

Physical Chemistry 1

Homework #3 solutions

1. (a) 단열 팽창이므로 $q = 0$

$$(b) \quad w = -p_{ex} \Delta V = -(1 \text{ atm}) \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \times (10 \text{ cm}^2) \times (20 \text{ cm}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \\ = -20.26 \text{ J}$$

$$(c) \quad \Delta U = q + w = 0 \text{ J} - 20.26 \text{ J} = -20.26 \text{ J}$$

(d) $\Delta U = n C_{V,m} \Delta T$ 이므로

$$\Delta T = \frac{\Delta U}{n C_{V,m}} = \frac{-20.26 \text{ J}}{(2 \text{ mol}) \times (28.8 \text{ J K}^{-1} \text{ mol}^{-1})} = -0.35 \text{ K}$$

(e) 위 과정은, 일정부피에서 온도를 낮추고 난 후 등온 팽창한 과정과 동일하다.
일정부피에서 온도에 따른 엔트로피 변화는

$$S(T_f) = S(T_i) + C_V \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_V \ln \left(\frac{T_f}{T_i} \right) \text{ 이므로}$$

$$\Delta S = n C_{V,m} \ln \left(\frac{T_f}{T_i} \right) \text{ 이고,}$$

이상기체의 등온 팽창에서 $\Delta S = nR \ln \left(\frac{V_f}{V_i} \right)$ 이다. 따라서

$$\Delta S = \Delta S_1 + \Delta S_2 = n C_{V,m} \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right)$$

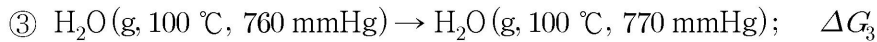
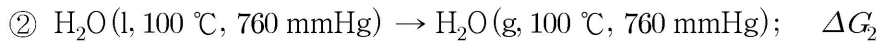
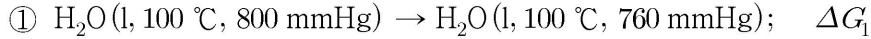
$$T_f = 298.15 \text{ K} - 0.35 \text{ K} = 297.80 \text{ K}$$

$$V_i = \frac{nRT_i}{p_i} = \frac{(2 \text{ mol}) \times (8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{10 \text{ atm}} \\ = 4.89 \text{ dm}^3$$

$$V_f = 4.89 \text{ dm}^3 + (10 \text{ cm}^2) \times (20 \text{ cm}) \times \left(\frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \right) \\ = 4.89 \text{ dm}^3 + 0.20 \text{ dm}^3 = 5.09 \text{ dm}^3$$

$$\begin{aligned}\Delta S &= (2 \text{ mol}) \times \left\{ (28.8 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{297.80}{298.15} \right) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln \left(\frac{5.09}{4.89} \right) \right\} \\ &= 2 \text{ mol} \times (-0.03 \text{ J K}^{-1} \text{ mol}^{-1} + 0.33 \text{ J K}^{-1} \text{ mol}^{-1}) = \mathbf{0.60 \text{ J K}^{-1}}\end{aligned}$$

2. G 는 상태함수이므로 다음과 같은 세 과정으로 나누어 생각할 수 있다.



$dG = Vdp - SdT$ 에서 T 는 일정하고, $n = 1 \text{ mol}$ 이므로

$$\begin{aligned}\Delta G_1 &= \int_{800}^{760} V_m^l dp = V_m^l \Delta p \\ &= (0.018 \text{ L mol}^{-1}) \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right) (760 - 800) \text{ mmHg} \left(\frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}} \right) = -0.10 \text{ J}\end{aligned}$$

$$\Delta G_2 = 0 \text{ (상전이)}$$

$$\begin{aligned}\Delta G_3 &= \int_{760}^{770} V_m^g dp = \int_{760}^{770} \frac{RT}{p} dp \text{ (이상기체)} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (373.15 \text{ K}) \ln \frac{770}{760} = 40.54 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{total}} &= \Delta G_1 + \Delta G_2 + \Delta G_3 = -0.10 \text{ J} + 0 \text{ J} + 40.54 \text{ J} \\ &= \mathbf{40.44 \text{ J}}\end{aligned}$$

ΔG_{total} 이 0보다 크므로 비자발적 과정이다.

