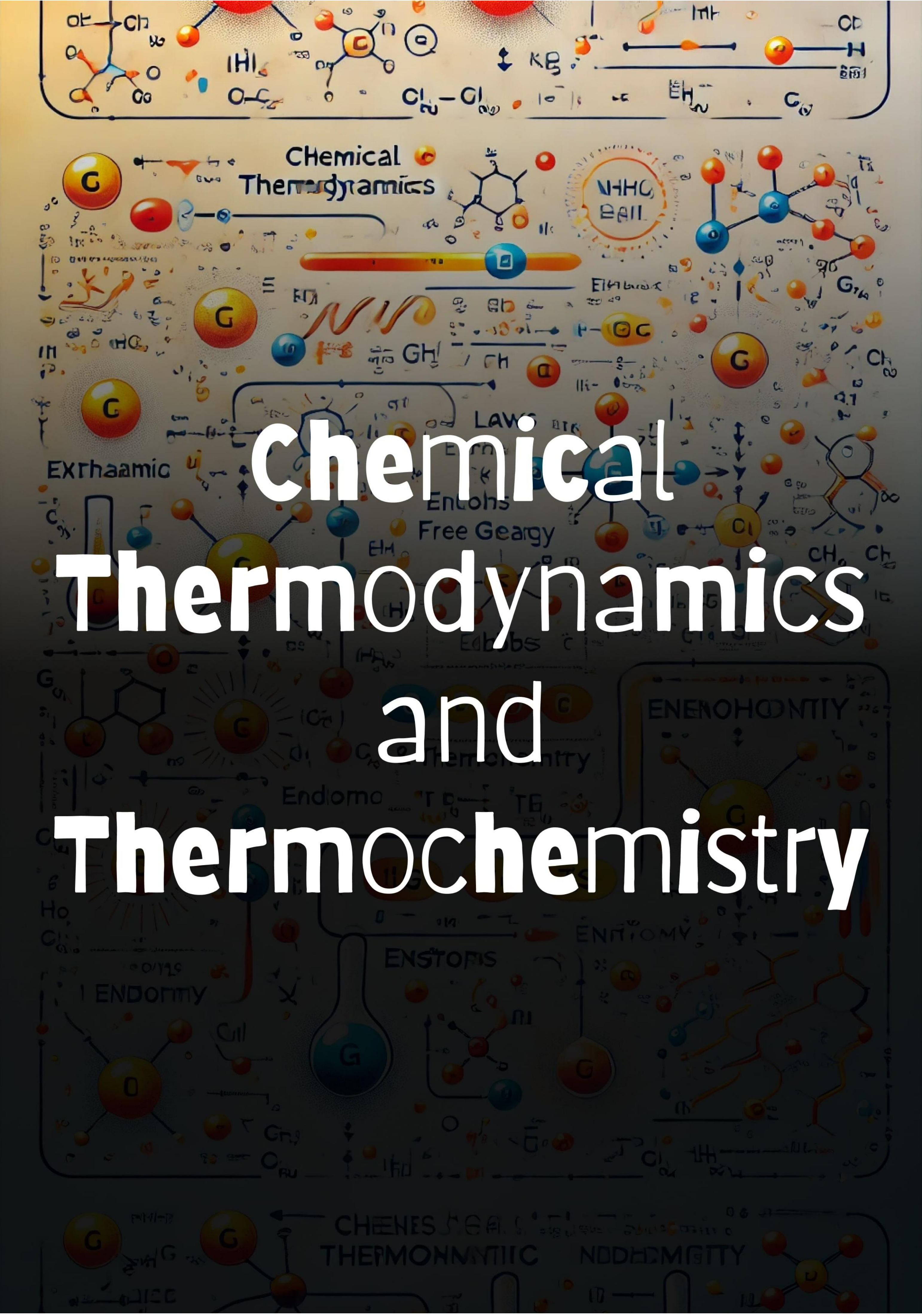
Chemical Thermodynamics and Thermochemistry



THERMODYNAMICS AND THERMOCHEMISTRY

Mass - E   Refractive index - I   Pressure of gas - I
Volume - E   Density of liquid or Solid - I   Resistance - E
Specific Resistance - I   -I
Spring force - E   M.P and B.P - E

TEMPERATURE - Intensive

THERMODYNAMIC FUNCTION

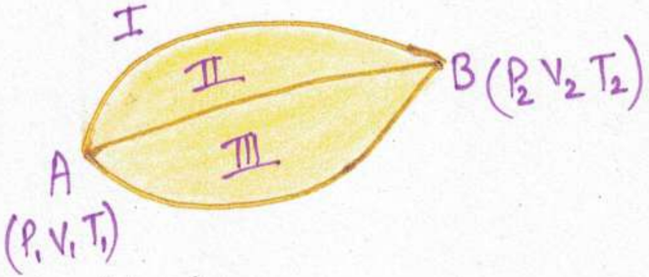
There are two types of thermodynamic functions—

1. STATE FUNCTION

2. PATH FUNCTION

1. Any Physical quantity which have same value for path I, II and III will be called state functions.

e.g:- Internal energy (ΔE or ΔU)



2. If it will depend on path like for path I, path II, path III. we have different value, then function will be path function.

e.g:- Heat, work

THERMODYNAMIC PROCESS

Isochoric process

Those process in which volume should be constant.

$\Delta V = 0$

$V =$ constant

$dV = 0$

$\boxed{P \propto T \text{ (Gray Lussac's Law)}}$

Isobaric process

Those process in which pressure will be constant.

$\Delta P = 0$ $P =$ constant

$dP = 0$

$V \propto T$ (Charles's Law)

Isothermal-process

Those process in which temperature will be constant.

$\Delta T = 0$

$dT = 0$ $\quad T = \text{constant}$

$PV = \text{constant}$

$P \propto \frac{1}{V}$ (Boyle's Law)

Adiabatic-process

The Process in which heat will be constant.

