Physical Chemistry 1

Homework #2 solutions

1. (1) $\triangle U = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$

$= \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$

이상기체에 대하여 $\left(\frac{\partial U}{\partial V}\right)_T = 0$ 이다.

O_2 (g)의 $C_{V,m}$ = 21.041 J K^{-1} mol^{-1} 를 대입한다.

$\triangle U = n C_{V,m} \triangle T$ = (1.0 mol) (21.041 J K^{-1} mol^{-1}) (398.15 K - 298.15 K)

= 2104.1 J

∴ $\triangle U$ = **2104.1 J**

(2) $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$

$\triangle U = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV$로부터 van der Waals gas에 대하여 적용하면, 두 번째 항은 아래와 같이 된다.

$$\int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \frac{an^2}{V^2} dV = -an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

a = 1.364 atm L^2 mol^{-2} = 1.382 bar L^2 mol^{-2} 이다.

$$\therefore \triangle U = n C_{V,m} \triangle T - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= 2104.1\ \text{J} - (1.382\ \text{bar L}^2\ \text{mol}^{-2})\ (1.0\ \text{mol})^2 \left(\frac{10^2\ \text{J}}{1\ \text{L bar}}\right)\left(\frac{1}{6.75\ \text{L}} - \frac{1}{5.00\ \text{L}}\right)$$

= 2104.1 J + 7.2 J = 2111.3 J

∴ $\triangle U$ = **2111.3 J**

2. (1) (a) $\triangle H = -241.818\,\mathrm{kJ\,mol^{-1}}$

$$= \frac{(-241.818\,\mathrm{kJ\,mol^{-1}})(1000\,\mathrm{g\,kg^{-1}})}{18\,\mathrm{g\,mol^{-1}}}$$

$$= -13.4\,\mathrm{MJ\ kg^{-1}}$$

$\therefore\ \boldsymbol{\triangle H = -13.4\ \mathrm{MJ\ kg^{-1}}}$

(b) $\triangle H = -638.49\,\mathrm{kJ\,mol^{-1}}$

$$= \frac{(-638.49\,\mathrm{kJ\,mol^{-1}})(1000\,\mathrm{g\,kg^{-1}})}{80\,\mathrm{g\,mol^{-1}}}$$

$$= -7.98\,\mathrm{MJ\,kg^{-1}}$$

$\therefore\ \boldsymbol{\triangle H = -7.98\ \mathrm{MJ\ kg^{-1}}}$

(c) $\triangle H = 2(-271.1) = -542.2\,\mathrm{kJ\,mol^{-1}}$

$$= \frac{(-542.2\,\mathrm{kJ\,mol^{-1}})(1000\,\mathrm{g\,kg^{-1}})}{40\,\mathrm{g\,mol^{-1}}}$$

$$= -13.6\,\mathrm{MJ\,kg^{-1}}$$

$\therefore\ \boldsymbol{\triangle H = -13.6\ \mathrm{MJ\ kg^{-1}}}$

(2) (a) $\dfrac{13.4}{18} = 0.744$

(b) $\dfrac{7.98}{80} = 0.0997$

(c) $\dfrac{13.6}{40} = 0.34$

$\therefore$ **(a) > (c) > (b)**

(문제 해석에 따라 풀이가 달라지므로 중복 답으로 인정)

반응물이 1kg이므로 생성물 또한 1kg이다.

(1)에서 구한 1kg당 $\triangle H$는 배출가스의 질량당으로 계산한 것과 일치한다.

$\therefore$ **(c) > (a) > (b)**

3. (1) $dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T$, $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$이므로, $\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = \boldsymbol{\alpha \pi_T V}$

(2) $C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$

$H = U + pV$에서, 이상기체이므로 pV 대신 nRT를 대입하면 $H = U + nRT$

따라서, $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (nRT)}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + nR$

$$\therefore \boldsymbol{C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P + nR - \left(\frac{\partial U}{\partial T}\right)_V}$$

이상기체일 때, $\pi_T = 0$ 즉, $\left(\frac{\partial U}{\partial V}\right)_T = 0$이다.

따라서 문제 (1)에서 구한 $\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$에서, 우변이 0이 된다. 즉, 이상기체일 때, $\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = 0$ 이다.

$$\therefore \text{이상기체에 대해서 } \boldsymbol{C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V + nR}$$
$$= \boldsymbol{nR}$$

(참조) 다른 풀이

$dH = d(U + pV) = dU + d(pV) = dU + d(nRT)$

$C_p dT = C_V dT + nR dT$

$C_p = C_V + nR$

$\therefore \boldsymbol{C_p - C_V = nR}$

4. $\triangle V = V(\mathrm{CO}) - [\,V(\mathrm{C}) + V(\mathrm{CO_2})]$

$$= \frac{(2\ \mathrm{mol})(8.314\ \mathrm{m^3\,Pa\,K^{-1}\,mol^{-1}})(298\ \mathrm{K})}{(1.00\ \mathrm{bar})[(10^5\ \mathrm{Pa})/(1\ \mathrm{bar})]} - \frac{(1\ \mathrm{mol})(12.01\ \mathrm{g\,mol^{-1}})}{(2.3\ \mathrm{g\,cm^{-3}})[(10^6\ \mathrm{cm^3}/(1\ \mathrm{m^3})]}$$
$$- \frac{(1\ \mathrm{mol})(8.314\ \mathrm{m^3\,Pa\,K^{-1}\,mol^{-1}})(298\ \mathrm{K})}{(1.00\ \mathrm{bar})[(10^5\ \mathrm{Pa})/(1\ \mathrm{bar})]}$$
$$= 0.04955\ \mathrm{m^3} - 0.05222 \times 10^{-4}\ \mathrm{m^3} - 0.02477\ \mathrm{m^3}$$
$$= 2.477 \times 10^{-2}\ \mathrm{m^3}$$

