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
   (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.]

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(a) 진공 자유팽창

→ $\Delta U = \Delta H = 0$

$\Delta S = nR\ln\frac{V_2}{V_1} = R\ln 2$

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

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

(b) 가역단열 팽창

→ $q = 0$

$\Delta U = nC_v dT = C_v(T_2 - T_1)$

$\Delta H = nC_p dT = C_p(T_2 - T_1)$

$\Delta S = \frac{q_{rev}}{T} = 0$

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

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

entropy의 absolute value가 필요함

(c) 등압 팽창

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

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

$\Delta S = \int \frac{C_p}{T} dT = C_p \ln\left(\frac{T_2}{T_1}\right)$

$\Delta F = \Delta U - \Delta(ST)$

$= \Delta U - (T_2S_2 - T_1S_1)$

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

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

$\Delta G = \Delta H - \Delta(ST)$

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

(d) 등적

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

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

$\Delta S = C_v \ln\left(\frac{T_2}{T_1}\right)$

$\Delta F = \Delta U - S_1(T_2 - T_1) - T_2\Delta S$

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

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.)

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

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

$$H_{N_2,800} = H_{N_2,298} + \int_{298}^{800} C_{PN_2}\,dT$$

$$= \left[27.87(800-298) + \frac{(4.27\times10^{-3})}{2}(800^2 - 298^2)\right]$$

$$= 15196.5\ J$$

$$H_{SiO_2,800} = H_{SiO_2,298} + \int_{298}^{800} C_{PSiO_2}\,dT$$

$$= -910900 + \left[43.89(800-298) + \frac{1.00\times10^{-3}}{2}(800^2 - 298^2) + (6.02\times10^5)\left(\frac{1}{800} - \frac{1}{298}\right)\right]$$

$$= -889859\ J$$

$$H_{O_2,800} = H_{O_2,298} + \int_{298}^{800} C_{PO_2}\,dT$$

$$= \left[29.96(800-298) + \frac{(4.18\times10^{-3})}{2}(800^2 - 298^2) + (1.67\times10^5)\left(\frac{1}{800} - \frac{1}{298}\right)\right]$$

$$= 15840.3\ J$$

$$H_{Si_3N_4,800} = H_{Si_3N_4,298} + \int_{298}^{800} C_{PSi_3O_4}\,dT$$

$$= -744800 + \left[70.54(800-298) + \frac{(98.74\times10^{-3})}{2}(800^2 - 298^2)\right]$$

$$= -682176\ J$$

$$\therefore \Delta H_{800} = 2\times15169.5 + 3\times(-889859) - 1\times(-682176) - 3\times15840.3$$

$$= -2004589\ J$$

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

$$S_{N_2,800} = S_{N_2,298} + \int_{298}^{800} \frac{C_{PN_2}}{T} dT$$

$$= 191.5 + \left[29.89 \ln\left(\frac{800}{298}\right) + (4.29 \times 10^{-3})(800 - 298) \right]$$

$$= 221.16 \text{ J/k·mol}$$

$$S_{SiO_2,800} = S_{SiO_2,298} + \int_{298}^{800} \frac{C_{PSiO_2}}{T} dT$$

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

$$= 82.4 \text{ J/k·mol}$$

$$S_{Si_3N_4,800} = S_{Si_3N_4,298} + \int_{298}^{800} \frac{C_{PSi_3N_4}}{T} dT$$

$$= 113.0 + \left[70.5 \ln\left(\frac{800}{298}\right) + (98.74 \times 10^{-3})(800 - 298) \right]$$

$$= 232 \text{ J/k·mol}$$

$$S_{O_2,800} = S_{O_2,298} + \int_{298}^{800} \frac{C_{PO_2}}{T} dT$$

$$= 205.1 + \left[29.96 \ln\left(\frac{800}{298}\right) + (4.18 \times 10^{-3})(800 - 298) - \frac{(1.67 \times 10^5)}{2}\left(\frac{1}{800^2} - \frac{1}{298^2}\right) \right]$$

$$= 236.2 \text{ J/k·mol}$$

$$\therefore \Delta S_{800} = 2 \times 221.16 + 3 \times 82.4 - 232 - 3 \times 236.2$$

$$= -250.2 \text{ J/K·mol}$$

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

$$= -2004587 - 800 \cdot (-250.2)$$

$$= -1804429 \text{ J}$$

if) $\Delta C_P = 0$

$$\Rightarrow \Delta H_{298} - T\Delta S_{298}$$

$$= (-3 \times 910900 + 744800) - (800)(2 \times 191.5 + 3 \times 41.5 - 3 \times 205.1 - 113.0)$$