$V = \text{constant}$

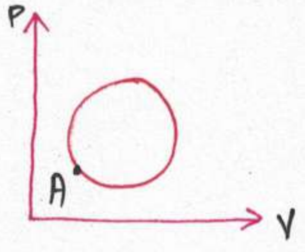
$dq = 0$

$\Delta q = 0$

Cyclic-process

The Process in which we have initial and final state the same. Graphically it will represent a close curve.

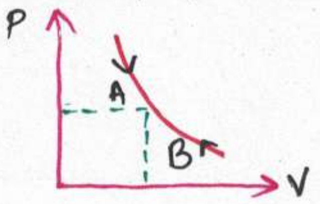
$\boxed{\Delta U = 0}$



Reversible-process

$R \rightleftharpoons P$

During reversible process system will be in thermal mechanical chemical etc equilibrium with surrounding. Graphically, if we have continuous curve, then it will be reversible process.



Irreversible process

When during process only equilibrium will be established at initial and final state. For irreversible process only external or constent pressure will be provided.

Graphically, we don't have continuous curve for irreversible proces

First Law of Thermodynamics

$dQ = dv + dw$

It is based on energy conservation

$$dq = du + dw$$

Where dq = Heat

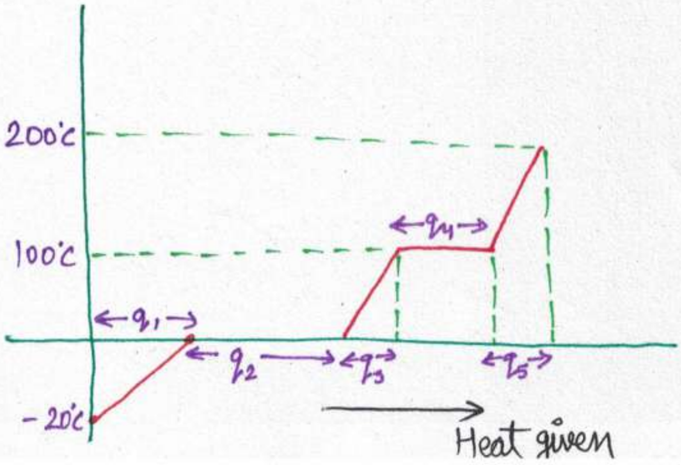
du = internal energy

dw = work

HEAT -

Principle of calorimetry

Heat given = Heat taken



We are expressing heat in terms of -

$$\boxed{Q = ms\Delta t} \rightarrow \boxed{\Delta t = L}$$

Where m = mass of substance
s = specific heat of substanc
Δt = change in temperature

Specific heat of water is "1 cal/gm."

$d = 1 g/ml$
$Q = mL$

i.e = amt of heat for phase transfer.

$Q = q_2 = mL_1$ (when solid → Liquid) L_1 = Latent heat of fusion
$Q = q_4 = mL_4$ (when Liquid → Vapour) L_4 = Latent heat of vapourisation

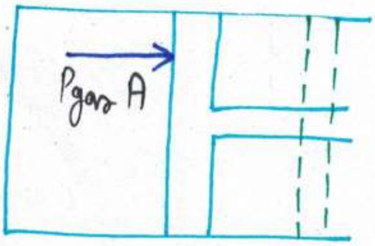
For gases, $\boxed{dq = nC_{process}\, dT}$

Where, n = no. of moles of gas
C = molar heat capacity of gas
dT = change in temperature

For water, $L_f = 80$ cal/gm
$L_v = 540$ cal/gm

WORK

$$dw = \vec{F}\cdot\vec{dx}$$
$$= P_{gas} A\, dx$$



$dw = P_{gas}\, dv$ = Area under the curve of "P" vs "V" graph $\frac{F}{A} = P$

Work by gas $\boxed{+ve}$
Expansion $\boxed{+ve}$

INTERNAL ENERGY

It is represent by "du or dE". It is the sum of all type of energies like kinetic energy, potential energy, rotational energy, vibrational energy etc.

For cyclic process, work will be area of closed loop.

"For Ideal gases" internal energy is a function of temperature only.

THERMODYNAMICS

ISOCHORIC PROCESS

The Volume is constant $(dV=0)$.

Work is $\oplus$ for expansion.

(i) $dW = PdV = 0$

(ii) $dQ = nC_v dT$

$dQ = dU + dW$

$\therefore dQ = dV$

$dU = nC_v dT$

ISOBARIC PROCESS

Pressure is constant.

(i) $dQ = nC_p dT$

(ii) $du = nC_v dT$

(iii) $dW = PdV$

$PV = nRT$

Differentiating

$Pdv + vdp = nRdT$

$Pdv = nRdT$

$dQ = dv + dW$

$nC_p dt = nC_v dt + nRdT$

$C_p = C_v + R$ (Mayer's Relation)

$$\boxed{C_p > C_v}$$

ADIABATIC EXPONENT

It is denoted by (γ).

$$\gamma = \frac{C_p}{C_v}$$

$C_p = \gamma C_v$

$C_p = C_v + R$

$\gamma C_v = C_v + R$

$C_v(\gamma - 1) = R$

$C_v = \frac{R}{\gamma - 1}$

$$\boxed{C_p = \frac{\gamma R}{\gamma - 1}}$$

ISOTHERMAL PROCESS

Temperature is constant.

i $dq = nC_{process}\,dT$

ii $du = 0 \;\{dT = 0\}$

iii $dq = \cancel{du} + dw$

$dq = dw$

$$C_{process} = \frac{dQ}{n\,dT}$$

$$dT = 0, \quad \boxed{C_{process} = \infty}$$

$$dW = P\,dV$$
$$dW = \frac{nRT}{V}\,dV$$
$$\int_0^W dW = nRT\int_{V_1}^{V_2}\frac{dV}{V}$$
$$W = nRT(\ln V_2 - \ln V_1)$$

$$\boxed{W = nRT\ln\left(\frac{V_2}{V_1}\right)}$$

$$W = 2{\cdot}303\,nRT\log\left(\frac{V_2}{V_1}\right)$$

$$\frac{0}{0} \text{ or } \frac{\infty}{\infty} \longrightarrow 1$$

ADIABATIC PROCESS

Heat is constant.

