

# Physical Chemistry 1

## Exam #1 solutions

1. 한 개의 플라스크 부피를  $V$ 라 할 때, 수소의 몰수  $n$ 은,

$$n = \frac{pV}{RT} = 0.8 = \frac{p \times 2V}{R \times 298} = \frac{1.3 \times 10^5 \times 2V}{R \times 298} \quad (V_1 = V_2 = V)$$

$$\frac{V}{R} = 0.8 \times 298 \times \frac{1}{2.6 \times 10^5}$$

$V_1, V_2$  플라스크에 들어있는 수소의 몰수를 각각  $n_1, n_2$ 라고 할 때, 전체 몰수는 0.8 mol로 변함이 없으므로

$$0.8 = n_1 + n_2$$

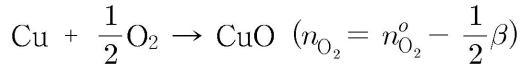
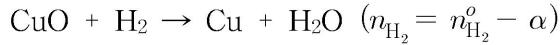
$$\begin{aligned} &= \frac{pV}{R} \left( \frac{1}{T_1} + \frac{1}{T_2} \right) \\ &= \frac{pV}{R} \left( \frac{1}{298} + \frac{1}{398} \right) \\ &= p \times (0.8 \times 298 \times \frac{1}{2.6 \times 10^5}) \times \left( \frac{1}{298} + \frac{1}{398} \right) \\ \therefore p &= 1.49 \times 10^5 \text{ Pa} \end{aligned}$$

$$\begin{aligned} n_1 &= \frac{pV}{R} \left( \frac{1}{298} \right) \\ &= 1.49 \times 10^5 \times (0.8 \times 298 \times \frac{1}{2.6 \times 10^5}) \times \left( \frac{1}{298} \right) \\ &= 0.458 \end{aligned}$$

$$\begin{aligned} n_2 &= \frac{pV}{R} \left( \frac{1}{398} \right) \\ &= 1.49 \times 10^5 \times (0.8 \times 298 \times \frac{1}{2.6 \times 10^5}) \times \left( \frac{1}{398} \right) \\ &= 0.342 \end{aligned}$$

$$\therefore n_1 = 0.458 \text{ mol}, n_2 = 0.342 \text{ mol}$$

2.  $n_{H_2}^o$ : 반응 전  $H_2$  몰 수,  $n_{O_2}^o$ : 반응 전  $O_2$  몰 수,  $n_{H_2}$ : 반응 후  $H_2$  몰 수,  $n_{O_2}$ : 반응 후  $O_2$  몰 수,  $n_{Cu}$ : 환원된 Cu 몰 수,  $\alpha$ :  $H_2$ 에 의해 환원된  $CuO$  몰 수,  $\beta$ :  $O_2$ 에 의해 재 산화된 Cu 몰 수라 하면,



$Cu$ 는  $O_2$ 에 의해 모두 산화되므로,  $\alpha = \beta$

마지막에 나온 기체는  $O_2$ 뿐이므로,  $n_{H_2} = n_{H_2}^o - \alpha = 0$

$$\therefore \alpha = n_{H_2}^o = \beta, \quad n_{O_2} = n_{O_2}^o - \frac{1}{2}n_{H_2}^o$$

174 °C, 750 Torr에서,

$V_1$  = 초기 혼합기체의 부피,  $V_2$  = 남아있는  $O_2$ 의 부피라 하면,

$$V_1 = (n_{H_2}^o + n_{O_2}^o) \frac{RT}{p}$$

$$V_2 = (n_{O_2}^o - \frac{1}{2}n_{H_2}^o) \frac{RT}{p}$$

$$\frac{V_2}{V_1} = \frac{n_{O_2}^o}{n_{H_2}^o + n_{O_2}^o} - \frac{\frac{1}{2}n_{H_2}^o}{n_{H_2}^o + n_{O_2}^o}$$

