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AMSE205 Thermodynamics I

due date: Oct. 12, 2021 | Prof. Byeong-Joo Lee

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.

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.

Let $P_1 = 10atm$, $P_2 = 5atm$

$dU = TdS - PdV$,

(a) $$dS = \frac{dU}{T} + \frac{PdV}{T} = \frac{C_v dT}{T} + \frac{R}{V}dV$$

isothermal : $dT = 0$

$$\Delta S = \int_{S_1}^{S_2} dS = R\int_{V_1}^{V_2} \frac{dV}{V} = R\ln\frac{V_2}{V_1}$$

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

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

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

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

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

(c) Let $T_1 = 300K$

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

$$dS = \frac{C_v dT}{T}.$$ $$\Delta S = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{C_v}{T} dT = C_v \ln\left(\frac{T_2}{T_1}\right)$$

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

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

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

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

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

$$\therefore \Delta S = -8.644\,(J/K)$$

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

$T_1 = 300k$.

$P_1 = 10\ atm$.

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

a. $V_2 = 3V_1 = 7.3854 (L)$ $\quad T_2 = 300k$

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

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

$q = 0$

$$dU = T \cdot dS - pdV \Rightarrow 0 = T \cdot dS - pdV$$

$$dS = \frac{P}{T} dV = \frac{1}{T} \cdot \frac{RT}{V} dV$$

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

b. constant volume : $V_3 = V_2 = 3V_1 = 7.3854 (L)$

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

$w = 0$ ($\because$ constant volume)

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

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

$q = \Delta U = 1247.1\ J$

$$dU = T \cdot dS - pdV \Rightarrow dU = T \cdot dS$$

$$dS = \frac{dU}{T}, \quad \Delta S = \int_{T_2}^{T_3} \frac{C_v \cdot dT}{T} = C_v \cdot \ln \frac{T_3}{T_2} = 3.588\ J/k$$

c. constant temperature, $T_4 = T_3 = 400K$

$V_4 = 3V_3 = 22.1562\ (L)$ $\quad$. $P_4 = \frac{P_3}{3} = 1.481\ (atm)$

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

$q = W$

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

$dU = T \cdot dS - pdV \Longrightarrow dS = \frac{P}{T} dV = \frac{R}{V} dV$

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

$= 9.134\ (J/K)$

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

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

$\Delta U = C_v \Delta T = 1.5 \times 8.314 \times (T_5 - T_4) = -1247.1\ J$

$\Delta H = C_p \Delta T = 2.5 \times 8.314 \times (T_5 - T_4) = -2078.5\ J$

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

$q_p = \Delta H = -2078.5\ J$

$dU = T \cdot dS - pdV \Longrightarrow dH = T \cdot dS$

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

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

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

$W_t = 2822.75\ J$ $\quad$ $q_t = 2822.15\ J$, $W_t \simeq q_t$, $\Delta S_t = 15.876\ (J/K)$

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

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

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

$$x + y = 1$$

(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.

$f_{xx} = 2$

$f_{yy} = 2$

$f_{xy} = 0$

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

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

$\Rightarrow$ that is relative minimum of f.

$f(2,2) = 4$ 가 극솟값이다.

(b) eliminating one variable

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

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

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

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

$y = \frac{1}{2},\ x = \frac{1}{2}$ 에서 최솟값 $z = \frac{17}{2}$ 갖는다.

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

(c) using Lagrange undetermined multiplier

Let $z = f(x,y)$, $h(x,y) = x+y-1$

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

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

$\Rightarrow$ $2x - 4 = \lambda$, $2y - 4 = \lambda$ 를 만족하는 점 (x,y) 를 (x_1, y_1) 이라 두자.

그런데, $x_1 + y_1 - 1 = 0$ 이므로

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

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

즉, $y = \frac{1}{2}$, $x = \frac{1}{2}$ 에서 최솟값 $z = \frac{17}{2}$ 갖는다.

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

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.

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

<rigid container>

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

(a)

A	B
V, 1mole	V, 1mole

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

(b)

A	B
V, 2moles	V, 1mole

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

(C) _ (a)

A	A
V, 1mole	V, 1mole

$\longrightarrow \Delta S = 0.$ (변화 없다)

(C) _ (b)

① A	② A
V, 2moles	V, 1mole

① $\Delta S_① = 2R\ln\frac{\frac{4}{3}V}{V}$

$\Delta S_② = R\ln\frac{\frac{2}{3}V}{V}$

$$\Delta S_{tot} = 2R\ln\frac{4}{3} + R\ln\frac{2}{3} = R\left(\ln\frac{16}{9} + \ln\frac{2}{3}\right)$$
$$= R\ln\frac{32}{27}$$