(i) $dQ = 0$

$$dQ = dW + dU$$
$$0 = dW + dU$$
$$dW = -dU$$
$$dW = -nC_V\,dT$$
$$dW = -n\left(\frac{R}{\gamma - 1}\right)(T_2 - T_1)$$

$$\boxed{dW = \frac{nRT_1 - nRT_2}{\gamma - 1}}$$

$$\boxed{dW = \frac{P_1V_1 - P_2V_2}{\gamma - 1}}$$

For adiabatic, $dQ = nC_{process}\,dT$

$$C_{process} = \frac{dQ}{n\,dT} = 0$$

$$\boxed{C_{process} = 0}$$

$dQ = dU + dW$

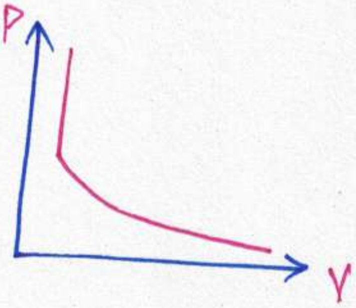
$dW = -dU$

$P\,dV = -nC_V\,dT$

$$\frac{nRT}{V}\,dV = -\frac{nR}{\gamma-1}\,dT$$

$$\frac{dV}{V} = \frac{-1}{\gamma-1}\,\frac{dT}{T}$$

$$\ln V = \frac{-1}{\gamma-1}\ln T + \ln C$$



$$V + \ln V = \ln\frac{1}{T} + \ln C$$

$$\ln\left(V^{\gamma-1}T\right) = \ln C$$

$$\boxed{\therefore V^{\gamma-1}T = \text{constant}} \Rightarrow PV = nRT$$

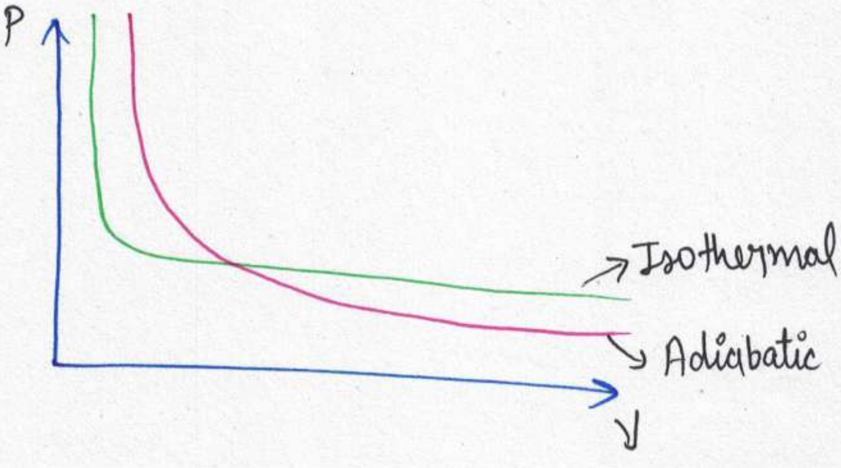
$$\frac{PV}{nR}V^{\gamma-1} = \text{constant}$$

$$\boxed{P^{1-\gamma}T^{\gamma} = \text{constant}}$$

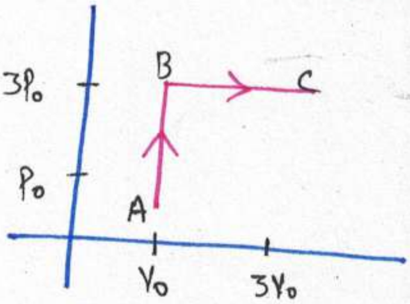
$$PV^{\gamma} = \text{constant}$$

THERMODYNAMICS

Graph of isothermal & adiabatic



Q For 2 mole He gas ($\gamma = 5/3$). Calculate heat internal energy, work for process AB & BC.



$n = 2$
$\gamma = 5/3$

$$C_V = \frac{R}{\gamma - 1} = \frac{R}{5/3 - 1} = \frac{3R}{2}$$

$$C_P = \gamma C_V = \frac{3\gamma R}{2} = \frac{\cancel{3}\times 5R}{2\times\cancel{3}} = \frac{5R}{2}$$

(i) AB is isochoric process (V = constant)

$dU = nC_V dT \Rightarrow 2\times\frac{3R}{2}dT = 3RdT$

$dW = PdV = 0$

$dq = dU$

$dU = 3R.dT$

$dT = T_B - T_A$

$T_B = \frac{3P_0V_0}{2R}$ $\quad T_A = \frac{P_0V_0}{2R}$

$$dT = \frac{2P_0V_0}{2R} = \frac{P_0V_0}{R}$$

$$dq = dU = 3R\frac{P_0V_0}{R} = 3P_0V_0$$

(ii) BC is isobaric process

$dq = dU + dW$

$dW = PdV$

$= 3P_0(3V_0 - V_0) = 6P_0V_0$

$dU = nC_V dT$

$= 2\times\frac{3R}{2}(T_C - T_B)$

$\cancel{2}\times\frac{3R}{\cancel{2}}\times\frac{\overset{3}{\cancel{6}}P_0V_0}{\cancel{2}R}$

$= 9P_0V_0$

$dq = 9P_0V_0 = 6P_0V_0$

$\boxed{dq = 15P_0V_0}$

Question ⇒ Calculate heat internal energy & work for AB, BC, CD & DA. What will be work, heat & internal for cyclic process ABCD ? ($\gamma = 5/3$, $n=2$).

(i) For AB, isochoric process

$$dW = PdV = 0$$

$$dV = nC_v dT$$

$$= 2 \times \frac{3R}{2}\left[\frac{4P_0V_0}{2R} - \frac{P_0V_0}{2R}\right]$$

$$= 3R\left[\frac{3P_0V_0}{2R}\right] = \frac{9P_0V_0}{2}$$

$$dQ = \frac{9P_0V_0}{2} + 0 = \boxed{\frac{9P_0V_0}{2}}$$ Ans.