$$= -1811000 \text{ J}$$

$$\text{오차} = \frac{1811000 - 1804429}{1804429} \times 100 = 0.36\%$$

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step a, b, c, d

a → b : 1 mole의 과냉된 액상이 590k → 600k로 heating

b → c : 액상 Pb가 600k에서 응고됨

c → d : 고체 Pb가 600k → 590k cooling 됨

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

$\Delta S_{a\to b} = \int_{590}^{600} \frac{C_p}{T} dT$

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

$= 32.4\ln\left(\frac{600}{590}\right) - 3.1\times10^{-3}(600-590) = 0.514\ J/K$

$\Delta S_{b\to c} = \frac{Q_{rev}}{T} = \frac{-4810}{600} = -8.017\ J/K$

$\Delta S_{c\to d} = \int_{600}^{590} \frac{23.6}{T} + 9.75\times10^{-3}\, dT = -0.494\ J/K$

$\Delta S_{a\to d} = 0.514 - 8.017 - 0.494 = -7.997\ J/K$

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

$\Delta H_{a\to b} = \int_{590}^{600} 32.4 - 3.1\times10^{-3}T\, dT$

$= 306\ J$

$\Delta H_{b\to c} = -4810\ J$

$\Delta H_{c\to d} = \int_{600}^{590} 23.6 + 9.75\times10^{-3}T\, dT$

$= -294\ J$

$\Delta H_{a\to d} = 306 - 4810 - 294$

$= -4799\ J$

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

$\Delta S_{res} = \frac{4799}{590} = 8.134\ J/K$

$\Delta S_{irr} = -7.999 + 8.314 = 0.317\ J/K > 0$

(2) $\Delta S_{irr} = 0.137\,J/K$ $\Delta S_{a\to d} = -7.997\,J/K$

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

$\Delta G = \Delta H - T\Delta S = -4799 - 590(0.137) \Rightarrow$ 전체 계

$= -4879.83\,J < 0$

$\Delta G = \Delta H - T\Delta S = -4799 - 590(-7.997) \Rightarrow$ system

$= -80.77\,J < 0$

(3) 550 K

$\Delta S_{a\to b} = 32.4 \ln\left(\frac{600}{550}\right) - 3.1\times10^{-3}(600-550)$

$= 2.664\,J/K$

$\Delta S_{b\to c} = -\frac{4810}{600} = -8.017\,J/K$

$\Delta S_{c\to d} = 23.6 \ln\left(\frac{550}{600}\right) + 9.75\times10^{-3}(550-600) = -2.54\,J/K$

$\Delta S_{tot} = -7.893\,J/K$

$\Delta H_{a\to b} = 32.4(600-550) - 1.55\times10^{-3}(600^2-550^2)$

$= 1530.875\,J$

$\Delta H_{b\to c} = -4810\,J$

$\Delta H_{c\to d} = 23.6(550-600) + \frac{9.75}{2}\times10^{-3}\times(550^2-600^2) = -1460.313\,J$

$\Rightarrow \Delta H_{tot} = -4939.438\,J$

$\Delta S_{heat\ reservoir} = \frac{4939.438}{550} = 8.617\,J$

$\Delta S_{irr} = -7.893 + 8.617 = 0.724\,J/K$

$0.724 > 0.137 \rightarrow$ 자발적이다.

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

$= 0 - 550\cdot 0.724$

$= -398.2\,J < 0$

$\Rightarrow$ more irreversible!

(4) 먼저, 가장 큰 차이는 ΔS는 계와 reservoir를 모두 고려해야하고,
ΔG는 계의 ΔH, ΔS 만으로 자발성을 확인할 수 있다는 점이다.
또한, ΔS는 0보다 크면 자발적이라는 것을 알 수 있지만, 무조건 $\Delta S > 0$ 라고
반응이 일어나지는 않는다. 그래서 보통 자발성을 확인할 때는 ΔG 값을 사용한다.
$\Delta G = \Delta H - T\Delta S$ 에서 ΔS가 (+) 값이라도 ΔH의 값까지 정확히 계산한 후,
자발성을 확인해야한다. 이 둘은 이러한 부분에서 차이가 난다.

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

isothermal의 경우
→ latent of heat (잠열)을 heat reservoir가 뺀다.

adiabatic의 경우
→ 상변화가 일어났을 때 열출입이 없으므로 잠열은 갈 곳이 없다.
→ 이 잠열은 온도를 600K 까지 올려지만, 모두 고상으로, 모두 액상으로 바뀌지는 않을 것이다.
⇒ 따라서 solid 상과 liquid 상이 공존을 이룰 것이다.