

(i) The question mentioned to be with generalized mathematical form of 1st law of thermodynamics, as taught in the class, it is

$$* \boxed{q = nC_v dT + \left[ p + \left( \frac{\partial u}{\partial v} \right)_T \right] dv} \quad \text{--- (1)}$$

For reversible process:-

As the condition is adiabatic,  $q = 0$ .  
eq<sup>n</sup> (1) becomes for ideal gas

$$\Rightarrow nC_v dT = -p dv$$

For ideal gas,  $p = \frac{nRT}{V}$

$$nC_v \frac{dT}{T} = -nR \frac{dv}{v} \quad \text{--- (2)}$$

Integrate the equation (2) to find the overall change.

$$\Rightarrow nC_v \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{v_1}^{v_2} \frac{dv}{v}$$

Given:  
( $v_2 = 2v_1$ )

$$\Rightarrow nC_v \ln \frac{T_2}{T_1} = -nR \ln \frac{v_2}{v_1} = -nR \ln \frac{2v_1}{v_1}$$

$$\Rightarrow C_v \ln \frac{T_2}{T_1} = -R \ln 2$$

$$\Rightarrow \frac{C_v}{R} \ln \frac{T_2}{T_1} = -\ln 2 = \ln \left( \frac{1}{2} \right)$$

$$\Rightarrow \ln \left( \frac{T_2}{T_1} \right)^{\frac{C_v}{R}} = \ln \left( \frac{1}{2} \right); \Rightarrow \left( \frac{T_2}{T_1} \right)^{\frac{C_v}{R}} = \frac{1}{2}$$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{1}{2} \right)^{\frac{R}{C_v}}$$

$$\Rightarrow \frac{T_2}{T_1} = \left( \frac{1}{2} \right)^{\frac{C_p - C_v}{C_v}} = \left( \frac{1}{2} \right)^{\gamma - 1}$$

$$\Rightarrow \boxed{T_2 = T_1 \left( \frac{1}{2} \right)^{\gamma - 1}}$$

Now, this generalized mathematical form of 1st law of thermodynamics is applicable to any system under any condition, but under infinitesimal change where state change does not occur and  $C_v = \left(\frac{\partial U}{\partial T}\right)_v$  remains same under no state change condition.

Now, however, as the question mentions that the volume change occurs against a constant  $P_{ext} = P_2$  this change is ideally an irreversible change. But it can be worked out under reversible approximation applying generalized 1st law.

Under adiabatic condition

$q=0$ , Eq<sup>n</sup> ① becomes for ideal gas,

$$0 = nC_v \Delta T + P \Delta V$$

$$nC_v \Delta T = -P \Delta V$$

Given:  $P_{ext} = P_2$ ,  $V_2 = 2V_1$

$$nC_v \Delta T = -P_2 (2V_1 - V_1)$$

$$nC_v (T_2 - T_1) = -P_2 V_1$$

Using ideal gas law,  $V_1 = \frac{nRT_1}{P_1}$

$$nC_v (T_2 - T_1) = -P_2 \left( \frac{nRT_1}{P_1} \right)$$

$$\Rightarrow C_v (T_2 - T_1) = -\frac{P_2}{P_1} RT_1$$

$$\Rightarrow T_2 - T_1 = -\frac{P_2}{P_1} \frac{RT_1}{C_v}$$

$$\Rightarrow T_2 = T_1 - \frac{P_2}{P_1} \frac{R}{C_v} T_1 \quad ; \Rightarrow \boxed{T_2 = T_1 \left[ 1 - \frac{P_2}{P_1} \frac{R}{C_v} \right]}$$

1. (a) A polytropic expansion follows the general relation  $PV^n = C$

General formula of w.d in a polytropic process is

$$W = - \int_{V_1}^{V_2} P dV \quad \text{--- (1)}$$

Using  $PV^n = C$

$$P = \frac{C}{V^n}$$

$$W = - \int_{V_1}^{V_2} \frac{C}{V^n} dV = \frac{C}{1-n} \left( V_2^{1-n} - V_1^{1-n} \right) \quad \text{--- (2)}$$

$$C = PV^n = \left( \frac{RT}{V} \right) \cdot V^n = RT \cdot V^{n-1}$$

$$C = RT_1 V_1^{n-1} = RT_2 V_2^{n-1}$$

Putting  $C$  in eq<sup>n</sup> (2)

