

AMSE205 Thermodynamics I

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Problem Set #2

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1. The initial state of one 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 (a) an isothermal decrease in the pressure to 5 atm , (b) a reversible adiabatic expansion to a pressure of 5 atm , (c) a constant-volume decrease in the pressure to 5 atm .
2. One mole of monatomic ideal gas is subjected to the following sequence of steps:
 - a. Starting at 300 K and 10 atm , the gas expands freely into a vacuum to triple its volume.
 - b. The gas is next heated reversibly to 400 K at constant volume.
 - c. The gas is reversibly expanded at constant temperature until its volume is again tripled.
 - d. The gas is finally reversibly cooled to 300 K at constant pressure.Calculate the values of q and w and the changes in U , H and S .
- 3.(a) Find the extreme value of the function,
$$z = (x - 2)^2 + (y - 2)^2 + 4.$$
Find the constrained maximum of this function corresponding to the condition
$$x + y = 1$$
(b) by eliminating one variable and (c) by using a Lagrange undetermined multiplier method.
4. A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm , and the other compartment contains 1 mole of ideal gas B at 1 atm .
 - (a) Calculate the entropy increase in the container if the partition between the two compartments is removed.
 - (b) If the first compartment had contained 2 moles of ideal gas A, what would have been the entropy increase due to gas mixing when the partition was removed?
 - (c) Calculate the corresponding entropy changes in each of the above two situations if both compartments had contained ideal gas A.

1. The initial state of one 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 (a) an isothermal decrease in the pressure to 5 atm , (b) a reversible adiabatic expansion to a pressure of 5 atm , (c) a constant-volume decrease in the pressure to 5 atm .

$$dU = Tds - PdV, \quad \text{Let } P_1 = 10 \text{ atm}, \quad P_2 = 5 \text{ atm}$$

$$(a) \quad ds = \frac{dU}{T} + \frac{PdV}{T} = \frac{C_V dT}{T} + \frac{R}{V} dV$$

isothermal : $dT = 0$

$$\Delta S = \int_{S_1}^{S_2} ds = R \int_{V_1}^{V_2} \frac{dV}{V} = R/n \frac{V_2}{V_1}$$

$$V_1 = \frac{RT}{P_1} = \frac{0.08206 \times 300}{10} = 2.4618 \text{ (L)}$$

$$V_2 = \frac{RT}{P_2} = \frac{0.08206 \times 300}{5} = 4.9236 \text{ (L)}$$

$$V_2 = 2V_1, \quad \therefore \Delta S = R/n \ln 2 = 8.314 \times \ln 2 = 5.763 \text{ (J/K)}$$

(b) reversible adiabatic ; $q = 0$. ($q_{\text{rev}} = 0$)

$$\Rightarrow \Delta S = \frac{q_{\text{rev}}}{T} = 0$$

(c) Let $T_1 = 300 \text{ K}$

$$ds = \frac{dU}{T} + \frac{PdV}{T} \quad dV = 0 \quad (\because \text{constant Volume})$$

$$ds = \frac{C_V dT}{T}, \quad \Delta S = \int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \ln \left(\frac{T_2}{T_1} \right)$$

$$P_1 \times V_1 = RT_1, \quad V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 300}{10} = 2.4618 \text{ (L)}$$

$$P_2 V_2 = P_2 V_1 = RT_2 \quad (\because \text{constant volume})$$

$$T_2 = \frac{P_2 V_1}{R} = \frac{5 \times 2.4618}{0.08206} = 150 \text{ (K)}$$

$$\Delta S = C_v \ln\left(\frac{150}{300}\right) = -C_v \ln 2$$

$$= -\frac{3}{2} \times 8.314 \times \ln 2$$

$$\therefore \Delta S = -8.644 \text{ (J/K)}$$

2. One mole of monatomic ideal gas is subjected to the following sequence of steps:
- Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.
 - The gas is next heated reversibly to 400 K at constant volume.
 - The gas is reversibly expanded at constant temperature until its volume is again tripled.
 - The gas is finally reversibly cooled to 300 K at constant pressure.

Calculate the values of q and w and the changes in U , H and S .

$$T_1 = 300 \text{ K} \quad V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 300}{10} = 2.4618 \text{ (L)}$$

$$P_1 = 10 \text{ atm}$$

a. $V_2 = 3V_1 = 7.3854 \text{ (L)} \quad T_2 = 300 \text{ K}$

$$P_2 = \frac{P_1}{3} = 3.333 \text{ (atm)}$$

freely expands $\Rightarrow w = 0$, $\Delta T = 0 \Rightarrow \Delta U = 0$, $\Delta H = 0$.