(ii) For BC isobaric process

$$dV = nC_v dT$$

$$2 \times \frac{3R}{2}\left[\frac{16\,P_0V_0}{2R} - \frac{4P_0V_0}{2R}\right]$$

$$3R\left[\frac{12P_0V_0}{2R}\right] = 18\,P_0V_0$$

$$dW = PdV = 4P_0\,(3V_0)$$

$$dW = PdV = 12\,P_0V_0$$

$$\boxed{dQ = 30\,P_0V_0}$$ Ans.

(iii) For CD, isochoric process

$$dV = nC_v dT$$

$$= 2 \times \frac{3R}{2}\left[\frac{4P_0V_0}{2R} - \frac{16\,P_0V_0}{2R}\right]$$

$$= 3R\left[-6\,P_0V_0\right] = -18\,P_0V_0$$

$$dW = PdV = 0$$

$$\boxed{dQ = -18P_0V_0}$$ Ans.

(iv) For DA, isobaric process,

$$dV = nC_v dT = \frac{3}{2}R\times 2\left[\frac{P_0V_0}{2R} - \frac{4P_0V_0}{2R}\right]$$

$$= \frac{-3}{2}\cancel{R}\times\cancel{2}\times -\frac{3P_0V_0}{\cancel{2R}} = -\frac{9P_0V_0}{2}$$

$$dW = PdV = P_0(-3V_0) = -3P_0V_0$$

$$dQ = -\frac{9P_0V_0}{2} - 3P_0V_0 = -\frac{15P_0V_0}{2}$$

$$\boxed{dQ = -\frac{15P_0V_0}{2}}$$ Ans.

(v) For ABCD

$$dU = 2\times\frac{3}{2}R[0] = 0$$

$$dQ = nC_{process}\,dT = 9P_0V_0$$

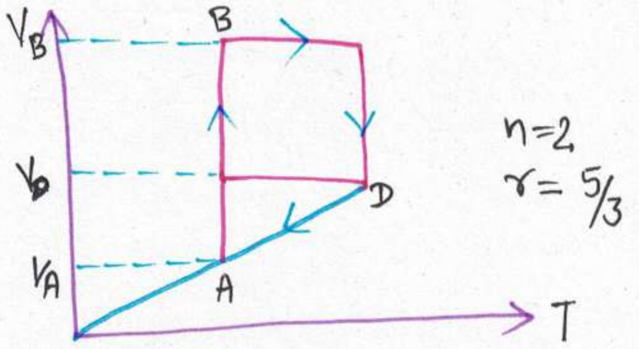
$$dW = 9P_0V_0$$

$$\boxed{dW = 9P_0V_0}$$ Ans.

- * For clockwise cycle, work will be positive for (P-V) graph.
- ★ For anticlockwise cycle, work will be negative for (P-V) graph.

THERMODYNAMICS

Que:-



$n = 2$

$\gamma = 5/3$

$$\frac{V_B}{V_D} = \frac{V_D}{V_A} = 2 \qquad T_A = 300K$$

Que. Calculate temp of point D.

Que. Find Q, U, W in all process AB, BC, CD, DA.

Que. Find Q, U, W, for entire cycle ABCDA.

Que. Make PV graph, PT, e_v, P & SvT.

$$dq = dv + dw$$

For AB, temperature constant (isothermal process)

$dU = 0$

$dq = dw$

$dw = Pdv$

$P(V_B - V_A)$

In DA process, $V \propto T$ ∴ P is constant so it is isobaric

$$\frac{V_D}{T_D} = \frac{V_B}{T_A}$$

$$T_D = \frac{V_D T_A}{V_A} = 2 \times 300$$

$$= \text{600 K} \quad \text{Ans.}$$

(i) For AB, $dv = 0$

$$dw = nRT \ln\left(\frac{V_B}{V_A}\right)$$

$$= 2 \times R \times T \ \ln 4$$

$$2 \times R \times 300 \ln 4$$

$$\boxed{dq = 600 R \ln 4}$$

$$\frac{V_B}{V_D} = \frac{V_D}{V_A} = 2$$

$$\frac{V_B}{V_D} \times \frac{V_D}{V_A} = \frac{V_B}{V_A} = 2 \times 2 = 4$$

$$600 \ln 4 = +1200 R \ln 2$$

(ii) For BC, isochoric process

$dW = 0$

$$dv = nC_v dT$$

$$= 2 \times \frac{3}{2} R (T_c - T_B)$$

$$= 3R(600 - 300)$$

$$\boxed{dv = 900R}$$

(iii) For CD, isothermal

$$dV = 0$$

$$dw = nRT \ln\left(\frac{V_D}{V_C}\right)$$

$$= 2 \times R \times 600 \ln\left(\frac{1}{2}\right)$$

$$\boxed{dw = -1200\, R \ln 2}$$

$V_B = V_C$

$\frac{V_D}{V_B} = \frac{1}{2}$

(iv) For DA, isobaric

$$dq = n C_p dT$$

$$dq = 2\, \frac{5}{2} R (300 - 600) = -1500K$$

$$dV = n C_V dT$$

$$= 2\, \frac{3}{2} R (-300) = -900R$$

$$\boxed{dW = -600R}$$

WORK CALCULATION FOR IRREVERSIBLE PROCESS

▷ For irreversible process, work $= P_{ext} (V_2 - V_1)$

I. ISOTHEMAL IRREVERSIBLE PROCESS

$$dV = 0$$

$$dV + dw = dq$$

$$dw = dq$$

$$\boxed{dq = P_{ext} (V_2 - V_1)}$$

II ADIABATIC IRREVERSIBLE PROCESS

We cannot apply $PV^{\gamma} = \text{constant}$ as process equation as the graph is discontinuous and we cannot apply integration.

$$dQ = 0$$

$$\text{work} = P_{ext}(V_2 - V_1)$$

$$dU = nC_v dT$$

$$dU = n\left(\frac{R}{\gamma-1}\right)(T_2 - T_1)$$

$$= \frac{nRT_2 - nRT_1}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

$$dQ = dU + dw$$

$$dw = -dU$$

$$\boxed{P_{ext}(V_2 - V_1) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}} \text{ —— } ①$$

eq. ① is used for calculation of process parameters (P, V, T)

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}} \text{ (State equation)}$$

The gas expands isothermally and reversibly → The work done is maximum.

