Physical Chemistry 1
Homework #3 solutions

1. (a) 단열팽창이므로 $\boldsymbol{q} = \mathbf{0}$

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

$= \mathbf{-20.26\,J}$

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

(d) $\Delta U = nC_{V,m}\Delta T$ 이므로

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

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

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

$\Delta S = nC_{V,m}\ln\left(\dfrac{T_f}{T_i}\right)$ 이고,

이상기체의 등온팽창에서 $\Delta S = nR\ln\left(\dfrac{V_f}{V_i}\right)$이다. 따라서

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

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

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

$= 4.89\,\text{dm}^3$

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

$= 4.89\ \text{dm}^3 + 0.20\,\text{dm}^3 = 5.09\,\text{dm}^3$

$$\Delta S = (2\,\text{mol}) \times \left\{ (28.8\,\text{J K}^{-1}\text{mol}^{-1}) \times \ln\left(\frac{297.80}{298.15}\right) + (8.314\,\text{J K}^{-1}\text{mol}^{-1}) \times \ln\left(\frac{5.09}{4.89}\right) \right\}$$

$$= 2\,\text{mol} \times (-0.03\,\text{J K}^{-1}\text{mol}^{-1} + 0.33\,\text{J K}^{-1}\text{mol}^{-1}) = \mathbf{0.60\,J\,K^{-1}}$$

2. G는 상태함수이므로 다음과 같은 세 과정으로 나누어 생각할 수 있다.

① H_2O (l, 100 ℃, 800 mmHg) → H_2O (l, 100 ℃, 760 mmHg); ΔG_1

② H_2O (l, 100 ℃, 760 mmHg) → H_2O (g, 100 ℃, 760 mmHg); ΔG_2

③ H_2O (g, 100 ℃, 760 mmHg) → H_2O (g, 100 ℃, 770 mmHg); ΔG_3

$dG = Vdp - SdT$ 에서 T는 일정하고, n = 1 mol이므로

$$\Delta G_1 = \int_{800}^{760} V_m^l\,dp = V_m^l\,\Delta p$$

$$= (0.018\,\text{L mol}^{-1})\left(\frac{10^{-3}\,\text{m}^3}{\text{L}}\right)(760-800)\,\text{mmHg}\left(\frac{1.01325\times10^5\,\text{Pa}}{760\,\text{mmHg}}\right) = -0.10\,\text{J}$$

$\Delta G_2 = 0$ (상전이)

$$\Delta G_3 = \int_{760}^{770} V_m^g\,dp = \int_{760}^{770} \frac{RT}{p}dp \text{ (이상기체)}$$

$$= (8.314\,\text{JK}^{-1}\text{mol}^{-1})(373.15\,\text{K})\ln\frac{770}{760} = 40.54\,\text{J}$$

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

ΔG_{total}이 0보다 크므로 **비자발적 과정**이다.

3. (1) i) a = 0일 때,

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

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

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

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

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

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

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

(2) ⅰ) b = 0일 때,

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

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

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

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

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

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

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

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

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

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

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

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

$$T = \frac{1}{2}(300\ ℃ + 25\ ℃) = 162.5\ ℃$$

각각의 $\triangle H = mC\triangle T$

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

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

$$\therefore \mathbf{\triangle H_{tot} = 0\ J}$$

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

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

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

$$\therefore \boldsymbol{\triangle S_{tot}} = \triangle S_1 + \triangle S_2 = \mathbf{54.46\ (J\,K^{-1})}$$

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

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

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

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

$$\boldsymbol{\Delta G} = \triangle H - \triangle(TS) = \triangle H - (T_2S_2 - T_1S_1)$$

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

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

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