$X_{H_2}^o$  와  $X_{O_2}^o$  를 각각 반응 전의  $H_2$ 와  $O_2$ 의 몰분율이라고 하면,

$$\frac{V_2}{V_1} = X_{O_2}^o - \frac{1}{2}X_{H_2}^o = (1 - X_{H_2}^o) - \frac{1}{2}X_{H_2}^o = 1 - \frac{3}{2}X_{H_2}^o$$

$$\therefore X_{H_2}^o = \frac{2}{3}(1 - \frac{V_2}{V_1}) = \frac{2}{3}(1 - \frac{225cm^3}{300cm^3}) = 0.167$$

$$X_{O_2}^o = 1 - X_{H_2}^o = 1 - 0.167 = 0.833$$

$\therefore H_2$ : 16.7 mol %,  $O_2$ : 83.3 mol %

3. (a) Critical point를 갖는다면  $p$ - $V$  도표에서 변곡점을 갖는다.

$$\therefore \frac{dp}{dV_m} = 0, \frac{d^2p}{(dV_m)^2} = 0$$

$$p = \frac{RT}{V_m} - \frac{B}{(V_m)^2} + \frac{C}{(V_m)^3}$$

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m)^2} + \frac{2B}{(V_m)^3} - \frac{3C}{(V_m)^4} = 0$$

$$-RT_c(V_c)^2 + 2BV_c - 3C = 0 \quad \text{①}$$

$$\frac{d^2p}{(dV_m)^2} = \frac{2RT}{(V_m)^3} - \frac{6B}{(V_m)^4} + \frac{12C}{(V_m)^5} = 0$$

$$RT_c(V_c)^2 - 3BV_c + 6C = 0 \quad \text{②}$$

①과 ②를 더하면,

$$-BV_c + 3C = 0 \quad \therefore V_c = \frac{3C}{B}, \quad T_c = \frac{B^2}{3RC}$$

$V_c$  및  $T_c$ 를 원식에 대입하면,

$$p_c = \frac{RT_c}{V_c} - \frac{B}{(V_c)^2} + \frac{C}{(V_c)^3}$$

$$p_c = \frac{RB^2}{3RC} \times \frac{B}{3C} - B\left(\frac{B}{3C}\right)^2 + C\left(\frac{B}{3C}\right)^3 = \frac{B^3}{27C^2}$$

$$\therefore Z_c = \frac{p_c V_c}{R T_c} = \left(\frac{B^3}{27C^2}\right)\left(\frac{3C}{B}\right)\left(\frac{1}{R}\right)\left(\frac{3RC}{B^2}\right) = \frac{1}{3}$$

(b)  $Z = \frac{V_m}{V_m^o}$  ( $V_m^o$  = molar volume of a perfect gas)

주어진 식,  $p(V-nb) = nRT$ 를 이용하여  $V_m$ 에 대해 정리하면,

$$V_m = \frac{RT}{p} + b = V_m^o + b$$

$$\therefore Z = \frac{b + V_m^o}{V_m^o} = 1 + \frac{b}{V_m^o}$$

$$\textcircled{1} \text{ 때, } V_m = 14b = b + V_m^o \text{ } \textcircled{1} \text{므로, } \frac{b}{V_m^o} = \frac{1}{13}$$

$$\therefore Z = 1 + \frac{b}{V_m^o} = 1 + \frac{1}{13} = 1 + 0.08 = 1.08$$

4. 문제를 다시 정리하면 다음과 같다.

initial state (1):  $p_1 = 122.6 \text{ kPa}$ ,  $T_1 = 30^\circ\text{C} = 303 \text{ K}$ , mol수 =  $n_1$ ,  $V_1$

final state (2):  $p_2 = p_{ex} = 101.9 \text{ kPa}$ ,  $T_2 = ?$ ,  $n_2 = n_1$ ,  $V_2 = ?$

(a) state (1)에서 단열팽창하여 state (2)로 된다. 그러므로,  $\mathrm{dq} = 0$ 이다.

