

AMSE205 Thermodynamics I

due date: Oct. 27, 2022

Problem Set #3

Prof. Byeong-Joo Lee
calphad@postech.ac.kr
Room 1- 311

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 .

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.)

3. 1 기압 하 Pb 의 melting point 는 600K 이다. 1 기압 하 590K 로 과냉된 액상 Pb 가 응고하는 것은 자발적인 반응이라는 것을 보이시오.

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

- (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?

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

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.]

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

(a) One mole of ideal gas at the pressure P and temperature T expands into a vacuum to double its volume.

$$\begin{aligned} \text{(a) constant } T, P \rightarrow \quad & \Delta U = \Delta H = 0 \\ \Rightarrow dT = dP = 0 \quad & \begin{cases} \Delta S = \frac{P}{T} dV = nR \int_{V_1}^{V_2} \frac{1}{V} dV = R \ln \left(\frac{V_2}{V_1} \right) = R \ln 2 \\ \Delta F = -PdV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -RT \ln \left(\frac{V_2}{V_1} \right) = -RT \ln 2 \\ \Delta G = \Delta H - TdS = RT \ln 2 \end{cases} \end{aligned}$$

$$\begin{cases} \Delta U = TdS - PdV \\ \Delta H = TdS + VdP \\ \Delta F = -SdT - PdV \\ \Delta G = -SdT + VdP \end{cases}$$

$$\Delta S = \frac{1}{T} dH - \frac{V}{T} dP$$

$$= \frac{1}{T} dU + \frac{P}{T} dV$$

(b) The reversible adiabatic expansion of 1 mole of an ideal gas from P_1, T_1 to P_2, T_2 .

$$\begin{aligned} \text{(b) adiabatic} \quad & \begin{cases} \Delta U = -w = nC_v dT = C_v (T_2 - T_1) \\ \Delta H = nC_p dT = C_p (T_2 - T_1) \\ \Delta S = 0 \\ \Delta F = \Delta H - SdT = C_p (T_2 - T_1) - S (T_2 - T_1) \\ \Delta G = \Delta U - SdT = C_v (T_2 - T_1) - S (T_2 - T_1) \end{cases} \\ \Rightarrow q = 0 \end{aligned}$$

(c) A constant-pressure expansion of 1 mole of an ideal gas from V_1, T_1 to V_2, T_2 .

$$\begin{aligned} \text{(c) constant } P \quad & \begin{cases} \Delta U = nC_v dT = C_v (T_2 - T_1) \\ \Delta H = nC_p dT = C_p (T_2 - T_1) \\ \Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right) = C_p \ln \left(\frac{T_2}{T_1} \right) \\ \Delta F = \Delta U - TdS - SdT = C_v (T_2 - T_1) - TC_p \ln \left(\frac{T_2}{T_1} \right) - S (T_2 - T_1) \\ \Delta G = \Delta H - TdS - SdT = C_p (T_2 - T_1) - TC_p \ln \left(\frac{T_2}{T_1} \right) - S (T_2 - T_1) \end{cases} \\ \Rightarrow dP = 0 \end{aligned}$$

(d) A constant-volume change of state of 1 mole of an ideal gas from P_1, T_1 to P_2, T_2 .

$$\begin{aligned} \text{(d) constant } V \quad & \begin{cases} \Delta U = q = C_v (T_2 - T_1) \\ \Delta H = C_p (T_2 - T_1) \\ \Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) = C_v \ln \left(\frac{T_2}{T_1} \right) \\ \Delta F = \Delta U - TdS - SdT = C_v (T_2 - T_1) - TC_v \ln \left(\frac{T_2}{T_1} \right) - S (T_2 - T_1) \\ \Delta G = \Delta H - TdS - SdT = C_p (T_2 - T_1) - TC_v \ln \left(\frac{T_2}{T_1} \right) - S (T_2 - T_1) \end{cases} \\ \Rightarrow dV = 0 \\ w = 0 \end{aligned}$$

