1. A one mole sample of gas follows the equation of state given by $pV_m = RT(1 + Bp)$. The gas is initially at 373 K. The gas then undergoes a Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = 5/2\ R$, $\mu_{JT} = 0.21$ K atm^{-1}, $B = -0.525(K/T)$ atm^{-1}. Assume that these values are constant over the temperature range involved. Derive the expression for ΔS for the gas and determine its value. [Hint: Consider the entropy as a function of temperature and pressure]

5

Ans:– Consider the temperature(T) as a function of pressure(p) and enthalpy (H):

$$T \equiv T(P, H)$$

So, $$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial H}\right)_P dH$$

As, Joule–thompson expansion is a constant enthalpy process,

Therefore, $$dT = \left(\frac{\partial T}{\partial P}\right)_H dp = \mu_{JT}\, dp \qquad \left[\text{where}, \left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT} \to \begin{array}{l}\text{Joule}\\\text{-Thomson}\\\text{coefficient}\end{array}\right]$$

$$\Rightarrow \Delta T = \mu_{JT}\int_{P_i}^{P_f} dp = \mu_{JT}\,\Delta P$$

$$\Rightarrow \Delta T = \mu_{JT}\,(P_f - P_i)$$

$$= 0.21\ \text{k·atm}^{-1} \times (1 - 100)\ \text{atm}$$

$$\Rightarrow \boxed{\Delta T = -21\ K}$$

Now, $\Delta T = T_f - T_i \Rightarrow \underline{T_f = T_i + \Delta T = (373 - 21)\ k = 352\ K}$ [Mean T = 363 K)

Consider the entropy(S) as a function of temperature(T) & Pressure(P):

$$S \equiv S(T, P)$$

So, $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \left[\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \ \& \ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\right]$$

Now, for $V_m = \dfrac{RT}{P}(1 + Bp)$

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{R}{P}(1 + Bp)$$

Then, $\Rightarrow dS_m = \dfrac{C_{p,m}}{T} dT - \dfrac{R}{P}(1 + Bp)\,dp$

from Maxwell's relation

or, $dS_m = \dfrac{C_{p,m}}{T} dT - \dfrac{R}{P}\,dp - R\cdot B\,dp$

Now, on integration,

$$\Delta S_m = \int_i^f dS_m = C_{p,m}\ln\left(\frac{T_f}{T_i}\right) - R\cdot\ln\left(\frac{P_f}{P_i}\right) - RB\,(P_f - P_i)$$

$$= \frac{5}{2}R\ln\left(\frac{352}{373}\right) - R\ln\left(\frac{1}{100}\right) - R\left(-\frac{0.525\ \text{atm·k}^{-1}}{363\,K}\right)\times(-99)\ \text{atm}$$

$$\boxed{\Delta S_m = +35.89\ J\,k^{-1}\,mol^{-1}}\ \text{Ⓐ}$$

2. A three step reversible cycle consists of (i) an isothermal expansion at T_1 (ii) a constant volume (isochoric) cooling to T_2 and (iii) an adiabatic compression to the initial state. Calculate the work done in each step considering 1 mole of an ideal gas. Show that the efficiency is given by:

$$\eta = 1 - \frac{T_1 - T_2}{T_1 \ln(T_1/T_2)}$$

Ans:-

(i) Isothermal expansion at T_1

(ii) Isochoric Cooling at to T_2

(iii) Adiabatic Compression to the initial state
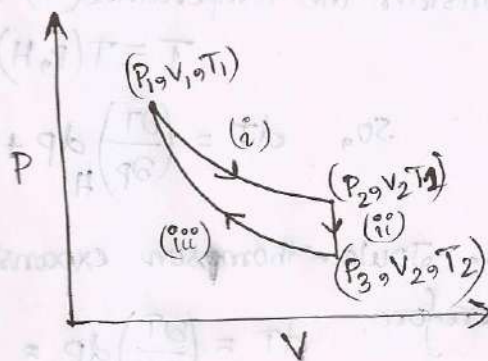
For, step(i), $W = -RT_1 \ln \frac{V_2}{V_1}$ & $q = RT_1 \ln \frac{V_2}{V_1}$

as, For isothermal reversible process $\Delta U = q_{rev} + W_{rev} = 0$

Therefore, $\boxed{q = -W}$

step(ii), $W = 0$ & $q = \Delta U = C_v(T_2 - T_1)$. $[T_2 < T_1]$

Since, for isochoric process $\Delta V = 0$ so, $W = P\Delta V = 0$, $\boxed{\Delta U = q}$.

step(iii), $q = 0$, $\boxed{W = \Delta U} = C_v(T_1 - T_2)$ $[T_1 > T_2]$

Since, for adiabatic process, $q = 0$

Now, Efficiency $\eta = \frac{|W|_{cycle}}{q} = \frac{-RT_1 \ln \frac{V_2}{V_1} + C_v(T_1 - T_2)}{RT_1 \ln \frac{V_2}{V_1}}$

$$\boxed{\eta = 1 - \frac{C_v(T_1 - T_2)}{RT_1 \ln\left(\frac{V_2}{V_1}\right)}}$$

