

1.

- 2.1 An monatomic ideal gas at 300 K has a volume of 15 liters at a pressure of 15 atm. Calculate
- The final volume of the system
 - The work done by the system
 - The heat entering or leaving the system
 - The change in the internal energy
 - The change in the enthalpy when the gas undergoes
 - A reversible isothermal expansion to a pressure of 10 atm
 - A reversible adiabatic expansion to a pressure of 10 atm
- The constant-volume molar heat capacity of the gas, c_v , has the value $1.5 R$.

$$P_i = 15 \text{ atm} \quad V_i = 15 \text{ L} \quad T_i = 300 \text{ K} \rightarrow n = \frac{P_i V_i}{R T_i} = \frac{15 \cdot 15}{0.08206 \cdot 300} = 9.16$$

i) reversible isothermal expansion to $P_j = 10$ (T = constant)

$$a. \quad P_i V_i = P_j V_j \quad , \quad V_j = \frac{P_i V_i}{P_j} = 22.5 \text{ L}$$

$$b. \quad w = \int_{V_i}^{V_j} P dV = \int_{V_i}^{V_j} \frac{nRT}{V} dV = nRT \ln \left(\frac{V_j}{V_i} \right) = 9.26 \text{ kJ}$$

$$c. \quad \Delta U = 0 \quad \therefore q = w = 9.26 \text{ kJ}$$

$$d. \quad \Delta U = n c_v \Delta T \quad , \quad P_i V_i = P_j V_j \rightarrow nRT_i = nRT_j \rightarrow \Delta T = 0 \quad \therefore \Delta U = 0$$

$$e. \quad \Delta H = \Delta U + P \Delta V = n c_p \Delta T = 0$$

$$a) 22.5 \text{ L} \quad b) 9.26 \text{ kJ} \quad c) 9.26 \text{ kJ} \quad d) 0 \quad e) 0$$

ii) reversible adiabatic expansion to $P_j = 10$

$$P_i V_i^\gamma = P_j V_j^\gamma \quad , \quad \gamma = \frac{5}{3} \quad V_j = \left(\frac{P_i V_i^\gamma}{P_j} \right)^{\frac{3}{5}} = 19.13 \text{ L}$$

$$T_j = \frac{P_j V_j}{nR} = 254.7 \text{ K}$$

$$\Delta U = q - w = -w = n c_v \Delta T = 9.16 \cdot \frac{3}{2} R \cdot (300 - 254.7) = 5.17 \text{ kJ}$$

$$\Delta H = \gamma \Delta U = 8.62 \text{ kJ}$$

$$a) 19.13 \text{ L} \quad b) -5.17 \text{ kJ} \quad c) 0 \quad d) 5.17 \text{ kJ} \quad e) 8.62 \text{ kJ}$$

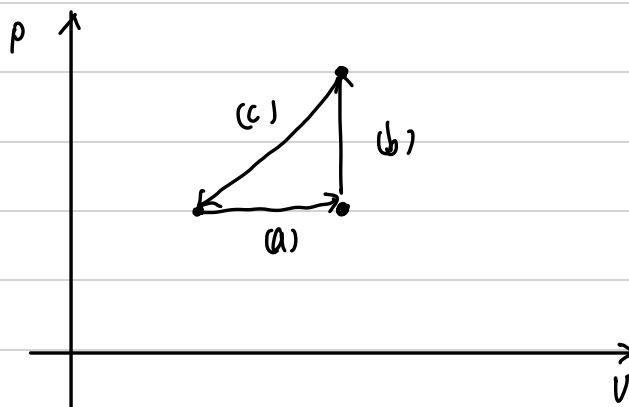
2.

2.2 One mole of a monatomic ideal gas, in the initial state $T = 273 \text{ K}$, $P = 1 \text{ atm}$, is subjected to the following three processes, each of which is conducted reversibly:

- A doubling of its volume at constant pressure,
 - Then a doubling of its pressure at constant volume,
 - Then a return to the initial state along the path $P = 6.643 \times 10^{-4} V^2 + 0.6667$.
- Calculate the heat and work effects which occur during each of the three processes.

