

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 $P = 10$ atm and $T = 300$ 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.

Thermodynamics I Problem Set #2. (Oct. 12, 2021)

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 .

$$\begin{array}{llll} P_1 = 10 & n_1 = 1 & \longrightarrow & P_2 = 5 \quad n_2 = 1 \\ T_1 = 300 & V_1 = 2.46 \text{ L} & & T_2 = 300 \quad V_2 = 4.92 \end{array}$$

a) isothermal $\rightarrow \Delta U = 0, q = w$

$$w = \int P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} \rightarrow q = -w = -nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{q}{T} = nR \ln \frac{V_2}{V_1} = 8.314 \times \ln \frac{4.92}{2.46} = 8.314 \ln 2 = \boxed{5.763 \text{ (J/K)}}$$

b) reversible adiabatic expansion

$$P_1 V_1^{\frac{5}{3}} = P_2 V_2^{\frac{5}{3}} \rightarrow V_2 = V_1 \left(\frac{P_1}{P_2} \right)^{\frac{3}{5}} = 3.73 \text{ (L)}$$

* adiabatic process 이니 $\Delta S = 0$

c) a constant-volume decrease in the pressure to 5 atm

$$dU = nC_v dT = \delta q - \delta w \rightarrow \delta q = nC_v dT + \delta w = nC_v dT$$

$$\int \frac{\delta q}{T} = \int dS = \int nC_v \frac{1}{T} dT = \frac{3}{2} \times 8.314 \ln \frac{T_2}{T_1} = \frac{3}{2} \times 8.314 \ln \frac{1}{2}$$

$$\begin{array}{llll} P_1 = 10 & n_1 = 1 & \longrightarrow & P_2 = 5 \quad n_2 = 1 \\ T_1 = 300 & V_1 = 2.46 & & T_2 = 150 \quad V_2 = 2.46 \end{array} \quad = \boxed{-8.64 \text{ (J/K)}}$$

2.

2. One mole of monatomic ideal gas is subjected to the following sequence of steps: 344.

- 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 .

$$w = 0$$

$$\begin{array}{llll} a) & 300 \text{ K}, 10 \text{ atm} \text{ 에서 시작. 진공으로 자유 팽창. } \Rightarrow \text{ 온도 그대로. 부피 3배 확장 } \Rightarrow \\ T_1 = 300 & V_1 = 2.46 \text{ (L)} & \longrightarrow & T_2 = 300 \quad V_2 = 7.38 \text{ (L)} \\ P_1 = 10 & n_1 = 1 & & P_2 = \frac{10}{3} \quad n_2 = 1 \end{array}$$

$$\boxed{q = 0, \quad \Delta U = 0, \quad \Delta H = \Delta U + \Delta(PV) = 0, \quad w = 0}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} = 8.314 \ln 3 = 9.134 \text{ (J/K)}$$

↳ Q. 왜 $\Delta S = 0$ 이 아닌가요? - 자유 팽창에서 온도가 균일하지 않아서가 맞을까요...??

b) reversibly heated 400K at constant Volume

$$T_2 = 300 \quad V_2 = 7.38 \quad T_3 = 400 \quad V_3 = 7.38 \text{ (L)}$$

$$P_2 = \frac{10}{3} \quad n_2 = 1 \quad \rightarrow \quad P_3 = \frac{40}{9} \quad n_3 = 1$$

$$P_3 = \frac{nRT}{V_3} = \frac{1 \times 0.082 \times 400}{7.38} = 4.44 \dots \left(\frac{40}{9} \right) \text{ (L)}$$

$$\Delta S = \int \frac{\delta q}{T} = \int n C_v \cdot \frac{1}{T} dT = \frac{3}{2} \times 8.314 \ln \frac{4}{3} = 3.588 \text{ (J/K)}$$

$$q = n C_v \Delta T = \frac{3}{2} \times 8.314 \times 100 = 1247.1 \text{ (J)}$$

$$w = P \Delta V = 0$$

$$\Delta U = q - w = 1247.1 \text{ (J)}$$

$$\Delta H = \Delta U + \Delta(PV) = 1247.1 + 830 = 2078.0$$

$$q = 1247.1 \text{ (J)}$$

$$w = 0 \text{ (J)}$$

$$\Delta U = 1247.1 \text{ (J)}$$

$$\Delta H = 2078.0 \text{ (J)}$$

$$\Delta S = 3.588 \text{ (J/K)}$$

c) 가역 & 등온, V × 3 (P₃V₃ = P₄V₄)

$$T_3 = 400 \quad V_3 = 7.38 \quad T_4 = 400 \quad V_4 = 22.14$$

$$P_3 = \frac{40}{9} \quad n_3 = 1 \quad \Rightarrow \quad P_4 = \frac{40}{27} \quad n_4 = 1$$

$$\Delta S = nR \ln \frac{V_4}{V_3} = 8.314 \ln 3 = 9.134 \text{ (J/K)}$$

$$\frac{\delta q}{T} \Rightarrow \Delta U = 0 \quad \rightarrow \quad \Delta U = q - w \Rightarrow q = 3653.5 \text{ (J)}$$