DEGREE OF FREEDOM

It is the directions in which atom or molecule will be free.

	f	$\gamma = \frac{f+2}{f}$	$C_V = \frac{R}{\gamma-1} = \frac{R}{\frac{f+2}{f}-1} = \frac{fR}{2}$	$C_p = C_V + R$
Monoatomic	3	5/3	$\frac{3}{2}R$	$\frac{5R}{2}$
Diaatomic	5	7/5	$\frac{5}{2}R$	$\frac{7R}{2}$
Polyatomic	6	4/3	$3R$	$4R$

MOLAR HEAT CAPACITY FOR FREEDOM

$$dq = dv + dw$$

$$C_{process} = \frac{dQ}{n\,dT}$$

$$dU = nC_v\,dT$$

$$dw = P\,dV$$

$$dq = dU + dw$$

$$\boxed{dq = nC_v\,dT + P\,dV}$$

To solve this we need equation of reaction.

$$PV^a = K$$

$$P = KV^{-a}$$

$$dw = P\,dV = \int_{V_1}^{V_2} (KV^{-a})\,dV = K\left(\frac{V^{1-a}}{1-a}\right)_{V_1}^{V_2}$$

$$dw = \frac{K}{1-a}\left(V_2^{1-a} - V_1^{1-a}\right)$$

$$PV^a = K$$

$$\frac{nRT}{V}\cdot V^a = K$$

$$nRT = KV^{1-a}$$

$$\frac{K}{1-a}\left[V_2^{1-a} - V_1^{1-a}\right] = \frac{nRT_2 - nRT_1}{1-a} = \frac{nRdT}{1-a}$$

$$dq = nC_V dT + \frac{nRdT}{1-a}$$

$$C_{process} = C_V + \frac{R}{1-a}$$

$$\boxed{C_{Process} = C_V + \frac{R}{1-a}}$$

Q. n=2 moles ideal gas, ($C_V = \frac{5R}{2}$ was compressed adiabatically against P_{ext} = 2 atm. T_P = 350K, P_i = 1 atm

Work done = ?

A. $P_{ext}\ (V_2 - V_1) = \left(\frac{5}{2}\right)\left[1(V_1) - 2(V_2)\right]$

$$(2)(V_2 - V_1) = (5/2)(V_2 - 2V_1)$$

apply $PV = nRT \rightarrow 9V_1 = 14V_2$ —— ①

$$(1)\ \left(\frac{14V_2}{9}\right) = nR(350)$$

$$(2)\ (V_2) = nR(T_F) \longrightarrow T_F = 450K$$

$$\therefore \text{Work} = (2)\left(\frac{5R}{2}\right)(450 - 350) = 500K$$

THERMOCHEMISTRY

In this section we will calculate heat in terms of enthalpy.

ENTHALPY - It is the heat at constant pressure. It is denoted by (ΔH or q_p).

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P(V_2 - V_1)$$

$$\Delta H = \Delta E + (P_2V_2 - P_1V_1)$$

H = enthalpy
E = internal energy

NOTE

▷ Enthalpy of reaction can be calculated but actual enthalpy of any reactan or product can not be calculated.

So, we will calculate enthalpy of reactant and enthalpy of product from any reference value. so, for any reaction

$$R \longrightarrow P$$

$$\boxed{\Delta H_{Reaction} \rightarrow \Delta H_P - \Delta H_R}$$

If $\Delta H_{Reaction} > 0$ endothermic

If $\Delta H_{Reaction} < 0$ exothermic

If exothermic $\Delta H_R > \Delta H_P$

If endothermic $\Delta H_P > \Delta H_R$

THERMODYNAMICS

HEAT OF FORMATION - It is the amount of heat added or evolved for the formation of one mole molecule from its constituent or native elements (most stable allotropic form).

e.g:- Some of most stable allotropic forms are -

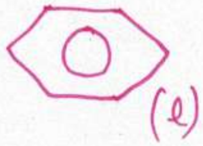
Carbon ⟶ graphit, Phosphorus ⟶ P_4 (white), H_2, N_2, O_2 gases

Sulphur ⟶ S_8, Cl_2 (gas), F_2 (gas) Br_2 (liq), I_2 (solid)

e.g:-

$$2C_{(graphite)(s)} + 2H_{2(g)} + O_{2(g)} \longrightarrow CH_3COOH_{(l)} \quad \text{——} ①$$

$$6C_{(graphite)(s)} + 3H_{2}\,(g) \longrightarrow$$



(l) ——— ②.

$$\tfrac{1}{2} I_{2\,(s)} + \tfrac{1}{2} H_{2\,(g)} \longrightarrow HI_{(l)} \quad \text{——} ③$$

STANDARD CONDITION

- Temperature is 25°C, pressure is 1 atm, molar concentration is assumed to be 1 molar at standard condition. heat of formation of most stable allotropic form is assumed to be zero.

eg:- In C ②
$$\Delta H^\circ = \Delta H^\circ_{f\,C_6H_6} - \cancel{3\Delta H^\circ_{f(H_2)}} - \cancel{6\Delta H^\circ_{graphite}}$$

$$\Delta H^\circ_{(reaction)} = \Delta H^\circ_{f\ C_6H_6}$$

MOST stable allotropic forms.

$$H_{2(g)} + \frac{1}{8}S_{8(s)} + 2O_{2(g)} \longrightarrow H_2SO_{4(l)}$$

$$\boxed{\Delta H^\circ_r = \Delta H^\circ_{H_2SO_4}}$$

$$\frac{1}{8}S_{8(g)} + \frac{3}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

$$\boxed{\Delta H^\circ_{reaction} = \Delta H^\circ_{SO_3}}$$

$$\frac{1}{4}\underset{white}{P_{4(s)}} + \frac{3}{2}H_{2(g)} \longrightarrow PH_{3(g)}$$

$$\boxed{\Delta H^\circ_{reaction} = \Delta H^\circ_{PH_3}}$$

Laws of Thermochemistry

Lavoisier and Laplace Law

According to it enthalpy or heat for the formation of any substance will be same in magnitude for decomposition of same substance but having opposite sign.