$$\therefore \triangle U = \triangle H - p\triangle V$$
$$= 162.15\ \mathrm{kJ} - (1.00\ \mathrm{bar})(2.477 \times 10^{-2}\ \mathrm{m^3})\left(\frac{10^5\ \mathrm{Pa}}{1\ \mathrm{bar}}\right)\left(\frac{1\ \mathrm{J}}{1\ \mathrm{m^3\,Pa}}\right)\left(\frac{1\ \mathrm{kJ}}{10^3\ \mathrm{J}}\right)$$
$$= 162.15\ \mathrm{kJ} - 2.477\ \mathrm{kJ} = \mathbf{159.673\ kJ}$$

5. $C_{V,m} = \frac{3}{2} \times 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} = 12.471\ \mathrm{J\,K^{-1}\,mol^{-1}}$

$C_{p,m} = \frac{5}{2} \times 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} = 20.785\ \mathrm{J\,K^{-1}\,mol^{-1}}$

$\gamma = \frac{C_p}{C_V} = 1.667$

(1) 단열압축 단계

$q = 0$

$$\Delta U = w = C_V \Delta T = n C_{V,m} \Delta T$$
$$= 1 \times 12.471\ \mathrm{J\,K^{-1}\,mol^{-1}} \times (573\ \mathrm{K} - 298\ \mathrm{K}) = 3429.525\ \mathrm{J}$$

$$\Delta H = C_p \Delta T = n C_{p,m} \Delta T$$
$$= 1 \times 20.785\ \mathrm{J\,K^{-1}\,mol^{-1}} \times (573\ \mathrm{K} - 298\ \mathrm{K}) = 5715.875\ \mathbf{J}$$

순차적인 세 가지 상태를 A, B, C라 할 때,

$$p_B = p_A(\frac{T_B}{T_A})^{\frac{\gamma}{\gamma-1}} = (1\text{bar})(\frac{573\,\text{K}}{298\,\text{K}})^{2.5} = 5.127\,\text{bar}$$

(2) 정압 단계

$$\Delta U = C_V \Delta T = n C_{V,m} \Delta T$$
$$= 1 \times 12.471\,\text{J K}^{-1}\,\text{mol}^{-1} \times (298\,\text{K} - 573\,\text{K}) = -3429.525\,\text{J}$$

$$\Delta H = q = C_p \Delta T = n C_{p,m} \Delta T$$
$$= 1 \times 20.785\,\text{J K}^{-1}\,\text{mol}^{-1} \times (298\,\text{K} - 573\,\text{K}) = -5715.875\,\text{J}$$

$$w = \Delta U - q = -3429.525\,\text{J} + 5715.875\,\text{J} = 2286.35\,\text{J}$$

(3) 등온팽창 단계

$$\Delta U = \Delta H = 0$$

$$w = -q = nRT\ln\frac{p_1}{p_3}$$

$$= 1\,\text{mol} \times 8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K} \times \ln\frac{1}{5.127} = -4049.643$$

∴ 전체과정에 대한 q, w, ΔU, ΔH 의 값은

$\boldsymbol{q} = 0 - 5715.875 + 4049.643 = \mathbf{-1666.232\,(J)}$

$\boldsymbol{w} = 3429.525 + 2286.35 - 4049.643 = \mathbf{1666.232\,(J)}$

$\boldsymbol{\Delta U} = 3429.525 - 3429.525 + 0 = \mathbf{0\,(J)}$

$\boldsymbol{\Delta H} = 5715.875 - 5715.875 + 0 = \mathbf{0\,(J)}$

각 상태에서의 부피는 다음과 같다.

$$V_A = \frac{nRT_A}{p_A} = \frac{1 \times 0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}}{1\,\text{bar} \times \frac{1\,\text{atm}}{1.013\,\text{bar}}} = 24.754\,\text{L}$$

$$V_B = \frac{nRT_B}{p_B} = \frac{1\,\text{mol} \times 0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 573\,\text{K}}{5.127\,\text{bar} \times \frac{1\,\text{atm}}{1.013\,\text{bar}}} = 9.295\,\text{L}$$

$$V_C = \frac{nRT_C}{p_C} = \frac{1\,\text{mol} \times 0.0821\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}}{5.127\,\text{bar} \times \frac{1\,\text{atm}}{1.013\,\text{bar}}} = 4.834\,\text{L}$$

$p-V$ 도표는 아래와 같다.