$$W = - \frac{RT_1 V_1^{n-1}}{1-n} \left( V_2^{1-n} - V_1^{1-n} \right)$$

~~or~~

$$= \frac{RT_1 V_1^{n-1}}{n-1} \left( V_2^{1-n} - V_1^{1-n} \right)$$

$$= \frac{R}{n-1} \left[ T_1 V_1^{n-1} V_2^{1-n} - T_1 V_1^{n-1} V_1^{1-n} \right]$$

$$W = \frac{RT_1}{n-1} \left[ V_1^{n-1} \left( V_2^{1-n} - V_1^{1-n} \right) \right]$$

$$V_1^{n-1} V_2^{1-n} = \left( \frac{V_1}{V_2} \right)^{n-1}$$

$$w = \frac{R \cdot T_1}{n-1} \left[ \left( \frac{V_1}{V_2} \right)^{n-1} - 1 \right]$$

$$\left( \frac{V_1}{V_2} \right)^{n-1} = \frac{T_2}{T_1}$$

$$\Rightarrow w = \frac{R T_1}{n-1} \left[ \frac{T_2}{T_1} - 1 \right]$$

$$\Rightarrow \boxed{w = \frac{R}{n-1} (T_2 - T_1)}$$

for  $T_1 = 300 \text{ K}$ ,  $T_2 = 200 \text{ K}$ , &  $n = 2$ ,  $R = 8.314 \text{ J/mol}\cdot\text{K}$

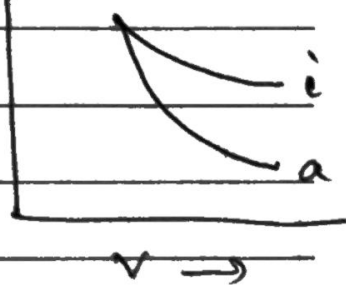
$$w = \frac{8.314}{2-1} (200 - 300)$$

$$w = -831.4 \text{ J}$$

(iii) ~~W.D~~

In a P-V diagram, the W.D by the gas during expansion is the area under the curve of the process from  $V_1$  to  $V_2$ .  $W.D = \text{Area under the curve}$

For the calculation of slope of the curves,  $P$  for isothermal process involving ideal gas,



$$W.D = \text{Area under the curve} = W = \int_{V_1}^{V_2} P dV$$

$PV = \text{Const.}$

$$\text{or, } PdV + VdP = 0$$

$$\text{or, } \left( \frac{dP}{dV} \right)_i = - \left( \frac{P}{V} \right) \quad \text{--- (A)}$$

for adiabatic process of ideal gas,  
 $PV^\gamma = \text{Const.}$

$$\Rightarrow \ln P + \gamma \ln V = \ln c$$

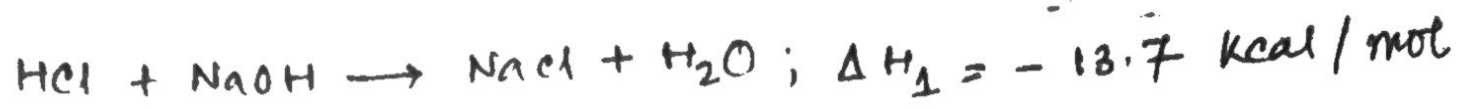
$$\Rightarrow \frac{1}{P} dP + \frac{\gamma}{V} \cdot dV = 0$$

$$\left( \frac{dP}{dV} \right)_a = -\gamma \left( \frac{P}{V} \right)$$

$$\text{Hence, } \left( \frac{dP}{dV} \right)_a > \left( \frac{dP}{dV} \right)_i$$

Hence, adiabatic curve is steeper than isotherm.

Since the adiabatic curve is steeper, the area under it is smaller than the isothermal curve for the same volume change. So, isothermal expansion does more work.



Volume = 10 ml

Normality = 0.1 (N)

Normality = 0.1 (N)  
Number of moles of  $\text{CH}_3\text{COOH}$  or  $\text{NaOH}$  used =  $0.1 \times 0.01 \text{ L}$   
= 0.001 mol