$A + B \longrightarrow C \qquad \Delta H = a$

$C \longrightarrow A + B \qquad \Delta H = -a$

one reversing a process, sign of heat of formation changes but magnitude is same.

Hess-Law-of-constant-heat-summation

If two or more reactions are added, then the net heat will be the sum of all individual heat of formations of different reactions.

$$\begin{tikzcd}
A \arrow[r, "q"] \arrow[d, "q_1"'] & D \\
B \arrow[r, "q_2"] & C \arrow[u, "q_3"']
\end{tikzcd}$$

$$\boxed{q = q_1 + q_2 + q_3 + q_4}$$

e.g.:- $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

I $C_{graphite} + 2H_{2(g)} \longrightarrow CH_{4(g)} \quad \Delta H^\circ_{f\,CH_4} = x$

$C_{graphite} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^\circ_{f\,CO_2} = Y$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H^\circ_{f\,H_2O} = Z$

II $CH_{4(g)} \longrightarrow \cancel{2H_2}_{(g)} + \cancel{C_{graphite}} \Rightarrow -x$

$\cancel{C_{graphite}} + O_{2(g)} \longrightarrow CO_{2(g)} \Rightarrow Y$

$\cancel{2H_2}_{(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \Rightarrow 2Z$

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

$$\boxed{\text{Net Heat} \Rightarrow y + 2z - x}$$

II^{nd} METHOD

NET HEAT = $\Delta H^\circ_{Product} - \Delta H^\circ_{Reactant}$

$$\Delta H^\circ_r = \Delta H^\circ_{fCO_2} + 2\Delta H^\circ_{fH_2O} - \Delta H^\circ_{fCH_4} - 2\cancel{\Delta H^\circ_{fO}}$$

↓ Most stable allotropic form

$$\boxed{\Delta H^\circ_r = y + 2z - x}$$

It can be generalised as:-

$$aA + bB \longrightarrow cC + dD$$

$$\boxed{\Delta H^\circ_{reaction} = \underbrace{\left(d\,\Delta H^\circ_{fD} + c\,\Delta H^\circ_{fC}\right)}_{\Delta H^\circ_{Products}} - \underbrace{\left(b\,\Delta H^\circ_{fB} \quad a\,\Delta H^\circ_{fA}\right)}_{-\ \Delta H^\circ_{reactants}}} \text{ — ①}$$

eq ① is equal to –

(Standard enthalpy of formation of product) – (standard enthalpy of formation of reactant).

Relationship b/w enthalpy and internal energy

$$aA_{(s)} + bB_{(l)} + cC_{(g)} \longrightarrow dD_{(g)} + eE_{(s)}$$

$$dw = P(V_2 - V_1)$$

$$= P(V_D + \cancel{V_E} - \cancel{V_A} - \cancel{V_B} - V_C)$$

$$= P(V_D - V_C)$$ [Vol. of solid & liquid is negligible w.r.t gas]

$= PV_D - PV_C$

$dw = dRT - cRT$

$dw = (d-c)RT$

$$\boxed{dW = \Delta nRT}$$

∴ It can be written as –

$\boxed{\Delta H = \Delta E + \Delta nRT}$ (Δn = no. of moles of gaseous products – No. of moles of gaseous reactants)

- Heat at constant volume is called "internal energy" $\underline{nC_VdT}$
  Heat at constant pressure is called "enthalpy".

e.g.:- $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$\Delta H = \Delta E + (2-4)RT$

$$\boxed{\Delta H = \Delta E - 2RT}$$

$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

$$\boxed{\Delta H = \Delta E + RT}$$

THERMODYNAMICS

THERMOCHEMISTRY

$2C_{graphite} + 3H_{2(g)} \longrightarrow C_2H_{6(g)}$

$4C_{graphite} + 4H_{2(g)} + O_{2(g)} \longrightarrow C_3H_7COOH_{(l)}$

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

HEAT OF COMBUSTION

- When one mole substance is completely burnt in presence of of oxygen the heat is evolved (in general). In general, combustion is an "exo thermic-reaction".

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $\Delta H < 0$

$C_{graphite} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H < 0$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H < 0$

- Combustion should always be for one mole.

e.g:- $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$ —— (I)

$C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$ —— (II)

- In these two reactions, I is correct because combustion always takes place for one mole not for two moles.

ENTHALPY OF NEUTRALISATION

- When one gram equivalent of an acid is completely neutralised with one gram equivalent of base, heat evolved is called "Heat of Neutralisation".

strong acid (1 eq) OR H^+ + strong Base (1 eq) OR OH^- $\longrightarrow$ Salt + water (H_2O)

$\boxed{\Delta H = (-13.7)\,K\,cal}$

(-ve) for exothermic

$\Delta H = (13.7)\,K\,Cal$

▨ Heat of formation will be calculated on the basis of no. of moles neutralised.

e.g:- 1 mole HCL + 0.5 mole NaOH
0.5 mole will be neutralised

Therefore, $\Delta H = \frac{-13.7}{2} = -6.85$ KCal

0.5 mole HCL + 0.5 mole NaOH
0.5 mole will be neutralised

Therfore, $\Delta H = -6.85$ KCal

$PH = 2$	$PH = 12$
$H^+ = 10^{-2}$	$OH^- = 10^{-2}$
$V = 2L$	$V = 3L$
$H^+ = 2\times10^{-2}$	$OH^- = 3\times10^{-2}$

(2×10^{-2}) will be neutralised

$\Delta H = -(2\times10^{-2} \times 13.7$ KCal$)$

Cal = 4.18J

▨ If either acid or base or both are weak, then evolved heat will be less than 13.7 KCal, because some heat will be lost in "ionization of acid."