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.)

$$\Delta H = 3\Delta H_{800}(\text{SiO}_2) + 2\Delta H_{800}(\text{N}_2) - \Delta H_{800}(\text{Si}_3\text{N}_4) - 3\Delta H_{800}(\text{O}_2)$$

$$\begin{aligned}\Delta H_{800}(\text{SiO}_2) &= \Delta H_{298}^{\circ}(\text{SiO}_2) + \int_{298}^{800} C_p dT \\ &= \Delta H_{298}^{\circ}(\text{SiO}_2) + \int_{298}^{800} 43.89 + 1.00 \times 10^{-3} T - 6.02 \times 10^5 T^{-2} dT \\ &= \Delta H_{298}^{\circ}(\text{SiO}_2) + \left[43.89 T + 0.50 \times 10^{-3} T^2 + 6.02 \times 10^5 T^{-1} \right]_{298}^{800} \\ &= -910,900 + 21,041 = \boxed{-889,859 \text{ J}}\end{aligned}$$

$$\begin{aligned}\Delta H_{800}(\text{N}_2) &= \Delta H_{298}^{\circ}(\text{N}_2) + \int_{298}^{800} C_p dT \\ &= \int_{298}^{800} 27.87 + 4.27 \times 10^{-3} T dT \quad (\because \Delta H_{298}^{\circ}(\text{N}_2) = 0) \\ &= \left[27.87 T + \frac{1}{2} \times 4.27 \times 10^{-3} T^2 \right]_{298}^{800} = \boxed{15,168 \text{ J}}\end{aligned}$$

$$\Rightarrow \Delta H_{\text{total}} = 3(-889,859) + 2 \times 15,168 + 682,196 - 3 \times 15,840 = \boxed{-2,004,585 \text{ J}}$$

$$\begin{aligned}\Delta H_{800}(\text{Si}_3\text{N}_4) &= \Delta H_{298}^{\circ}(\text{Si}_3\text{N}_4) + \int_{298}^{800} C_p dT \\ &= \Delta H_{298}^{\circ}(\text{Si}_3\text{N}_4) + \int_{298}^{800} 70.54 + 98.74 \times 10^{-3} T dT \\ &= -744,800 + 62,624 = \boxed{-682,176 \text{ J}}\end{aligned}$$

$$\begin{aligned}\Delta H_{800}(\text{O}_2) &= \Delta H_{298}^{\circ}(\text{O}_2) + \int_{298}^{800} C_p dT \\ &= \int_{298}^{800} 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} dT \\ &= \boxed{15,840 \text{ J}}\end{aligned}$$

$$\Delta S_{800} = 3\Delta S_{800}(\text{SiO}_2) + 2\Delta S_{800}(\text{N}_2) - \Delta S_{800}(\text{Si}_3\text{N}_4) - 3\Delta S_{800}(\text{O}_2)$$

$$\begin{aligned}\Delta S_{800}(\text{SiO}_2) &= \Delta S_{298}^{\circ}(\text{SiO}_2) + \int_{298}^{800} \frac{C_p}{T} dT \\ &= \Delta S_{298}^{\circ}(\text{SiO}_2) + \int_{298}^{800} 43.89 \cdot T^{-1} + 1.00 \times 10^{-3} - 6.02 \times 10^5 T^{-3} dT \\ &= \Delta S_{298}^{\circ}(\text{SiO}_2) + \left[43.89 \cdot \ln T + 1.00 \times 10^{-3} T + \frac{1}{2} \times 6.02 \times 10^5 T^{-2} \right]_{298}^{800} \\ &= 41.5 + 40.9 = \boxed{82.4 \text{ J/K}}\end{aligned}$$