$$w = \int P dV = nRT \ln \frac{V_4}{V_3} = 3653.5 \text{ (J)}$$

$$\Delta H = \Delta U + \Delta(PV) = 0$$

$$q = 3653.5 \text{ (J)}$$

$$w = 3653.5 \text{ (J)}$$

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

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

d) reversibly cooled to 300K at constant pressure

$$T_4 = 400 \quad V_4 = 22.14 \quad T_5 = 300 \quad V_5 = 16.61$$

$$P_4 = \frac{40}{27} \quad n_4 = 1 \quad \Rightarrow \quad P_5 = \frac{40}{27} \quad n_5 = 1$$

$$\Delta U = \delta q - \delta w \rightarrow \delta q = dU + \delta w$$

$$\int \frac{\delta q}{T} = \int \frac{1}{T} dU + \int \frac{1}{T} \delta w$$

$$= \int \frac{n C_v dT}{T} + \int \frac{P}{T} dV = \int \frac{n C_v dT}{T} + nR \ln \frac{V_2}{V_1}$$

$$= n C_v \ln \frac{T_5}{T_4} + nR \ln \frac{V_5}{V_4}$$

$$= -3.588 + (-2.389) = -5.977 \text{ (J/K)}$$

$$w = P \Delta V = \frac{40}{27} \times (16.61 - 22.14) = -830.1 \text{ (J)}$$

$$q = n C_p \Delta T = \frac{5}{2} \times 8.314 \times (300 - 400) = -2078.5 \text{ (J)}$$

$$\Delta H = \Delta U + \Delta(PV) = -2078.5 \text{ (J)}$$

$$\Delta S = -5.977 \text{ (J/K)}$$

$$w = -830.1 \text{ (J)}$$

$$q = -2078.5 \text{ (J)}$$

$$\Delta H = -2078.5 \text{ (J)}$$

$$\Delta U = -1248.4 \text{ (J)}$$

3.

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

$$x + y = 1 \rightarrow y = 1 - x$$

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

$$a) f(x, y) = (x-2)^2 + (y-2)^2 + 4$$

$$f_x = 2(x-2) = 2x-4 \quad f_y = 2(y-2) = 2y-4$$

$$\rightarrow x = 2, y = 2 \text{ 일 때 extreme value } \boxed{z=4}$$

$$f_{xx} = 2, f_{yy} = 2, f_{xy} = 0 \Rightarrow D = 4 - 0 = 4 > 0.$$

$$f_{xx} > 0 \Rightarrow \text{minimum value is not.}$$

$$b) y = 1 - x$$

$$z = (x-2)^2 + (-1-x)^2 + 4 = x^2 - 4x + 4 + x^2 + 2x + 1 + 4 = 2x^2 - 2x + 9$$

$$\frac{dz}{dx} = 4x - 2 = 0 \rightarrow x = \frac{1}{2} \text{ 일 때 } \boxed{z = \frac{17}{2}} \text{ minimum.}$$

c) by using Lagrange undetermined multiplier method.

$$dz = 2(x-2)dx + 2(y-2)dy, \quad dy = -dx$$

$$= 2(x-2)dx - 2(y-2)dx$$

$$\begin{cases} 2x-4 = \lambda \\ 2y-4 = \lambda \\ x+y=1 \end{cases}$$

$$2-2x-4 = 2x-4 \quad x = \frac{1}{2}, y = \frac{1}{2}, \lambda = -3$$

$$\therefore x = \frac{1}{2}, y = \frac{1}{2} \text{ 일 때 } \boxed{z = \frac{17}{2}}$$

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.
- (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.

$$a) \overset{A}{1 \text{ mol. } P=1 \text{ atm.}} \quad \overset{B}{1 \text{ mol. } P=1 \text{ atm.}}$$

$$i) A \text{ 입장: } \Delta S_A = R \ln \frac{V_2}{V_1} = R \ln 2 \Rightarrow \Delta S = \boxed{2R \ln 2}$$

$$ii) B \text{ 입장: } \Delta S_B = R \ln 2$$

b) A 2mol, $P=2\text{atm}$, B 1mol, $P=1\text{atm}$

i) A 팽창: $\Delta S_A = 2R \ln \frac{V_B}{V_A} = 2R \ln 2$

ii) B 팽창: $R \ln 2 \rightarrow \Delta S = \boxed{3R \ln 2}$

c) Calculate the corresponding entropy changes if both have A

a)

A 1atm, 1mol	A 1atm, 1mol
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 \rightarrow mixture $\rightarrow \Delta S = 0$

b)

A 2atm, 2mol	A 1atm, 1mol
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 $\xrightarrow{①}$

A 1atm, 2mol	A 1atm, 1mol
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 $\xrightarrow{②}$

A $\frac{5}{3}\text{atm}, 3\text{mol}$

①: $\Delta S = 2R \ln 2$

②: $\Delta S = 3R \ln \frac{2}{3} \Rightarrow \Delta S_{\text{tot}} = R \ln 4 + R \ln \frac{8}{27}$
 $= \boxed{R \ln \frac{32}{27}}$