AMSE205 Thermodynamics I

due date: Oct. 27, 2022 — Prof. Byeong-Joo Lee

Problem Set #3

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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

$$Si_3N_4 + 3\ O_2 = 3\ SiO_2\ (\alpha\text{-quartz}) + 2\ N_2$$

   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.)

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

   (1) Use the maximum entropy criterion
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   (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.

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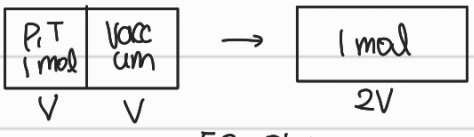
Sol) (a) 

$\Delta U = q - W$

자유팽창 ⇒ 등온, 일 X

$\therefore \Delta U = 0$, $\Delta H = 0$

ΔS는 상태함수 이므로 등온팽창일 경우로 생각가능 $\Delta S = \frac{nRT\ln 2}{T} = nR\ln 2$ ← $W = \int pdV \Rightarrow nRT\ln\frac{2V}{V} = nRT\ln 2 = q$

$\Rightarrow n = 1\,mol$ $\therefore \Delta S = R\ln 2$

$\Delta G = \Delta H - T\Delta S = 0 - RT\ln 2 = -RT\ln 2$

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

(b) 가역단열 팽창. 1mol $P \to P_2$ $T_1 \to T_2$

단열이므로 $q = 0$ $\Delta U = -W$

$\Delta U = nC_V\Delta T = C_V(T_2 - T_1)$ $\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$

$\Delta S = \int \frac{dq_{rev}}{T} = 0$ $(\because q = 0)$

$dG = dH - TdS - SdT \to \int dG = \Delta H - S\int_{T_1}^{T_2} dT = \Delta H - S(T_2 - T_1) = (T_2 - T_1)(C_p - S)$

$dF = dU - TdS - SdT \to \Delta F = \int_{U_1}^{U_2} dU - S\int_{T_1}^{T_2} dT$

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

(c) constant pressure expansion 1mol $V_1 \to V_2$ $T_1 \to T_2$

$\Delta U = nC_V\Delta T = C_V(T_2 - T_1)$ $\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$ $q = \Delta U + W$, $dq = dU + pdV = C_V dT + pdV$

$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{C_V dT + pdV}{T} = C_V\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$

$= C_V\ln\frac{T_2}{T_1} + R\ln\frac{T_2}{T_1}$ $\left(\frac{T_2}{T_1} = \frac{V_2}{V_1}\right)$

$= C_p\ln\frac{T_2}{T_1}$

$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2S_2 - T_1S_1)$

$= \Delta H - (T_2(S_1 + \Delta S) - T_1S_1)$

$= \Delta H - S_1(T_2 - T_1) - T_2\Delta S$

$$\Delta F = \Delta U - \Delta(TS)$$
$$= \Delta U - (T_2S_2 - T_1S_1)$$
$$= \Delta U - (T_2(S_1 + C_p \ln\frac{T_2}{T_1}) - T_1S_1)$$
$$= \Delta U - S_1(T_2 - T_1) - T_2 C_p \ln\frac{T_2}{T_1}$$

(d) constant volume $P_1 \to P_2$ $T_1 \to T_2$

$$\Delta U = nC_v\Delta T = C_v(T_2 - T_1)$$
$$\Delta H = nC_p\Delta T = C_p(T_2 - T_1)$$
$$\Delta S = \int \frac{\delta q_{rev}}{T} = \int \frac{\delta q_v}{T} = \int_{T_1}^{T_2} \frac{C_v}{T} dT = C_v \ln\frac{T_2}{T_1}$$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2S_2 - T_1S_1)$$
$$= \Delta H - (T_2(S_1 + \Delta S) - T_1S_1)$$
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2. Calculate the value of ΔG for the reaction

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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.)