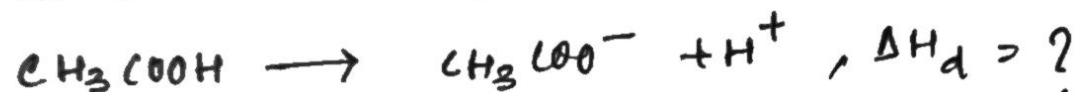
For, 0.001 moles, Heat of neutralisation is  $= -12.5 \text{ cal}$

$$11 \quad 1 \quad " \quad " \quad " \quad " \quad " = \frac{-12.5}{0.001}$$

$$= -12500 \text{ cal/mol}$$

$$= -12.5 \text{ Kcal/mol.}$$

For the dissociation of Acetic Acid—

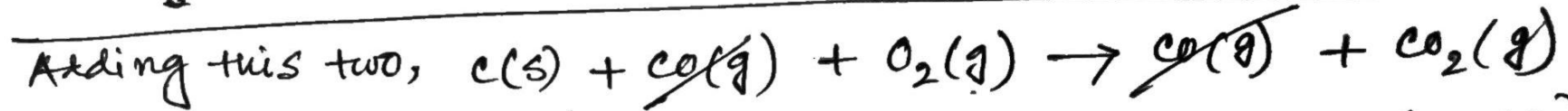
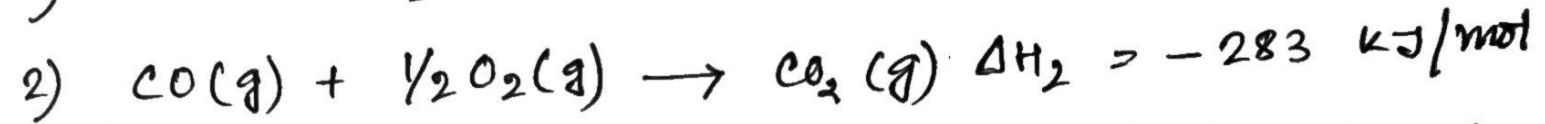
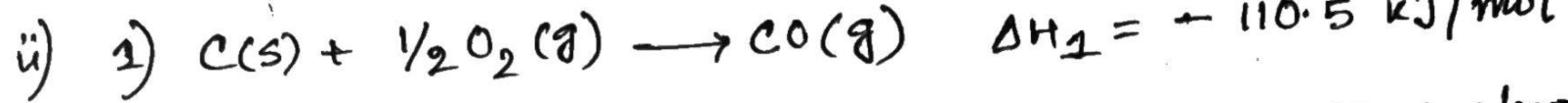


Therefore, applying Hess's law —

$$\Delta H_d \text{ (Endo-thermic process)} = (\text{Heat of neutralisation of W.A}) - (\text{Heat of neutralisation of S.A})$$

or,  $\Delta H_d = -12.5 - (-13.7) \text{ Kcal/mol}$

$$\Delta H_1 = 1.2 \text{ Kcal/mol}$$



$$\Delta H = -110.5 + (-283)$$



$$\Delta H = -393.5 \text{ kJ/mol.}$$



Q:2) ii) Hess's Law:

For a chemical reaction, the net heat change ( $\Delta H$  or  $\Delta U$ ) will be same whether the process occurs in one step or in several steps.

Acc. to

2 (iii) 1<sup>st</sup> Law of Thermodynamics:-  
 $dU = dq + dw$

Clausius inequality:-

$$dq \leq Tds$$

Substituting Clausius inequality in 1<sup>st</sup> law

$$dU \leq Tds + dw$$

$$dU - dw \leq Tds \quad \text{--- (1)}$$

$$-dw \leq Tds - dU$$

Definition of Helmholtz free energy

$$A = U - TS$$

$$dA = dU - Tds$$

$$-dA = Tds - dU \quad \text{--- (2)}$$

Equating (1) & (2)

