Physical Chemistry 1

Homework #4 solutions

1. (1) 이 물질의 증기가 이상기체이며 몰 증발엔탈피($\Delta_{vap}H_m$)가 온도에 따라 변하지 않으므로 Clausius-Clapeyron 식을 적용한다.

$$p = p^* \exp\left\{\frac{-\Delta_{vap}H_m}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right\} \text{ -------①}$$

$\Delta_{vap}H_m = 32.7\,\mathrm{kJ\,mol^{-1}}$, $T^* = 293.15\,\mathrm{K}$, $p^* = 58.0\,\mathrm{kPa}$, $p = 66.0\,\mathrm{kPa}$ 이므로

①식을 정리하면

$$\ln\left(\frac{p}{p^*}\right) = \frac{-\Delta_{vap}H_m}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)$$

$$\therefore \frac{1}{T}-\frac{1}{T^*} = -\frac{R}{\Delta_{vap}H_m} ln\left(\frac{p}{p^*}\right)$$

$$\frac{1}{T} = \frac{1}{293.15\,\mathrm{K}} - \frac{8.314\,\mathrm{J\,K^{-1}mol^{-1}}}{32.7\times10^3\,\mathrm{J\,mol^{-1}}}\ln\left(\frac{66.0\,\mathrm{kPa}}{58.0\,\mathrm{kPa}}\right) = 3.32\times10^{-3}$$

$\therefore$ **T = 296 K**

(2) (a) $$\left(\frac{\partial\mu(l)}{\partial T}\right)_p - \left(\frac{\partial\mu(s)}{\partial T}\right)_p = -S_m(l) + S_m(s)$$

$$= -\Delta_{fus}S = \frac{-\Delta_{fus}H}{T_f}$$

$$= \frac{-6.01\,\mathrm{kJ\,mol^{-1}}}{273.15\,\mathrm{K}} = -22.0\,\mathrm{J K^{-1}mol^{-1}}$$

(b) $$\left(\frac{\partial\mu(g)}{\partial T}\right)_p - \left(\frac{\partial\mu(l)}{\partial T}\right)_p = -S_m(g) + S_m(l)$$

$$= -\Delta_{vap}S = \frac{-\Delta_{vap}H}{T_b}$$

$$= \frac{-40.6\,\mathrm{kJ\,mol^{-1}}}{373.15\,\mathrm{K}} = -108.8\,\mathrm{J K^{-1}mol^{-1}}$$

2. (a) $\boldsymbol{\Delta H_{sub}} = \dfrac{RT_1T_2}{T_2 - T_1}\ln\dfrac{p_2}{p_1}$

$$= \frac{(8.314\,\mathrm{J\,K^{-1}mol^{-1}})\times(146.65\,\mathrm{K})\times(161.15\,\mathrm{K})}{14.5\,\mathrm{K}}\ln\frac{352}{35}$$

$$= \mathbf{31278.3\,J\,mol^{-1} = 31.3\,kJ\,mol^{-1}}$$

(b) $\boldsymbol{\Delta H_{vap}} = \dfrac{(8.314\,\mathrm{J\,K^{-1}mol^{-1}})\times(173.15\,\mathrm{K})\times(193.15\,\mathrm{K})}{20\,\mathrm{K}}\ln\dfrac{7830}{1590}$

$$= \mathbf{22164.0\,J\,mol^{-1} = 22.2\,kJ\,mol^{-1}}$$

(c) $\boldsymbol{\Delta H_{fus}} = \Delta H_{sub} - \Delta H_{vap}$

$$= 31.3\,\mathrm{kJ\,mol^{-1}} - 22.2\,\mathrm{kJ\,mol^{-1}} = \mathbf{9.1\,kJ\,mol^{-1}}$$

(d) 고체에 대하여 ------①

$$\ln p = \ln 352 + \frac{31278.3}{8.314}\left(\frac{1}{161.15} - \frac{1}{T}\right)$$

$$= 29.21 - \frac{3762.12}{T}$$

액체에 대하여 ------②

$$\ln p = \ln 1590 + \frac{22164}{8.314}\left(\frac{1}{173.15} - \frac{1}{T}\right)$$

$$= 22.77 - \frac{2665.86}{T}$$

삼중점에서 ① = ②이므로

$$29.21 - \frac{3762.12}{T} = 22.77 - \frac{2665.86}{T}$$

$$T = \frac{1096.26}{6.44} = \mathbf{170.2\,K = -103.0\,℃}$$

3. $\dfrac{dp}{dT} = \dfrac{\Delta_{fus}H}{T\Delta_{fus}V}$: Clapeyron 식

$\Delta_{fus}V$를 먼저 구하면

$$V_{water} = \frac{18.0\,\mathrm{g\,mol^{-1}}}{1.00\,\mathrm{g\,cm^{-3}}} = 18.0\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$$

$$V_{ice} = \frac{18.0\ \text{g mol}^{-1}}{0.92\ \text{g cm}^{-3}} = 19.6\times10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

$$\Delta_{fus}V = V_{water} - V_{ice} = -1.6\times10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

