590}^{600} \frac{n C_{p(s)}}{T} dT = \int_{590}^{600} \left(\frac{23.6}{T} + 9.75 \times 10^{-3} \right) dT = -0.49 \text{ J/K} \end{aligned}$$

$$\Rightarrow \Delta S_{a \rightarrow d} = -8.00 \text{ J/K}$$

$$\therefore \Delta S_{\text{sys}} = -8.00 \text{ J/K}$$

$$\begin{aligned} \Delta H_{a \rightarrow b} &= \int_{590}^{600} C_{p(l)} dT = \int_{590}^{600} (32.4 - 3.1 \times 10^{-3} T) dT = 905.6 \text{ J} \\ \Delta H_{b \rightarrow c} &= -4810 \text{ J} \\ \Delta H_{c \rightarrow d} &= \int_{590}^{600} C_{p(s)} dT = \int_{590}^{600} (23.6 + 9.75 \times 10^{-3} T) dT = -294 \text{ J} \end{aligned}$$

$$\Rightarrow \Delta H_{a \rightarrow d} = -4798.4 \text{ J}$$

$$\therefore \Delta S_{\text{sur}} = -\frac{\Delta H}{T} = \frac{4798.4}{590} = 8.13 \text{ J/K}$$

$$\Delta S_{\text{irr}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0.13 \text{ J/K} > 0 \rightarrow \text{자발적}$$

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

$$= -4798.4 - 590 \times (-8.00) = -80.17 < 0 \rightarrow \text{자발적}$$

$$\begin{aligned} \Delta S_{a \rightarrow b} &= \int_{550}^{600} \frac{n C_{p(l)}}{T} dT = \int_{550}^{600} \left(\frac{32.4}{T} - 3.1 \times 10^{-3} \right) dT = 2.66 \text{ J/K} \\ \Delta S_{b \rightarrow c} &= \frac{\Delta Q}{T} = \frac{-4810}{600} = -8.02 \text{ J/K} \\ \Delta S_{c \rightarrow d} &= \int_{550}^{600} \frac{n C_{p(s)}}{T} dT = \int_{550}^{600} \left(\frac{23.6}{T} + 9.75 \times 10^{-3} \right) dT = -2.54 \text{ J/K} \end{aligned}$$

$$\Rightarrow \Delta S_{a \rightarrow d} = -7.89 \text{ J/K}$$

$$\Delta S_{\text{sys}} = -7.89 \text{ J/K}$$

$$\begin{aligned} \Delta H_{a \rightarrow b} &= \int_{550}^{600} C_{p(l)} dT = \int_{550}^{600} (32.4 - 3.1 \times 10^{-3} T) dT = 1931 \text{ J} \\ \Delta H_{b \rightarrow c} &= -4810 \text{ J} \\ \Delta H_{c \rightarrow d} &= \int_{550}^{600} C_{p(s)} dT = \int_{550}^{600} (23.6 + 9.75 \times 10^{-3} T) dT = -1460 \text{ J} \end{aligned}$$

$$\Rightarrow \Delta H_{a \rightarrow d} = -4739 \text{ J}$$

$$\Delta S_{\text{sur}} = \frac{4739}{550} = 8.62 \text{ J/K}$$

$$\Delta S_{\text{irr}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0.72 \text{ J/K}$$

(4) entropy criterion은 $\Delta S_{\text{sys}}, \Delta S_{\text{sur}}$ 모두 계산해야 하지만

Gibbs energy criterion은 ΔS_{sys} 만으로 계산한다

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

단열 용기이므로 잠열이 남아있을 것이고 이 때문에 생긴 액체와
자발적으로 만들어진 고체가 모두 존재하는 것이다.

고체 질량: 액체 (1.7)톤.

$$\Delta H_{A \rightarrow C} = 0 \quad (\because \text{단열 과정})$$

$$\left(\begin{array}{l} \Delta H_{A \rightarrow B} = \int_{590}^{600} C_p dT = \int_{590}^{600} (32.4 - 3.1 \times 10^{-3} T) dT = 305.6 \text{ J} \\ \Delta H_{B \rightarrow C} = -4810 \text{ J} \end{array} \right.$$

$$x = \frac{305.6}{4810} = 0.064 \text{ mol}$$

고체 0.064 mol, 액체 0.936 mol 존재