▨ Ionization means "breaking into ions."

$$\underset{1\,\text{mole}}{CH_3COOH} + \underset{1\,\text{mole}}{NaOH} \longrightarrow \underset{1\,\text{mole}}{CH_3COONa} + \underset{1\,\text{mole}}{H_2O} \quad (\Delta H = 12.3\,\text{KCal})$$

E.g:- 200 ml 1M HCL + 500 ml 0.5M NaOH

$H^+ = \frac{200\times1}{1000} = 1/5$ $\qquad OH^- = \frac{500\times0.5}{1000} = 1/4$

$1/5$ mole will be neutralised.

$$\Delta H = -13.7\times 1/5 = \boxed{\frac{-13.7}{5}\,\text{KCal}}$$

Q. The heat of combustion of ethylene at 18°C at constant volume is −335.8 KCal when water is obtained in Liquid state. Calculate heat of combustion at constant pressure at 18°C.

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)}$$

$$\Delta E = -335.8 \text{ KCal}$$

$$\Delta E = (-335.8 - 2 \times 2 \times 291) \text{ KCal}$$

$$\Delta E = \left(-335.8 - \frac{1164}{1000}\right) \text{ KCal}$$

$$\Delta E = -335.8 - 1.164$$

$$\Delta E = -336.964$$ Ans.

Q. The enthalpy of formation of methane at constant pressure and 300K is −75.83 KJ? what will be heat of formation at constant volume?

$$C_{graphite} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$

$$\Delta H = \Delta E + \Delta n RT$$

$$-75.83 = \Delta E + (1-2)RT$$

$$-75.83 = \Delta E - RT$$

$$\Delta E = RT - 75.83$$

$$\Delta E = \left(\frac{8.31 \times 300}{1000} - 75.83\right) \text{ KJ}$$

$$\Delta E = -(2.493 - 75.83) \text{ KJ}$$

$$\Delta E = -73.337 \text{ KJ}$$ Ans.

Q. The standard heat of formation at 298 K for $CCl_{4(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$ & $HCL_{(g)}$ are (−25.5, −57.8, −94.1 & −22.1) kal/mole respectively. Calculate ΔH° for reaction -

$$CCl_{4(g)} + 2H_2O_{(g)} \longrightarrow CO_{2(g)} + 4HCL_{(g)}$$

$$\Delta H^\circ = [94.1 - 4(22.1)] - [2(-57.8) - 25.5]$$

$$= (-94.1 - 88.4) - (-115.6 - 25.5)$$

$$= -182.5 + 141.1$$

$$\boxed{\Delta H^\circ = -41.4\ K.Cal}$$ Ans.

Q. The Molal heat of formation of $NH_4NO_{3(s)}$ is −367.5 KJ and those of $N_2O_{(o)}$ and $H_2O(l)$ are 81.46 KJ and −285.78 KJ respectively at 25°C and 1 atm pressure. Calculate ΔH and ΔE for reaction.

$$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)} \quad — ①$$

$$N_2O_{(g)} + 2H_2O_{(l)} \longrightarrow NH_4NO_3$$

$$\Delta H = (-367.5) - [-285.78 + (81.46)]$$

$$\Delta H = (-367.5) - (-285.78 + 162.92)$$

$$\Delta H = -367.5 + 122.86$$

$$\Delta H = 144.64\ KJ$$

ΔH of I is 144.64 KJ

$$\Delta H = \Delta E + \Delta nRT$$

$$144.64 = \Delta E + \frac{8.31}{1000} \times 298$$

$$\boxed{\Delta E = -125\ KJ}$$ Ans.

THERMODYNAMICS

THERMOCHEMISTRY

Bomb calorimeter is used to burn a fuel.

If heat is added or evolved from a closed container, that "heat is ΔE."

$$m_1 s_1 t_1 + m_2 s_2 t_2 + m_3 s_3 t_3 - - - - - m_n s_n t_n = (m_1 + m_2 + --) s_{sol.} J$$

s. - specific heat of water = 1 g/ml

CALORIFIC VALUE

- This is used for fuels. This is heat of combustion per gram of particular fuel.

The heat of combustion for CH_4 and C_4H_{10} are -890.3 kJ, -2878.7 kJ/mole respectively. which of the two has greater efficiency as fuel per given? (calorific value).

Calorific fuel $\propto$ efficiency of fuel

For 16 gm, $\Delta H = -89.3$ kJ

For 1 gm, $\Delta H = -\frac{890}{16}$

$C.F = -55.56$ kJ/gm

For 58 gm, $\Delta H = -2878.7$ kJ

For 1 gm, $\Delta H = \frac{-2878.7}{58} = -99.6$ kJ/gm.

For comparing, only magnitude is compared or we check the heat evolved. The more the heat evolved, higher is the calorific value.

CH_4 is more efficient.

Q. When 2 mole C_2H_6 completely burnt, 3129 KJ heat is liberated. Calculate heat of formation of C_2H_6 if standard heat of formation for CO_2 & H_2O are 395 & 286 KJ.

$$C_2H_{6(g)} + \tfrac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O$$

$$\Delta H = \Delta H_{Product} - \Delta H_{reactant}$$

$$-3129 = (2\times-395-3\times 286)-(H_{C_2H_6})$$

$$\frac{-3129}{2} = (-790-858)-H_{C_2H_6}$$

$$H_{C_2H_6} = +1564.5-1648$$

$$\boxed{H_{C_2H_6} = -83.5\,KJ}$$ Ans.