Sol)

$$Si_3N_4 + 3O_2 \rightleftarrows 3SiO_2(\alpha) + 2N_2$$

$$\Delta H^\circ_{298} = 3\Delta H^\circ_{SiO_2} - \Delta H^\circ_{Si_3N_4} = -3 \times 910900 + 744800$$
$$= -1987900\ J/mol$$

$$\Delta S^\circ_{298} = 3S^\circ_{SiO_2} + 2S^\circ_{N_2} - S^\circ_{Si_3N_4} - 3S^\circ_{O_2}$$
$$= 3 \times 41.5 + 2 \times 191.5 - 113.0 - 3 \times 205.1$$
$$= -220.8\ J/mol \cdot K$$

$$\Delta C_p = 2C_{p,N_2} + 3C_{p,SiO_2} - C_{p,Si_3N_4} - 3C_{p,O_2}$$
$$= 2(27.87 + 4.27 \times 10^{-3}T) + 3(43.89 + 1 \times 10^{-3}T - 6.02 \times 10^5 T^{-2})$$

$$-(70.54+98.74\times10^{-3}T)-3(29.96+4.18\times10^{-3}T-1.67\times10^{5}T^{-2})$$

$$=26.99-99.74\times10^{-3}T-13.05\times10^{5}T^{-2}$$

$$\Delta G^{\circ}_{800}=\Delta H^{\circ}_{298}-800\Delta S^{\circ}_{298}+\underbrace{\int_{298}^{800}\Delta C_p dT}_{-16687.1}-800\underbrace{\int_{298}^{800}\frac{\Delta C_p}{T}dT}_{-29.7445}$$

$$=-198790+800\times220.8-16681.1+800\times29.7445$$

$$=-1.804\times10^{6}\ J$$

If $\Delta C_p=0$, $\Delta G^{\circ\prime}_{800}=-198790+800\times220.8=-1.81126\times10^{6}$

$$=\Delta H^{\circ}_{298}-800\Delta S^{\circ}_{298}$$

$$\therefore error=\frac{\Delta G^{\circ\prime}_{800}-\Delta G^{\circ}_{800}}{\Delta G^{\circ}_{800}}=\text{약 } 0.4\%$$

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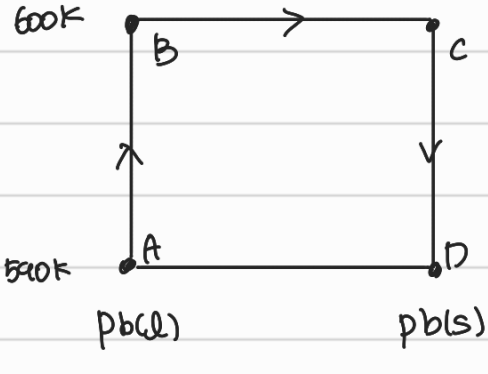

Liquid Pb n mol 가정.

단열X → 모두 자연적으로 응고.

3.

Sol) (1) $A \to B \to C \to D$ 경로

$$\Delta S_{(A\to D)} = \Delta S_{(A\to B)} + \Delta S_{(B\to C)} + \Delta S_{(C\to D)}$$

$$\Delta S_{(A\to B)} = \int_{590}^{600} \frac{n C_{p(g)}}{T} dT = \int_{590}^{600} n\left(\frac{32.4}{T} - 3.1\times10^{-3}\right) dT$$

$$= 0.514 \times n \ J/K$$

$$\Delta S_{(B\to C)} = \frac{q_p}{T} = \frac{\Delta H_m}{T} = \frac{-4810}{T} \times n = \frac{-4810}{600} n = -8.017 n \ J/K$$

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

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

$\therefore \Delta S_{(A\to D)} = 0.514n - 8.017n - 0.494n = -7.997n \ J/K$

$\hookrightarrow \Delta S_{계}$

$\Delta S_{주위}$ 구하기!

$$\Delta H_{(A\to D)} = \Delta H_{(A\to B)} + \Delta H_{(B\to C)} + \Delta H_{(C\to D)}$$

$$\Delta H_{(A\to B)} = \int_{590}^{600} n C_{p(g)} dT = \int_{590}^{600} n(32.4 - 3.1\times10^{-3}T) dT$$

$$= 306 n$$

$$\Delta H_{(B\to C)} = -n \times 4810 J$$

$$\Delta H_{(C\to D)} = \int_{600}^{590} n C_{p(s)} dT = \int_{600}^{590} n(23.6 + 9.75\times10^{-3}T) dT$$

$$= -294 n$$

$$\Delta H_{(A\to D)} = 306n - 4810n - 294n = -4798n$$

$$\Delta S_{주위} = n\frac{4798}{590} = 8.132n \ J/K$$

$\Delta S_{계} + \Delta S_{주위} = \Delta S_{tot} = -7.997n + 8.312n = 0.315n \ J/K > 0$

$\therefore$ 자발적 reaction.