$$-dw \leq -dA$$

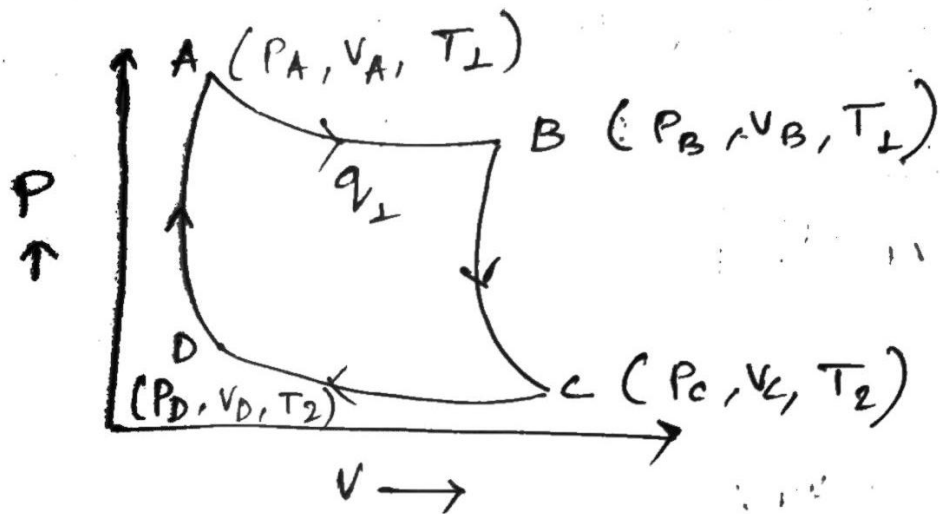
for an isothermal process,

$$w_{\max} = \Delta A \quad (05)$$

This indicates free energy is the freely accessible max. work done.

Q: 3) Carnot engine operates between temperatures 600 K and 300 K using one mole of  $O_2$  gas.

$$T_1 = 600 \text{ K} \quad T_2 = 300 \text{ K}, \quad n = 1 \text{ mole.}$$



A  $\rightarrow$  B (Reversible) Isothermal Expansion)

B  $\rightarrow$  C (Reversible Adiabatic Expansion)

C  $\rightarrow$  D (Reversible Isothermal Compression)

D  $\rightarrow$  A (Reversible Adiabatic Compression)

1) Efficiency of Carnot cycle,  $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{600}$   
 $= 0.5$   
 $= 50\%$

ii) The gas undergoes expansion from  $V_A$  to  $V_B$  such as pressure  $P_A = 20 \text{ atm}$  drops to  $P_B = 5 \text{ atm}$ .

Assuming ideal gas behaviour —

$$P_A V_A = nRT_1$$

$$P_B V_B = nRT_1$$

As,  $A \rightarrow B$  is an Iso-thermal process, so temp<sup>r</sup> remains same.

$$\frac{P_A V_A}{P_B V_B} = \frac{nRT_1}{nRT_1} \Rightarrow \frac{V_A}{V_B} = \frac{P_B}{P_A}$$

$$\Rightarrow \frac{V_A}{V_B} = \frac{5}{20} = \frac{1}{4}$$

$$\Rightarrow \boxed{\frac{V_B}{V_A} = 4}$$

$$W_{\text{iso-rev-expansion}} = -nRT_1 \ln\left(\frac{V_B}{V_A}\right)$$

$$= -1 \times 8.314 \times 600 \times \ln(4)$$

$$= -6915 \text{ J} = -6.915 \text{ KJ}$$

iii) We know,  $\eta = \frac{|W|}{Q_h}$  by the system

So, the net work done per cycle =  $(-6.915 \times 0.5)$

$$= -3.4575 \text{ KJ}$$

As for the Isothermal rev.expansion

process,  $du = 0$  &  $Q_h = W_{AB} = W_1$

Another Way

$$W_{\text{net}} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$= -nRT_1 \ln\left(\frac{V_B}{V_A}\right) + C_V(T_2 - T_1)$$

$$-nRT_2 \ln\left(\frac{V_D}{V_C}\right) + C_V(T_1 - T_2)$$

$$W_{\text{net}} = -nRT_1 \ln\left(\frac{V_B}{V_A}\right) - nRT_2 \ln\left(\frac{V_D}{V_C}\right)$$

Now, for adiabatic process —

$$TV^{\gamma-1} = \text{constant}$$

$$\text{So, } T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1} \quad \text{and} \quad T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1}$$

$$\therefore \left( \frac{V_B}{V_A} \right)^{\gamma-1} = \left( \frac{V_C}{V_D} \right)^{\gamma-1} \Rightarrow \left( \frac{V_B}{V_A} \right) = \left( \frac{V_C}{V_D} \right)$$

Therefore—

$$W_{\text{net}} = -nRT_1 \ln \left( \frac{V_B}{V_A} \right) - nRT_2 \ln \left( \frac{V_A}{V_B} \right)$$

$$= -nRT_1 \ln \left( \frac{V_B}{V_A} \right) + nRT_2 \ln \left( \frac{V_B}{V_A} \right)$$

$$= nR \ln \left( \frac{V_B}{V_A} \right) (T_2 - T_1)$$

$$= 1 \times 8.314 \times \ln(4) \times (300 - 600)$$

$$= -3457.69 \text{ J}$$

$$\boxed{W_{\text{net}} = -3.45 \text{ kJ}}$$