In step(iii) $TV^{\gamma - 1} = $ Const. [for adiabatic reversible process]

So, $T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$

or $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = \left(\frac{V_2}{V_1}\right)^{\frac{C_p}{C_v} - 1}$

$\Rightarrow \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{R/C_v}$ or, $\boxed{\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^{C_v/R}}$

Now, $\eta = 1 - \dfrac{C_v(T_1 - T_2)R}{RT_1 \ln\left(\dfrac{T_1}{T_2}\right)C_v}$

$$\boxed{\eta = 1 - \dfrac{T_1 - T_2}{T_1 \ln\left(\dfrac{T_1}{T_2}\right)}} \quad (\text{Proved})$$

---

3. Derive the thermodynamic equation of state $\left(\dfrac{\partial H}{\partial P}\right)_T = V - T\left(\dfrac{\partial V}{\partial T}\right)_P$ 2

Ans:-   from Fundamental equation of Thermodynamics,

$$dH = Tds + VdP.$$

Now, differentiating the eqⁿ. by w.r.t P at constant T.

we get,

$$\left(\dfrac{\partial H}{\partial P}\right)_T = T\left(\dfrac{\partial S}{\partial P}\right)_T + V$$

$$= -T\left(\dfrac{\partial V}{\partial T}\right)_P + V \quad \left[\text{from Maxwell's relation, } \left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P\right]$$

or

$$\boxed{\left(\dfrac{\partial H}{\partial P}\right)_T = V - T\left(\dfrac{\partial V}{\partial T}\right)_P} \quad (\text{Proved}).$$

4. Calculate the change of entropy when 200 g of ice at 0°C is added to 200 g of water at 363 K in an insulated vessel. The molecular weight of water is 18.0 gm/mole, the enthalpy of fusion for ice is 6.01 kJ/mole, and assume the heat capacity for water is 75.5 J K^{-1} mole^{-1}, independent of temperature.

Ans:- For, Heat exchange process, $Q_{lost} = Q_{gained}$.

In this case, Heat lost by water (Q_{lost}) = Heat gained by ice (Q_{gained}) where, the temperature change ΔT.

$$\Delta T = (T_{org} - T_{final}) = (\text{original temp.} - \text{final temp.})$$

Now, $\underset{lost}{Q} = M_{water} \cdot S \cdot (T_{org} - T_{final}) \quad \text{—①} \quad \left[\begin{array}{l} S = \text{heat capacity} \\ \text{for water.} \\ \rightarrow c_p \end{array} \right]$

$$Q_{gained} = M_{ice} \cdot \Delta H_{fus} + M_{ice} \cdot S (T_{final} - 0°c) \quad \text{—②}$$

Combi from ① & ②

$\Rightarrow \quad M_{water} \cdot S \cdot (T_{org} - T_f) = M_{ice} \cdot \Delta H_{fus} + M_{ice} \cdot S (T_f - 0°c)$

$\Rightarrow \quad \dfrac{200g}{18g/mol} \times 75.5 \; J\,K^{-1}mol^{-1} \times (363 - T_f)K = \dfrac{200}{18} \times 6.01 \times 10^3 \; J$

$$+ \dfrac{200}{18} \times 75.5 \times (T_f - 273)$$

$\Rightarrow \quad 75.5 \times (636 - 2T_f) = 6.01 \times 10^3$

$\Rightarrow \quad 2T_f = + 556.39 \, K$

or $\boxed{T_f = 278.19 \, K}$ Ⓐ

So, change in entropy $\quad \overset{ice}{\downarrow} \quad\quad \overset{water}{\downarrow}$

$$\Delta S = \left(\dfrac{\Delta H_{fus}}{T} + c_p \cdot \ln\dfrac{T_f}{T_i} + c_p \cdot \ln\dfrac{T_f}{T_i} \right) \times n$$

$$= \left(\dfrac{6010 J\,mol^{-1}}{273 K} + \underset{J\,K^{-1}mol^{-1}}{75.5 \times \ln\dfrac{278.19}{273K}} + \underset{J\,K^{-1}mol^{-1}}{75.5 \times \ln\dfrac{278.19}{363}} \right) \times \dfrac{200 \, g}{18 g\,mol^{-1}}$$

$$= (22.014 + 1.4218 - 20.09) \times \dfrac{200}{18} \; J\,K^{-1}$$

$\boxed{\Delta S = 37.17 \, J\,K^{-1}}$ Ⓐ

$$\pm 1.5 \, J\,K^{-1}.$$

5. An Otto cycle is the cycle involved in the operation of an internal combustion engine. In this case air can be considered to be the working substance that is assumed to behave like an ideal gas. The cycle consists of the following steps:

Step I: reversible adiabatic compression from A to B;

Step II: reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel;
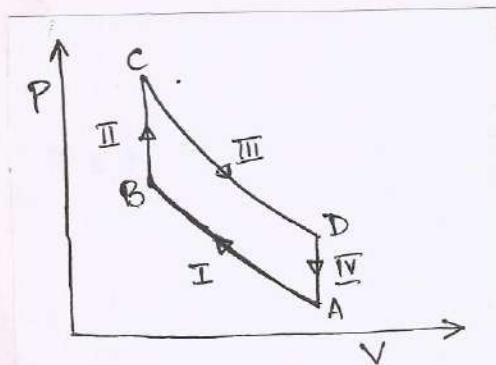
Step III: reversible adiabatic expansion from C to D;

Step IV: reversible and constant-volume pressure decrease back to state A.