$$q = 0$$

$$dU = T \cdot ds - p \cdot dV \Rightarrow 0 = T \cdot ds - p \cdot dV$$

$$ds = \frac{p}{T} dV = \frac{1}{T} \cdot \frac{RT}{V} dV$$

$$\Delta S = R \int_{V_1}^{V_2} \frac{dV}{V} = R \cdot \ln \frac{V_2}{V_1} = 8.314 \times \ln 3 = 9.134 \text{ (J/K)}$$

b. constant volume : $V_3 = V_2 = 3V_1 = 7.3854 \text{ (L)}$

$$T_3 = 400 \text{ K} \quad P_3 = \frac{RT_3}{V_3} = 4.444 \text{ (atm)}$$

$$w = 0 \quad (\because \text{constant volume})$$

$$\Delta U = C_v \Delta T = \frac{3}{2} R \times (T_3 - T_2) = 1.5 \times 8.314 \times 100 = 1247.1 \text{ J}$$

$$\Delta H = C_p \Delta T = \frac{5}{2} R \times (T_3 - T_2) = 2.5 \times 8.314 \times 100 = 2078.5 \text{ J}$$

$$q = \Delta U = 1247.1 \text{ J}$$

$$dU = T \cdot ds - p \cdot dV \Rightarrow dU = T \cdot ds$$

$$ds = \frac{dU}{T} \quad \Delta S = \int_{T_2}^{T_3} \frac{C_v \cdot dT}{T} = C_v \cdot \ln \frac{T_3}{T_2} = 3.588 \text{ J/K}$$

c. constant temperature, $T_4 = T_3 = 400\text{K}$

$$V_4 = 3V_3 = 22.1562\text{ (L)}$$

$$P_4 = \frac{P_3}{3} = 1.481\text{ (atm)}$$

$$\Delta T = 0 \Rightarrow \Delta U = \Delta H = 0$$

$$q = w$$

$$q = w = \int_{V_3}^{V_4} \frac{RT_4}{V} dV = RT_4 \ln \frac{V_4}{V_3} = 8.314 \times 400 \times \ln 3 = 3653.55\text{ J}$$

$$dU = T \cdot ds - p dV \Rightarrow ds = \frac{p}{T} dV = \frac{R}{V} dV$$

$$\Delta S = \int_{V_3}^{V_4} R \cdot \frac{1}{V} dV = R \ln \left(\frac{V_4}{V_3} \right)$$

$$= 9.134\text{ (J/K)}$$

d. constant pressure, $P_5 = P_4 = 1.481\text{ (atm)}$

$$T_5 = 300\text{K}, \quad V_5 = \frac{RT_5}{P_5} = \frac{0.08206 \times 300}{1.481} = 16.62\text{ (L)}$$

$$\Delta U = C_V \Delta T = 1.5 \times 8.314 \times (T_5 - T_4) = -1247.1\text{ J}$$

$$\Delta H = C_P \Delta T = 2.5 \times 8.314 \times (T_5 - T_4) = -2078.5\text{ J}$$

$$w = \int p dV = P_5 \Delta V = 1.481 \times (V_5 - V_4) \times 101.325 \left(\frac{\text{J}}{\text{L} \cdot \text{atm}} \right) = -830.8\text{ J}$$

$$q_r = \Delta H = -2078.5\text{ J}$$

$$dU = T \cdot ds - p dV \Rightarrow dH = T \cdot ds$$

$$ds = \frac{dH}{T}$$

$$\Delta S = \int_{T_4}^{T_5} \frac{C_P dT}{T} = C_P \ln \frac{T_5}{T_4} = -5.98\text{ J/K}$$

Total: $\Delta U_t = 0, \quad \Delta H_t = 0$

$$w_t = 2822.75\text{ J} \quad q_t = 2822.15\text{ J}, \quad w_t \approx q_t, \quad \Delta S_t = 15.876\text{ (J/K)}$$

3.(a) Find the extreme value of the function,

$$z = (x - 2)^2 + (y - 2)^2 + 4.$$

Find the constrained ~~maximum~~ of this function corresponding to the condition

~~minimum~~

$$x + y = 1$$

(b) by eliminating one variable and (c) by using a Lagrange undetermined multiplier method.

(a) Let $z = f(x, y)$

$$f_x = 2(x - 2)$$

$$f_y = 2(y - 2)$$

$$f_x = 0, f_y = 0 \Rightarrow x = 2, y = 2$$

(2, 2) is critical point.

$$f_{xx} = 2$$

$$f_{xx}(2, 2), f_{yy}(2, 2) > 0,$$

$$f_{yy} = 2$$

$$f_{xy} = 0$$

$$D = f_{xx}(2, 2) \cdot f_{yy}(2, 2) - (f_{xy}(2, 2))^2 > 0$$

$\Rightarrow$

that is relative

minimum of f .