$$T_i = 273 \text{ K}, P_i = 1 \text{ atm} \quad V_i, n_i = 1 \rightarrow ? \quad \text{heat, work effect.}$$

$$a) V_j = 2V_i, P_j = P_i \quad b) P_j = 2P_i, V_j = V_i \quad c) P = 6.643 \times 10^{-4} V^2 + 0.6667$$



$$V_i = \frac{n_i R T_i}{P_i} = 22.4$$

$$(a) \Delta U = n C_V \Delta T, \quad T_j / T_i = \frac{P_j V_j}{P_i V_i} = 2, \quad T_j = 546 \text{ K}$$

$$= \frac{3}{2} R \cdot 273 = 3.40 \text{ kJ}$$

$$w = P \Delta V = 1 \text{ atm} \cdot 22.4 \text{ L} = 22.4 \text{ atm} \cdot \text{L} \cdot \frac{105 \text{ N/m}^2}{1 \text{ atm}} \times \frac{1 \text{ m}^3}{10^3 \text{ L}}$$

$$= 2.24 \text{ kJ}$$

$$q = \Delta U + w = 5.64 \text{ kJ}$$

$$\therefore w = 2.24 \text{ kJ}, q = 5.64 \text{ kJ}, \Delta U = 3.40 \text{ kJ}$$

$$(b) P_i = 1 \text{ atm} \quad V_i = 44.8 \quad n = 1 \quad T_i = 546 \text{ K}$$

$$P_j = 2 \text{ atm} \quad V_j = \quad \quad \quad T_j = 1092 \text{ K}$$

$$\Delta U = n C_V \Delta T = \frac{3}{2} R \cdot 546 = 6.81 \text{ kJ}$$

$$\Delta U = q - w, \quad w = 0, \quad \Delta U = q = 6.81 \text{ kJ}$$

$$\therefore w = 0, q = 6.81 \text{ kJ}, \Delta U = 6.81 \text{ kJ}$$

$$(c) P = 6.643 \times 10^{-4} V^2 + 0.6667, \quad P_i = 2 \text{ atm} \quad V_i = 44.8 \text{ L}, \quad n = 1 \quad T_i = 1092 \text{ K}$$

$$T_{\text{initial}} = T_{\text{final}} \rightarrow \Delta U = n C_V \Delta T = \frac{3}{2} R \cdot 0 = 0$$

$$w = \int P dV = \int [6.643 \times 10^{-4} \cdot \frac{1}{3} V^3 + 0.6667 V]_{44.8}^{22.4} \cdot 10^{-1} \frac{\text{kJ}}{\text{atm} \cdot \text{L}} = -3.24 \text{ kJ}$$

$$q = \Delta U + w = -3.24 \text{ kJ}$$

$$\therefore w = -3.24 \text{ kJ}, q = -3.24 \text{ kJ}, \Delta U = 0$$

3.

- 3.1 The initial state of 1 mole of a monatomic ideal gas is $P = 10 \text{ atm}$ and $T = 300 \text{ K}$. Calculate the change in the entropy of the gas for
- An isothermal decrease in the pressure to 5 atm
 - A reversible adiabatic expansion to a pressure of 5 atm
 - A constant-volume decrease in the pressure to 5 atm

$$P_i = 10 \text{ atm} \quad T_i = 300 \text{ K} \quad n = 1 \text{ mol.} \quad V_i = \frac{nRT_i}{P_i} = 2.46 \text{ L}$$

a.) $P_j = 5 \text{ atm} \quad V_j = 4.92 \text{ L} \quad T_j = 300 \text{ K} \text{ (isothermal)}$

$$\textcircled{1} \quad dS = \frac{dq}{T}$$

$$\textcircled{2} \text{ Isothermal} \quad \Delta U = 0 \quad q = w$$

$$w = \int p dV = \int \frac{nRT}{V} dV = nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$\textcircled{2} \leftarrow \textcircled{1} \quad \Delta S = \int \frac{dq}{T} = nR \ln \frac{V_f}{V_i} = 16.62 \text{ J/K.}$$

b) adiabatic : $\Delta q = 0 \rightarrow \Delta S = \int \frac{dq}{T} = 0.$

c) constant volume, decrease in pressure of $P_f = 5 \text{ atm}$

$$\Delta V = 0 \rightarrow w = 0 \rightarrow dq = dU = nC_v dT$$

$$\Delta S = \int \frac{dq}{T} = \int_{300}^{150} \frac{nC_v}{T} dT = -nC_v \ln 2 = -\frac{3}{2}R \ln 2 = -8.64 \text{ J/K.}$$

4.

3.4 Calculate the change in the enthalpy and the change in entropy when 1 mole of SiC is heated from 25°C to 1000°C. The constant-pressure molar heat capacity of SiC varies with temperature as

$$c_p = 50.79 + 1.97 \times 10^{-3} T - 4.92 \times 10^6 T^{-2} + 8.20 \times 10^8 T^{-3} \text{ J/mole} \cdot \text{K}$$

$$\textcircled{1}. \Delta H = \int n C_p dT \quad , \quad n=1 \quad , \quad T_f = 1273 \quad T_i = 289$$

$$= \left[50.79 T + \frac{1}{2} \times 1.97 \times 10^{-3} T^2 + 4.92 \times 10^6 T^{-1} - \frac{1}{2} \cdot 8.20 \times 10^8 T^{-2} \right]_{289}^{1273}$$

$$= 4.30 \text{ kJ/mol.}$$

$$\textcircled{2}. \Delta S = \int \frac{dq}{T}$$

- entropy는 상태함 $\rightarrow$ 경로 상관 X.