[Assume that in State A, $V = 4.00$ dm^3, $p = 1.00$ atm, and $T = 300$ K; $p_C/p_B = 5$, $C_{p,m} = 7/2$ R.]

(i) On a PV diagram indicate the individual steps of the cycle marking each step   1

(ii) Determine the change in entropy (of the system and of the surroundings) for *Step II* of the cycle.   2

(iii) Evaluate the efficiency for a compression ratio of 10:1 meaning that $V_A = 10V_B$ assuming that the heat is supplied in *Step II*.   5

Ans :- (i)

$PV = nRT \rightarrow n = \dfrac{PV}{RT} = \dfrac{1 \times 4}{0.082 \times 300} = 0.1624$ mol

$\rightarrow$ PV diagram.

step I : Reversible adiabatic Compression

step II : Reversible isochoric pressure increase

step III : Reversible adiabatic expansion

Step IV : Reversible isochoric pressure decrease.

(ii) For step II, i.e for Constant volume process.

entropy change $= \Delta S_{II} = n C_V \ln\left(\dfrac{T_C}{T_B}\right)$ [Where, $C_{V,m} = C_{p,m} - R$

as at Constant volume $\dfrac{T_C}{T_B} = \dfrac{P_C}{P_B} = 5$. $= 7/2 R - R$

                                                   $\boxed{C_{V,m} = \dfrac{5}{2} R}$

$\therefore \Delta S_{II} = \dfrac{5}{2} \times 8.314 \, JK^{-1} mol^{-1} \times \ln 5 \times 0.1624$ mol

$\Rightarrow \boxed{\Delta S_{II} = +5.36 \, JK^{-1}}$ $\rightarrow$ entr change in entropy of the system

Therefore, ΔS_{II} for Surroundings $= -\Delta S_{II}$ [as, $\Delta S_{Total} = \Delta S_{sys} + \Delta S_{surroundings}$

or, $\underline{\Delta S_{II, sur}} = -\underline{\Delta S_{II, sys}} = -5.36 \, JK^{-1}$ (A) $= 0$. for reversible Process.

(iii). Efficiency is the quotient of the net work from the system, to the heat added to the system.

$$\text{So,} \quad \eta = \frac{|W|_{cycle}}{|q_2|} \qquad [q_2 = q_{II}].$$

$$W_{cycle} = W_1 + W_3 = \Delta U_1 + \Delta U_3 \quad [\text{as, } q_1 = q_3 = 0]$$

$$= C_V(T_B - T_A) + C_V(T_D - T_C)$$

$$q_2 = \Delta U_2 = C_V(T_C - T_B)$$

$$\text{Therefore, } \eta = \frac{|T_B - T_A + T_D - T_C|}{|T_C - T_B|} = 1 - \left(\frac{T_D - T_A}{T_C - T_B}\right).$$

for reversible adiabatic process, It is true that,

$$TV^{\gamma - 1} = \text{Constant} \quad \left[\text{where, } \gamma = \frac{C_P}{C_V}\right]$$

& T = absolute temperature

$$\text{So, } T_A V_A^{\gamma - 1} = T_B V_B^{\gamma - 1} \quad \text{and} \quad T_C V_C^{\gamma - 1} = T_D V_D^{\gamma - 1}.$$

$$\text{or } \frac{T_A}{T_B} = \left(\frac{V_B}{V_A}\right)^{\gamma - 1} - ① \quad \text{or} \quad \frac{T_C}{T_D} = \left(\frac{V_D}{V_C}\right)^{\gamma - 1} - ②$$

Given that, $C_{P,m} = \frac{7}{2}R$ & $C_{V,m} = \frac{5}{2}R$, So, $\gamma = \frac{7}{5}$

from ① & ②

since, $V_B = V_C$ and $V_A = V_D$,

$$\frac{T_A}{T_B} = \frac{T_D}{T_C} \quad \text{or, } T_D = \frac{T_A T_C}{T_B}$$

$$\text{Then, } \eta = 1 - \frac{\frac{T_A T_C}{T_B} - T_A}{T_C - T_B} = 1 - \frac{T_A}{T_B}$$

$$\text{or } \eta = 1 - \left(\frac{V_B}{V_A}\right)^{\gamma - 1}$$

$$\& \text{ for, } V_A = 10 V_B, \quad \eta = 1 - \left(\frac{1}{10}\right)^{\frac{7}{5} - 1} = 1 - \left(\frac{1}{10}\right)^{\frac{2}{5}} = 0.60$$

$$\boxed{\eta = 0.60} \quad Ⓐ.$$