$$\begin{aligned}\Delta S_{800}(\text{N}_2) &= \Delta S_{298}^{\circ}(\text{N}_2) + \int_{298}^{800} \frac{C_p}{T} dT \\ &= \Delta S_{298}^{\circ}(\text{N}_2) + \int_{298}^{800} 27.87 \cdot T^{-1} + 4.27 \times 10^{-3} dT \\ &= \Delta S_{298}^{\circ}(\text{N}_2) + \left[27.87 \cdot \ln T + 4.27 \times 10^{-3} T \right]_{298}^{800} \\ &= 191.5 + 29.7 = \boxed{221.2 \text{ J/K}}\end{aligned}$$

$$\begin{aligned}\Delta S_{800}(\text{Si}_3\text{N}_4) &= \Delta S_{298}^{\circ}(\text{Si}_3\text{N}_4) + \int_{298}^{800} \frac{C_p}{T} dT \\ &= 113.0 + \int_{298}^{800} 70.54 T^{-1} + 98.74 \times 10^{-3} dT \\ &= 113.0 + 119.2 = \boxed{232.2 \text{ J/K}}\end{aligned}$$

$$\begin{aligned}\Delta S_{800}(\text{O}_2) &= \Delta S_{298}^{\circ}(\text{O}_2) + \int_{298}^{800} \frac{C_p}{T} dT \\ &= 205.1 + \int_{298}^{800} 29.96 T^{-1} + 4.18 \times 10^{-3} - 1.67 \times 10^5 T^{-3} dT \\ &= 205.1 + 30.9 = \boxed{236.0 \text{ J/K}}\end{aligned}$$

$$\Rightarrow \Delta S_{\text{total}} = 3 \times 82.4 + 2 \times 221.2 - 232.2 - 3 \times 236.0 = \boxed{-250.6 \text{ J/K}}$$

$$\Delta G = \Delta H - T\Delta S = -2,004,585 \text{ J} + 800 \text{ K} \times 250.6 \text{ J/K} = -1,804,105 \text{ J}$$

$$\rightarrow \Delta C_p = 0 \text{ ok then } \Delta H_{800} = \Delta H_{298}^{\circ}, \Delta S_{800} = \Delta S_{298}^{\circ} \text{ 0/02}$$

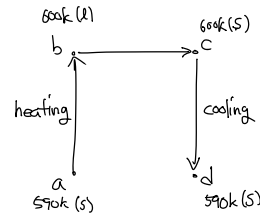
$$\Delta G = \Delta H_{800} - T\Delta S_{800} = -1,947,900 \text{ J} + 800 \text{ K} \times 220.8 \text{ J/K} = -1,811,260 \text{ J}$$

$$\Rightarrow \text{error} = \frac{|1,804,105 - 1,811,260|}{1,804,105} = 0.4\% \text{ error}$$

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



(1) 과정을 나누어 생각해보자.

- a → b : super-cooling 된 1mol의 액상이 590K에서 600K까지 heating 될.
- b → c : 액상 Pb가 600K에서 응고됨
- c → d : 과냉 Pb가 600K에서 590K로 cooling 될

$$\Delta S_{ad} = \Delta S_{ab} + \Delta S_{bc} + \Delta S_{cd}$$

$$\begin{aligned} \Delta S_{ab} &= \int_{590}^{600} \frac{C_p}{T} dT \quad (\text{Pb}_l \text{에 대한 } C_p = 32.4 - 3.1 \times 10^{-3} T \text{ J/K}) \\ &= \int_{590}^{600} (32.4 T^{-1} - 3.1 \times 10^{-3}) dT \\ &= \left[32.4 \ln T - 3.1 \times 10^{-3} T \right]_{590}^{600} \\ &= 0.514 \text{ J/K} \end{aligned}$$

$$\Delta S_{bc} = \frac{q_{rev}}{T} = \frac{-4810 \text{ (응고열)}}{600} = -8.017 \text{ J/K}$$

$$\begin{aligned} \Delta S_{cd} &= \int_{600}^{590} \frac{C_p}{T} dT \quad (\text{Pb}_s \text{에 대한 } C_p = 23.6 + 9.75 \times 10^{-3} T \text{ J/K}) \\ &= \int_{600}^{590} (23.6 T^{-1} + 9.75 \times 10^{-3}) dT \\ &= -0.494 \text{ J/K} \end{aligned}$$

