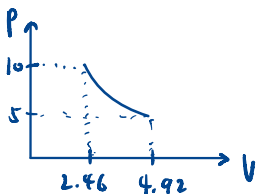


1. The initial state of one mole of a monatomic ideal gas is $P = 10 \text{ atm}$ and $T = 300 \text{ K}$. Calculate the change in the entropy of the gas for (a) an isothermal decrease in the pressure to 5 atm, (b) a reversible adiabatic expansion to a pressure of 5 atm, (c) a constant-volume decrease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

(a). by ideal gas law, $10 V_1 = 0.082 \times 300$, $V_1 = 2.46 \text{ L}$

$V_2 = 4.92 \text{ L} \therefore$ Isothermal process, $PV = \text{Constant}$

Plot P-V Graph,



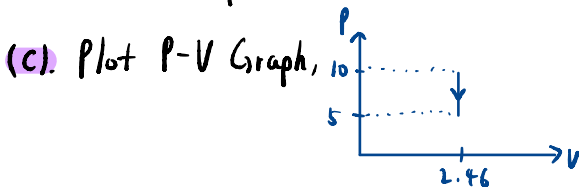
$$\Delta S = \frac{q}{T}, \quad q = w \therefore \Delta U = 0 \text{ in isothermal process}$$

$$w = q = \int P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} = 8.314 \times 300 \times \ln 2$$

$$\therefore \Delta S = \frac{q}{T} = 8.314 \times \ln 2 = 5.76, \quad \text{Ans) } 5.76 \text{ J/K}$$

(b). In adiabatic process, $q = 0$

$$\text{Since } \Delta S = \frac{q}{T}, \quad \Delta S = 0 \quad \text{Ans) } 0$$



$$\Delta U = q = nC_v \Delta T \therefore \text{Constant volume}$$

by ideal gas law, $T_2 = 150 \text{ K}$ also $C_v = 1.5 R \therefore$ monatomic ideal gas

$$\Delta S = \int_{300}^{150} \frac{nC_v}{T} dT = 1.5 \times 8.314 \times (-\ln 2) = -8.64 \quad \text{Ans) } -8.64 \text{ J/K}$$

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 .

By ideal gas law, $10 V_1 = 300 \times 0.082$, $V_1 = 2.46 \text{ L}$

$V_2 = 7.38 \text{ L}$, $P_2 = 3.33 \text{ atm}$ by process (a), $P_3 = 4.44 \text{ atm}$ by process (b)

$V_3 = 22.1 \text{ L}$, $P_3 = 1.49 \text{ atm}$ by process (c), $V_4 = 16.6 \text{ L}$ by process (d)

Process (a). $q = w = \Delta U = \Delta H = 0$ \therefore Free expansion, $\Delta S = nR \ln \frac{V_2}{V_1} = 9.13 \text{ J/K}$

Process (b). $w = 0$, $\Delta U = q = nC_v \Delta T$ \therefore Constant volume, $C_v = 1.5R$ \therefore monatomic ideal gas $\therefore \Delta U = q = 1.5 \times 8.314 \times 100 = 1247 \text{ J}$, $\Delta H = nC_p \Delta T = 2.5 \times 8.314 \times 100 = 2079 \text{ J}$, $\Delta S = \int_{300}^{400} \frac{nC_v}{T} dT = 1.5 \times 8.314 \times \ln \frac{4}{3} = 3.59 \text{ J/K}$

Process (c). $q = w = nRT \int_{V_2}^{V_3} \frac{1}{V} dV$ \therefore isothermal, $q = w = 8.314 \times 400 \times \ln 3 = 3654 \text{ J}$, $\Delta U = 0$, $\Delta H = 0$, $\Delta S = 9.13 \text{ J/K}$

Process (d). $w = P \Delta V = 1.49 \times (-5.5) \times 101.325 = -831 \text{ J}$, $\Delta U = nC_v \Delta T = -1247 \text{ J}$, $q = \Delta H = nC_p \Delta T = -2079 \text{ J}$, $\Delta S = \int_{400}^{300} \frac{nC_p}{T} dT = 2.5 \times 8.314 \times \ln \frac{3}{4} = -5.98 \text{ J/K}$

Ans) $q_{\text{tot}} = 2822 \text{ J}$, $w_{\text{tot}} = 2822 \text{ J}$, $\Delta U_{\text{tot}} = 0$, $\Delta H_{\text{tot}} = 0$, $\Delta S_{\text{tot}} = 15.9 \text{ J/K}$

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

$$x + y = 1$$

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

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

\therefore we get extreme value at $(2, 2)$

Ans) 4 (when $x=2, y=2$)

(b). Plug $y = 1-x$, then $z = (x-2)^2 + (1-x)^2 + 4 = 2x^2 - 2x + 9$

We can get extreme value when $\frac{dz}{dx} = 0$, $\therefore 4x - 2 = 0$, $x = \frac{1}{2}$

then $y = \frac{1}{2}$, \therefore Condition fulfilled

Ans) 8.5 (when $x = \frac{1}{2}, y = \frac{1}{2}$)

(c). Let $f(x, y, \lambda) = (x-2)^2 + (y-2)^2 + 4 + \lambda(x+y-1)$

$$\left. \begin{aligned} \frac{\partial f}{\partial x} &= 2x-4 + \lambda = 0 \\ \frac{\partial f}{\partial y} &= 2y-4 + \lambda = 0 \\ \frac{\partial f}{\partial \lambda} &= x+y-1 = 0 \end{aligned} \right\} \begin{aligned} 2x + \lambda &= 4 \\ 2y + \lambda &= 4 \\ x + y &= 1 \end{aligned} \quad \left(x = \frac{1}{2}, y = \frac{1}{2}, \lambda = 3 \right)$$

Ans) 8.5 (when $x = \frac{1}{2}, y = \frac{1}{2}$)

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

Total PV is constant \therefore partial pressure decreases by increased volume.

$$\therefore \Delta U = 0, q = w, \Delta S = \int \frac{P dV}{T} = nR \ln \frac{V_f}{V_i}$$

$$(a). \Delta S_A = R \ln 2, \Delta S_B = R \ln 2$$

$$\therefore \Delta S_{\text{tot}} = 2R \ln 2$$

$$\text{Ans) } \Delta S = 2R \ln 2$$

$$(b). \Delta S_A = 2R \ln 2, \Delta S_B = R \ln 2$$

$$\therefore \Delta S_{\text{tot}} = 3R \ln 2$$

$$\text{Ans) } \Delta S = 3R \ln 2$$

(c)-(i). A is distributed uniformly both partition is removed and not.

\therefore Not mixing of different gases.

$$\therefore \Delta S = 0$$

$$\text{Ans) } \Delta S = 0$$

(c)-(ii). Assume that left compartment has 2 moles of A

$$\Delta S_A = 2R \ln \frac{4}{3}, \Delta S_B = R \ln \frac{2}{3} \quad \therefore \Delta S_{\text{tot}} = R \ln \frac{32}{27}$$

$$\text{Ans) } \Delta S = R \ln \frac{32}{27}$$