$$\mathrm{d}U = \mathrm{dq} + \mathrm{dw}, \quad \mathrm{dq} = 0$$

$$\mathrm{d}U = \mathrm{dw}$$

$$n_1 C_{V,m} \mathrm{d}T = -p_{ex} \mathrm{d}V$$

$$\int_{T_1}^{T_2} n_1 C_{V,m} \mathrm{d}T = -p_{ex} \int_{V_1}^{V_2} \mathrm{d}V$$

$$n_1 C_{V,m} (T_2 - T_1) = -p_{ex} (V_2 - V_1) \quad n_1 = n_2 \text{ } \textcircled{1} \text{므로}$$

$$n_1 C_{V,m} (T_2 - T_1) = -p_{ex} \left( \frac{n_1 R T_2}{p_2} - \frac{n_1 R T_1}{p_1} \right)$$

양변을  $n_1$ 로 나누어 주고,  $T_1$ 과  $T_2$ 에 대해 정리하면,

$$\left( C_{V,m} + \frac{p_{ex}R}{p_2} \right) T_2 = \left( C_{V,m} + \frac{p_{ex}R}{p_1} \right) T_1$$

$$p_{ex} = p_2 \text{ } \textcircled{1} \text{므로,}$$

$$T_2 = \left( \frac{C_{V,m} + \frac{p_{ex}}{p_1} R}{C_{V,m} + R} \right) T_1$$

위 식에 각 값을 대입하면,

$$T_2 = \left( \frac{1.5R + \frac{101.9 \text{ kPa}}{122.6 \text{ kPa}} R}{1.5R + R} \right) (303 \text{ K}) = 282.5 \text{ K}$$

$$\therefore T_2 = 282.5 \text{ K}$$

(b)  $p_1 V_1 = n_1 R T_1$ ,  $p_{ex} V_2 = n_1 R T_2$  으로 두식을 나누면,

$$\begin{aligned} \left( \frac{p_1}{p_{ex}} \right) \left( \frac{V_1}{V_2} \right) &= \frac{T_1}{T_2} \\ V_2 &= \left( \frac{p_1}{p_{ex}} \right) \left( \frac{T_2}{T_1} \right) V_1 = \left( \frac{122.6}{101.9} \right) \left( \frac{282.5}{303} \right) V_1 = 1.12 V_1 \end{aligned}$$

$$\therefore 1.12 \text{ 배}$$

$$\begin{aligned} 5. dH &= \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp \\ &= \left( \frac{\partial H}{\partial p} \right)_T dp \quad (\because \text{constant } T, \left( \frac{\partial H}{\partial T} \right)_p dT = 0) \end{aligned}$$

$$\begin{aligned} \left( \frac{\partial H}{\partial p} \right)_T &= \mu_T = -\mu C_p = -\mu n C_{p,m} = -n \left( \frac{2a}{RT} - b \right) \\ &= -1 \text{ mol} \times \left( \frac{2 \times 3.60 \text{ L}^2 \text{ atm mol}^{-2}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}} - 0.044 \text{ L mol}^{-1} \right) \\ &= -0.1754 \text{ L} \end{aligned}$$

$$\Delta H = \int_{p_i}^{p_f} dH = -0.1754 \int_{p_i}^{p_f} dp = -0.1754(p_f - p_i)$$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$p_i = \frac{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{30 \text{ L mol}^{-1} - 0.044 \text{ L mol}^{-1}} - \frac{3.60 \text{ L}^2 \text{ atm mol}^{-2}}{(30 \text{ L mol}^{-1})^2} = 1.0917 \text{ atm}$$

$$p_f = \frac{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{15 \text{ L mol}^{-1} - 0.044 \text{ L mol}^{-1}} - \frac{3.60 \text{ L}^2 \text{ atm mol}^{-2}}{(15 \text{ L mol}^{-1})^2} = 2.1787 \text{ atm}$$

$$\Delta H = (-0.1754 \text{ L}) \times (2.1787 \text{ atm} - 1.0917 \text{ atm})$$

$$= -0.1907 \text{ L atm}$$

$$= (-0.1907 \text{ L atm}) \left( \frac{101325 \text{ N m}^{-2}}{\text{atm}} \right) \left( \frac{\text{m}^3}{1000 \text{ L}} \right) \left( \frac{\text{J}}{\text{N m}} \right)$$

$$= \mathbf{-19.32 \text{ J}}$$