$$\Rightarrow \Delta S_{ad} = 0.514 - 8.017 - 0.494 = -7.997 \text{ J/K}$$

system의 총 엔탈피는 열역학 제 1 법칙에 의해 계산 됨

$$\Delta H_{ad} = \Delta H_{ab} + \Delta H_{bc} + \Delta H_{cd}$$

$$\begin{aligned} \Delta H_{ab} &= \int_{590}^{600} C_p dT \\ &= \int_{590}^{600} (32.4 - 3.1 \times 10^{-3} T) dT \\ &= 306 \text{ J} \end{aligned}$$

$$\Delta H_{bc} = -4810 \text{ J}$$

$$\begin{aligned} \Delta H_{cd} &= \int_{600}^{590} C_p dT \\ &= \int_{600}^{590} (23.6 + 9.75 \times 10^{-3} T) dT \\ &= -294 \text{ J} \end{aligned}$$

$$\Rightarrow \Delta H_{ad} = 306 - 4810 - 294 = -4798 \text{ J}$$

$$\rightarrow \Delta H_{\text{heat reservoir}} = 4799 \text{ J}$$

$$\Rightarrow \Delta S_{\text{res}} = \frac{4799}{590} = 8.134 \text{ J/K}, \quad \Delta S_{\text{univ}} = -7.997 + 8.134 = 0.137 \text{ J/K} > 0, \text{ 즉 자발적 reaction}$$

(2) Use the minimum Gibbs Energy criterion

$$\Delta S_{\text{univ}} = 0.137 \text{ J/K}, \quad \Delta H_{ad} = -4799 \text{ J}, \quad \Delta S_{ad} = -7.997 \text{ J/K}$$

$$\Delta G_{\text{system}} = \Delta H - T \Delta S = -4799 - 590 \times (-7.997) = -80.11 \text{ J} < 0 \text{ 이므로 자발적 반응}$$

(3) Show that the reaction becomes more irreversible at 550K.

$$\Delta S_{ab} = \int_{550}^{600} 32.4 T^{-1} - 3.1 \times 10^{-3} dT = 2.664 \text{ J/K}$$

$$\Delta S_{bc} = -\frac{4810}{600} = -8.017 \text{ J/K}$$

$$\Delta S_{cd} = \int_{600}^{550} 23.6 T^{-1} + 9.75 \times 10^{-3} dT = -2.541 \text{ J/K}$$

$$\Delta S_{total} = 2.664 - 8.017 - 2.541 = -7.894$$

$$\Delta H_{ab} = \int_{550}^{600} 32.4 - 3.1 \times 10^{-3} T dT = 1530.88 \text{ J}$$

$$\Delta H_{bc} = -4.810 \text{ J}$$

$$\Delta H_{cd} = \int_{600}^{550} 23.6 + 9.75 \times 10^{-3} T dT = -1460.31 \text{ J}$$

$$\Delta H_{total} = 1530.88 - 4.810 - 1460.31 = -4.739.43 \text{ J}$$

$$\Rightarrow \Delta G = \Delta H - T\Delta S = -4.739.43 - 550 \times (-7.894) = -397.73 \text{ J} < 0 \text{ 이므로 } -80.77 \text{ J/mol 이므로 more irreversible 하다.}$$

(4) What is the difference between the entropy criterion and Gibbs energy criterion?

$\Rightarrow \Delta S$ 는 오히려 크면 자발적인 반응, but ΔS 가 positive 값을 가져도 항상 해당 반응이 일어나는 것은 아니다.

하지만 ΔG 는 부호에 따라 해당 반응의 자발/비자발이 확실히 구분 가능하다.

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

위와 같은 adiabatic 상황이라면, 액상과 고상이 혼재하는 상태가 될 것이다.

(잠열로 인한 현상)