(2) $\Delta G = \Delta H_{(A\to D)} - T\Delta S_{(A\to D)}$ ($\Delta S_{계}$)

$$= -4798n - 590(-7.997n)$$

$$= -9.03n < 0 \quad \therefore \text{자발적 반응}$$

(3) 550K

Equal 하게 풀기

$\Delta S_{(A\to D)} = \Delta S_{(A\to B)} + \Delta S_{(B\to C)} + \Delta S_{(C\to D)}$ $\quad 2.664n$

$\Delta S_{(A\to B)} = \int_{550}^{600} \frac{nC_p}{T} dT = \int_{550}^{600} n \frac{32.4}{T} - 3.1\times10^{-3}\, dT$

$\Delta S_{(B\to C)} = \frac{Q_p}{T} = \frac{\Delta H_m}{T} = -8.01n$

$\Delta S_{(C\to D)} = \int_{600}^{550} \frac{nC_p}{T} dT = \int_{600}^{550} n\left(\frac{23.6}{T} + 9.75\times10^{-3}\right) dT$

$= -2.541n$

$\Delta S_{(A\to D)} = 2.664n - 8.01nn - 2.541n = -n.894n$ J/K

$\Delta H_{(A\to D)} = \Delta H_{(A\to B)} + \Delta H_{(B\to C)} + \Delta H_{(C\to D)}$

$\Delta H_{(A\to B)} = \int_{550}^{600} n(32.4 - 3.1\times10^{-3}T)\, dT = 1531n$ J/K

$\Delta H_{(B\to C)} = -4810n$

$\Delta H_{(C\to D)} = \int_{600}^{550} n(23.6 + 9.75\times10^{-3}T) dT$

$= -1460n$ J/K

$\Delta H_{(A\to D)} = 1531n - 4810n - 1460n = -4n39n$ J/K

$\Delta S_{surr} = \frac{+4n39n}{T} = \frac{+4n39n}{550} = 8.616n$ J/K

$\Delta S_{irr} = \Delta S_{(A\to D)}^{sys} + \Delta S_{surr} = 8.616n - n.894n$

$= 0.n22n$ J/K

∴ $\Delta S_{irr,500} > \Delta S_{irr,590}$ 이므로 더욱 Irreversible

(4) Entropy criterion은 주위와 계 모두의 ΔS를 구하여 우주의 엔트로피 변화를 통해 자발성을 확인하였으며, Gibbs energy criterion은 계(system의) ΔH와 ΔS 만으로도 자발성을 확인할 수 있다.

4.

Sol) 단열용기이기 때문에 보온되어 있었다면 자발적으로 만들어진 고체와 빠져나가지 못한 잠열로인한 액체상의 공존이 이루어 질것 이다.

이때 n몰의 납이 있고, 몰을 x만큼 응고되어있다 할때,

A→B→C 과정을 가정하였을때.

$$\Delta H_{(A\to C)} = \Delta H_{(A\to B)} + \Delta H_{(B\to C)} = q_p = 0 \quad (\text{Adiabatic})$$

$$\Delta H_{(A\to B)} = \int_{590}^{600} nC_{p(l)}\,dT$$

$$= \int_{590}^{600} n(32.4 - 3.1\times10^{-3}T)\,dT$$

$$= 306n$$

$$\Delta H_{(B\to C)} = -4810 \cdot nx$$

$$\Delta H_{(A\to B)} = -\Delta H_{(B\to C)}$$

$$306 = +4810x$$

$$x = +\frac{306}{4810} = 0.064$$

└ 몰을 0.064 만큼 응고↑ & 나머지 액체와 공존.