$$f(2, 2) = 4 \text{ 가 극값이다.}$$

(b) eliminating one variable

$$x = 1 - y, \quad z = (-y - 1)^2 + (y - 2)^2 + 4$$

$$= y^2 + 2y + 1 + y^2 - 4y + 4 + 4$$

$$= 2y^2 - 2y + 9$$

$$= 2(y^2 - y + \frac{1}{4}) - \frac{1}{2} + 9 = 2(y - \frac{1}{2})^2 + \frac{17}{2}$$

$$y = \frac{1}{2}, \quad x = \frac{1}{2} \text{ 이라 하면 } z = \frac{17}{2} \text{ 가 된다.}$$

$$z = f(\frac{1}{2}, \frac{1}{2}) = \frac{17}{2}$$

(c) using Lagrange undetermined multiplier

$$\text{let } z = f(x, y), \quad h(x, y) = x + y - 1$$

$$\nabla f = \langle 2(x-2), 2(y-2) \rangle, \quad \nabla h = \langle 1, 1 \rangle$$

$$\nabla f = \lambda \cdot \nabla h$$

$$\Rightarrow 2x - 4 = \lambda, \quad 2y - 4 = \lambda \text{ 를 만족하는 점 } (x, y) \text{ 를 } (x_1, y_1) \text{ 이라 두라.}$$

$$\text{그런데, } x_1 + y_1 - 1 = 0 \text{ 이므로}$$

$$\left. \begin{array}{l} 2x_1 - 4 = \lambda \\ 2y_1 - 4 = \lambda \\ x_1 = 1 - y_1 \end{array} \right\} \Rightarrow \left. \begin{array}{l} 2(1 - y_1) - 4 = \lambda \\ 2y_1 - 4 = \lambda \end{array} \right\} \quad \left. \begin{array}{l} -2y_1 - 2 = \lambda \\ 2y_1 - 4 = \lambda \end{array} \right\}$$

$$2\lambda = -6, \quad \lambda = -3, \quad x_1 = \frac{1}{2}, \quad y_1 = \frac{1}{2}$$

$$\frac{z}{7}, \quad y = \frac{1}{2}, \quad x = \frac{1}{2} \text{ 에서 최댓값 } z = \frac{17}{2} \text{ 가 된다.}$$

$$z = f\left(\frac{1}{2}, \frac{1}{2}\right) = \frac{17}{2}$$

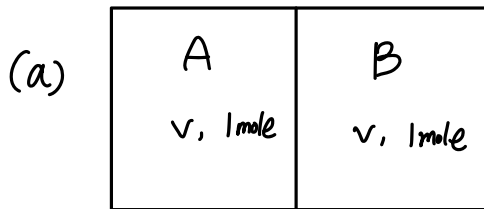
4. A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm.

- (a) Calculate the entropy increase in the container if the partition between the two compartments is removed.
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 (c) Calculate the corresponding entropy changes in each of the above two situations if both compartments had contained ideal gas A.

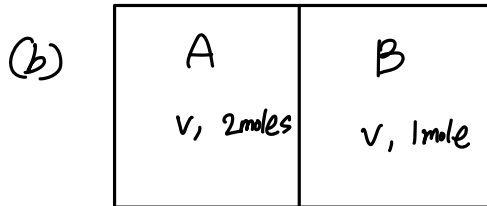
$$dU = T \cdot dS - P \cdot dV \Rightarrow dS = \frac{P}{T} dV \Rightarrow dS = \frac{nR}{V} dV$$

<rigid container>

$$\therefore \Delta S = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln\left(\frac{V_2}{V_1}\right)$$

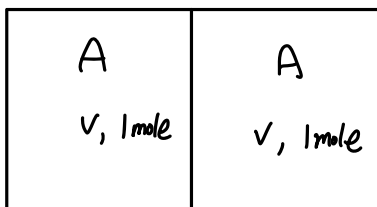


$$\begin{aligned}\Delta S_A &= R \ln \frac{2V}{V} = R \ln 2 \\ \Delta S_B &= R \ln \frac{2V}{V} = R \ln 2 \\ \Delta S &= \Delta S_A + \Delta S_B = R \ln 4\end{aligned}$$



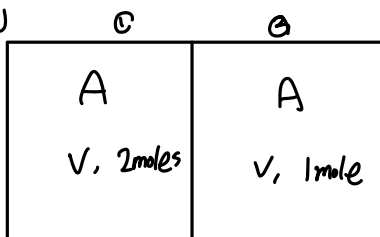
$$\begin{aligned}\Delta S_A &= 2R \ln \frac{2V}{V} = 2R \ln 2 \\ \Delta S_B &= R \ln \frac{2V}{V} = R \ln 2 \\ \Delta S &= \Delta S_A + \Delta S_B = R \ln 8\end{aligned}$$

(c) - (a)



$$\rightarrow \Delta S = 0. \quad (\text{변화 없다})$$

(c) - (b)



$$\textcircled{1} \Delta S_0 = 2R \ln \frac{\frac{4}{3}V}{V}$$

$$\Delta S_{\textcircled{2}} = R \ln \frac{\frac{5}{3}V}{V}$$

$$\begin{aligned}\Delta S_{\text{tot}} &= 2R \ln \frac{4}{3} + R \ln \frac{5}{3} = R \left(\ln \frac{16}{9} + \ln \frac{5}{3} \right) \\ &= R \ln \frac{80}{27}\end{aligned}$$