스케이트 날에 의해 가해지는 압력을 구하면

$$p = \frac{63\ \text{kg}\times9.8\ \text{m s}^{-2}}{1.0\times10^{-5}\ \text{m}\times0.15\ \text{m}\times2} = 2.06\times10^{8}\ \text{Pa}$$

Clapeyron 식을 양변 적분하면

$$\int_{T_1}^{T_2}\frac{1}{T}dT = \int_{p_1}^{p_2}\frac{\Delta_{fus}V}{\Delta_{fus}H}\,dp,$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{\Delta_{fus}V}{\Delta_{fus}H}(p_2-p_1)$$

$\Delta_{fus}V$, $\Delta_{fus}H$가 변하지 않으므로

$$\boldsymbol{T_2} = 273.15\ \text{K}\times\exp\left[\frac{-1.6\times10^{-6}\ \text{m}^3\,\text{mol}^{-1}}{6009\ \text{J mol}^{-1}}(2.06\times10^{8}-1.103\times10^{5})\text{Pa}\right] = \mathbf{258.6\,K}$$

4. At 1.00 atm, $T_{fus} =$ 427.15 K, $V_m(s) =$ 130.15 $\text{cm}^3\,\text{mol}^{-1}$

At 1.20 MPa, $T_{fus} =$ 429.26 K, $V_m(l) =$ 152.62 $\text{cm}^3\,\text{mol}^{-1}$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{fus}H_m}{T_{fus}\,\Delta_{fus}V_m}$$

$$\int_{p^*}^{p} dp = \int_{T^*}^{T}\frac{\Delta_{fus}H_m}{T_{fus}\,\Delta_{fus}V_m}\,dT$$

$$p - p^* = \frac{\Delta_{fus}H_m}{\Delta_{fus}V_m}\ln\left(\frac{T}{T^*}\right)$$

$$p = p^* + \frac{\Delta_{fus}H_m}{\Delta_{fus}V_m}\ln\left(\frac{T}{T^*}\right)$$

이 때, $\Delta V_m = V_m(l) - V_m(s)$

$= 152.62\ \text{cm}^3\,\text{mol}^{-1} - 130.15\ \text{cm}^3\,\text{mol}^{-1}$

$= 22.47\ \text{cm}^3\,\text{mol}^{-1}$

$$\therefore\ \boldsymbol{\Delta_{fus}H_m} = \frac{(p-p^*)\,\Delta_{fus}V_m}{\ln\left(\frac{T}{T^*}\right)}$$

$$= \frac{\{(1.20\times10^{6}-1.013\times10^{5})\mathrm{Pa}\times(22.47\times10^{-6}\ \mathrm{m^3\ mol^{-1}})\}}{\ln\left(\frac{429.26}{427.15}\right)}$$

$$= \mathbf{5010.2\ (J\ mol^{-1})}$$

$$\therefore \Delta_{fus}S_m = \frac{\Delta_{fus}H_m}{T_{fus}} = \frac{5015.15}{427.15} = \mathbf{11.7\ (J\ mol^{-1}K^{-1})}$$

5. Clapeyron 식에 의해, $\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T\Delta V_{\mathrm{m}}}$

$\Delta V_{\mathrm{m}} = V_{\mathrm{g,m}} - V_{\mathrm{l,m}} = \frac{Z_{\mathrm{g}}RT}{p} - \frac{Z_{\mathrm{l}}RT}{p} = \frac{RT}{p}(Z_{\mathrm{g}} - Z_{\mathrm{l}})$ · · · · · · · · · ①

$\frac{\mathrm{d}(1/T)}{\mathrm{d}T} = -\frac{1}{T^2}$로부터, $\mathrm{d}T = -T^2\mathrm{d}(1/T)$ · · · · · · · · · ②

$\frac{\mathrm{d}(\ln p)}{\mathrm{d}p} = \frac{1}{p}$로부터, $\mathrm{d}p = p\,\mathrm{d}\ln p$ · · · · · · · · · ③

식 ②와 ③으로부터, $\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{p}{T^2}\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}$ · · · · · · · · · ④

식 ①과 ④를 Clapeyron 식에 대입하면,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{p}{T^2}\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T}\frac{1}{\frac{RT}{p}(Z_{\mathrm{g}} - Z_{\mathrm{l}})}$$

$$\therefore \Delta_{\mathrm{vap}}H_{\mathrm{m}} = -\frac{p}{T^2}\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)} \times \frac{RT^2}{p}(Z_{\mathrm{g}} - Z_{\mathrm{l}})$$

$$= -\boldsymbol{R(Z_{\mathrm{g}} - Z_{\mathrm{l}})\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}}$$