$$f = \Delta U + w = \Delta U + p \Delta V = \Delta H.$$

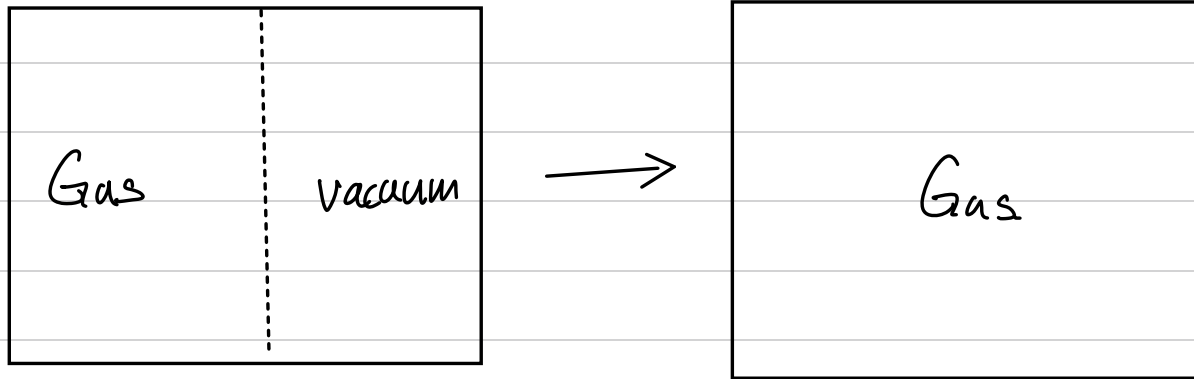
$$\Delta S = \int \frac{dq}{T} = \int \frac{\Delta H}{T} dT = \int \left[50.79 + \frac{1}{2} \times 1.97 \times 10^{-3} T + 4.92 \times 10^6 T^{-2} - \frac{1}{2} \cdot 8.20 \times 10^8 T^{-3} \right] dT$$

$$= \left[50.79 T + \frac{1}{4} \times 1.97 \times 10^{-3} T^2 - 4.92 \times 10^6 T^{-1} + \frac{1}{4} \cdot 8.20 \times 10^8 T^{-2} \right]_{289}^{1273}$$

$$= 6.16 \text{ kJ/K}$$

→ 대기압은 1atm 이나, 이쯤에서 water 의 partial volume 은 대략 낮다.
대략 차 안의 space 이 A 라 가라치 H_2O 의 상태는 Vapor 이 응결한 상태고,
차가운 상태인 창과 접촉 시 liquid 로 응결하기까지 값이 내려가 된다.
만약 T 를 내려가면 이펙트를 커면 liquid 가 응결한 상태로 바뀌고
 Vapor 의 partial pressure 이 낮아져 값이 내려가게 된다.

6.



- statistical 관점 : $\Delta S = k_B \ln \Omega_2 / \Omega_1$ 으로 정의한다.
 Ω 이 gas 입자가 공간 내에 존재하는 양의 수이므로,
 2배의 공간이 존재시 $\Omega_2 > \Omega_1$
 $\therefore \Delta S = k_B \ln \Omega_2 / \Omega_1 > 0 \rightarrow$ 자발적인
 gas가 확산된다.

- dynamics 관점 : isolated이므로 $\Delta U = \Delta H = 0$, 다만 irreversible 하므로
 q와 w를 적용할 수 없음

$$\Delta S = \frac{q_{\text{irreversible}}}{T} + \Delta S_{\text{irr}} = \frac{q_{\text{rev}}}{T} \text{ 일 때}$$

reversible adiabatic 경로로 생각시

$$q_{\text{rev}} = RT \ln \frac{V_2}{V_1} > 0, \text{ 자발적이다.}$$

반응의 극 한계에 irreversible한 과정에 reversibly 하면
 가능한 과정이 존재 (전통이 일어나지 않음)가 있다 가정시
 $\Delta S > 0$ 으로 자발적

17. Microscopically reversible, Macroscopically irreversible.

- Macroscopic: P, T state
- Microscopic: 분자들의 각각의 속력.

- Microscopic state의 경우 분자의 속력을 따지는 경우로, 실제로는 분자의 속력을 모두 알 수 없는 random 이기 reversible한 상태와 유사하다.
- Macroscopic state의 경우 방향성이 존재하며, 이로 인해 irreversible 한 상태라고 할 수 있다.