3. (1) i) $a = 0$ 일 때,

$$p = \frac{nRT}{V - nb} = \frac{RT}{(V_m - b)}, \quad V_m = \frac{RT}{p} + b$$

$$\text{따라서, } Z = \frac{pV_m}{RT} = 1 + \frac{bp}{RT}$$

$$\ln \phi = \int_0^p \frac{(Z-1)}{p} dp = \int_0^p \left(\frac{b}{RT} \right) dp = \frac{bp}{RT}$$

$$\therefore \phi = \exp\left(\frac{bp}{RT}\right)$$

$$\text{ii) } f = p \times \exp\left(\frac{bp}{RT}\right)$$

$$p = 10.00 \text{ atm}, T = 298.15 \text{ K}, b = 3.707 \times 10^{-2} \text{ L mol}^{-1} \text{ 이므로, } \frac{bp}{RT} = 0.015$$

$$\therefore f = p \times \exp\left(\frac{bp}{RT}\right) = (10.00 \text{ atm}) \times e^{0.015} = \mathbf{10.15 \text{ atm}}$$

(2) i) $b = 0$ 일 때,

$$\left(p + a \frac{1}{V_m^2}\right) V_m = RT \text{ 에서, } pV_m^2 - RTV_m + a = 0 \text{ 이 된다.}$$

$$\text{그러면 } V_m = \frac{RT \pm \sqrt{R^2 T^2 - 4pa}}{2p} \text{ 이고,}$$

$$Z = \frac{pV_m}{RT} = \frac{1 + \sqrt{1 - \frac{4pa}{R^2 T^2}}}{2}$$

$$\frac{4pa}{R^2 T^2} \ll 1 \text{ 이므로, } \left(1 - \frac{4pa}{R^2 T^2}\right)^{\frac{1}{2}} \approx 1 - \frac{2pa}{R^2 T^2}$$

$$\therefore Z = \frac{1 + 1 - \frac{2pa}{R^2 T^2}}{2} = 1 - \frac{pa}{R^2 T^2}$$

$$Z - 1 = -\frac{pa}{R^2 T^2}$$

$$\ln \phi = \int_0^p \frac{(Z-1)}{p} dp = \int_0^p -\left(\frac{a}{R^2 T^2}\right) dp = -\frac{ap}{R^2 T^2}$$

$$\therefore \phi = \exp\left(-\frac{ap}{R^2 T^2}\right)$$

ii) $f = p \times \exp\left(-\frac{ap}{R^2 T^2}\right)$ 이므로, $p = 10.00 \text{ atm}, T = 298.15 \text{ K},$

$$a = 4.225 \text{ L}^2 \text{ atm mol}^{-1} \text{ 를 대입하면, } \frac{ap}{R^2 T^2} = 0.07$$

$$\therefore f = p \times \exp\left(-\frac{ap}{R^2 T^2}\right) = (10.00 \text{ atm}) \times e^{-0.07} = \mathbf{9.32 \text{ atm}}$$

4. 두 개의 iron block의 질량이 같고 열용량이 상수이기 때문에 최종상태의 온도는 초기 두 온도의 평균과 같다.

$$T = \frac{1}{2}(300 \text{ }^\circ\text{C} + 25 \text{ }^\circ\text{C}) = 162.5 \text{ }^\circ\text{C}$$

$$\text{각각의 } \Delta H = mC\Delta T$$

$$= (1 \times 10^3 \text{ g}) \times (0.519 \text{ JK}^{-1}\text{g}^{-1}) \times (\pm 137.5 \text{ K})$$

$$= \pm 71362.5 \text{ J} = \pm \mathbf{71.4 \text{ kJ}}$$

$$\therefore \Delta H_{tot} = \mathbf{0 \text{ J}}$$

$$\Delta S = mC \left(\ln \frac{T_f}{T_i} \right)$$

$$\Delta S_1 = (1 \times 10^3 \text{ g}) \times (0.519 \text{ JK}^{-1}\text{g}^{-1}) \times \ln \left(\frac{435.65}{298.15} \right) = 196.83 \text{ J K}^{-1}$$

$$\Delta S_2 = (1 \times 10^3 \text{ g}) \times (0.519 \text{ JK}^{-1}\text{g}^{-1}) \times \ln \left(\frac{435.65}{573.15} \right) = -142.37 \text{ J K}^{-1}$$

$$\therefore \Delta S_{tot} = \Delta S_1 + \Delta S_2 = \mathbf{54.46 \text{ (JK}^{-1}\text{)}}$$

5. 상태 1, 2를 각각 150 °C, 270 °C 때의 상태라 할 때,

$$\Delta S = S_2 - S_1 = nC_p \ln \left(\frac{T_2}{T_1} \right) = (1) \frac{5R}{2} \ln \left(\frac{543.15}{423.15} \right) = \mathbf{5.19 \text{ (J K}^{-1}\text{)}}$$

$$S_2 = 135 + 5.19 = 140.19 \text{ (JK}^{-1}\text{)}$$

$$\Delta H = nC_p \Delta T = (1) \frac{5R}{2} (120) = \mathbf{2494.20 \text{ (J)}}$$

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2 S_2 - T_1 S_1)$$

$$= 2494.20 - [(543.15)(140.19) - (423.15)(135)]$$

$$= \mathbf{-16524.75 \text{ (J)}}$$

ΔG 가 음의 부호를 나타내지만 spontaneous process 여부를 알 수 없다. 왜냐하면, ΔG 는 T, p 모두 일정한 반응에서 음의 부호를 나타낼 때 spontaneous process인데, 위 반응은 일정한 압력은 유지되고 있지만, 온도가 변하는 반응이기 때문이다.