Q. The standard heat of formation of CH_4 gas, CO_2 gas & $H_2O_{(g)}$ are -76.2, -398.8, -241.6 KJ/mole. Calculate the amt. of heat evolved by burning $1m^3$ of CH_4 gas measured at STP condn.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$$

$$\Delta H = [2(-241.6)-398.8]-[-76.2]$$

$$\Delta H = -483.2-398.8+76.2$$

$$\Delta H = 882.0+76.2$$

$$\Delta H = -805.8\,KJ$$

$T = 25°C \qquad P = 1\,atm$

$1m^3 = 1000L$

$V = 1000L$

$$n = \left(\frac{1000}{22.4}\right) = 44.1$$

$$\boxed{\Delta H = (-805.8\times 44.1)\,KJ}$$

Q. A gaseous mixture of 3·67L of ethylene & methane combustion at 25°C produces 6·11L of CO_2. Find out the heat evolved on burning 1L of gaseous mixture. The heat of combustion of ethylene and methane are (−1423 & −891) KJ/mole at 25°C.

$$\text{Glucose} \begin{array}{l} \xrightarrow{\text{Scheff's}} \\ \xrightarrow{NaHSO_3} \\ \xrightarrow{2,4,DNP} \end{array} (NR) \text{ as there are reversible}$$

$$\underset{(3\cdot61-V)}{CH_4} + 2O_2 \longrightarrow \underset{(36\cdot1-V)}{CO_2} + 2H_2O$$

$$\underset{V}{C_2H_4} + 3O_2 \longrightarrow \underset{2V}{2CO_2} + 2H_2O$$

$$2V + 3\cdot67 - V = 6\cdot11$$

$$V = 6\cdot11 - 3\cdot67 = 2\cdot44L$$

Vol. of $C_2H_4 = 2\cdot44L$

Vol. of $CH_4 = 3\cdot67 - 2\cdot44$

$= 1\cdot23L$

C_2H_4 will be $\frac{2}{3}$rd part & CH_4 will be $\frac{1}{3}$rd part

So for 1L, $C_2H_4 = \frac{2}{3} \times 1 = 0\cdot66L = \frac{2}{3}L$

$CH_4 = \frac{1}{3} \times 1 = 0\cdot33L = \frac{1}{3}L$

$PV = nRT$

$1 \times \frac{2}{\cancel{3}} = n \times \frac{1}{\underset{4}{\cancel{12}}} \times 298$

$n = \frac{8}{298} = \frac{4}{149}$

$PV = nRT$

$1 \times \frac{1}{3} = n \times \frac{1}{12} \times 298$

$n = \frac{2}{149}$

$(\Delta H)_{C_2H_4} = \left(\frac{4}{149} \times -423\right)$

$(\Delta H)_{CH_4} = \left(\frac{2}{149} \times -891\right)$

$$\text{Total} = \left[\left(\frac{4}{149} \times -1423\right) + \left(\frac{2}{149} \times -891\right)\right] \text{KJ}$$

$$= \frac{2}{149}\left\{2 \times -1423 - 891\right\}$$

$$\frac{2}{149} \times -3737 = -50.81\text{J} \quad \text{Ans.}$$

Q. Calculate heat evolved for the following –

i 0.5 mole of HCL sol. is neutralised by 0.5 mole NaOH

ii 0.5 mole of HNO_3 sol. is neutralised by 0.3 mole KOH

iii 100 ml 0.2 M HCL sol. is neutralised by 0.3M NaOH

iv 100 ml 0.2 M H_2SO_4 sol. is neutralised by 0.7M KOH

i Moles neutralised = 0.5

Heat evolved $= \frac{13.7}{2}$ K.Cal

ii Moles neutralised $= 0.3 = 3/10$

Heat evolved $= \frac{3 \times 13.7}{10} = \frac{41.4}{10} = \boxed{4.11 \text{ KCal}}$

iii Moles neutralised $= \frac{2\cancel{0}}{10\cancel{0}} = 1/50$

Heat evolved $= \boxed{\frac{13.7}{50} \text{ KCal}}$ Ans.

iv 400 ml 0.2 M H_2SO_4 & 600 ml 0.1 KOH

Moles of $H_2SO_4 = 2 \times 400 \times 0.2 = 40 \times 4 = 160$

Moles of KOH $= 600 \times 0.1 = 60$

Moles neutralised = 60

Heat evolved $= \left(\frac{-60}{1000} \times 13.7\right)$ KCal

THERMODYNAMICS

ANTHALPY OF HYDRATION

It is amt. of heat evolved for one mole anhydrous salt to convert to its hydrated salt.

E.g:- $CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$

$\Delta H = -18.89$ KCal

$CaCl_2 + 6H_2O \longrightarrow CaCl_2 \cdot 6H_2O$

$\Delta H = -18.8$ KCal

ANTHALPY OF SOLUTION

When one mole anhydrous salt or partially hydrated salt is added to excess amt. of water, heat evolved is called "heat of solution".

E.g:- $CuSO_4 + aq \longrightarrow CuSO_4(aq)$

$CaCl_2 + aq \longrightarrow CaCl_2(aq)$

Q. one mole $CuSO_4$ is added to 5 mole H_2O, heat evolved is 18.69 KCal. If one mole $CuSO_4$ is added to 1000 moles of water, heat evolved is 19.8 KCal. what will be change in enthalpy if solution containing 5 mole water & ·1 mole $CuSO_4$ is added with 995 mole of water?

$CuSO_4 + 5H_2O \longrightarrow CuSO_4$

$\Delta H = -18.69$ KCal

$CuSO_4 + 1000H_2O \longrightarrow CuSO_4 \cdot 1000\,H_2O$

$\Delta H = -19.8$ Cal

$$CuSO_4 \cdot 5H_2O + 995H_2O \longrightarrow CuSO_4 \cdot 1000H_2O$$

change in enthalpy $= -19.8 + 18.69$
$= -1.11$ KCal

$\boxed{-1.11 \text{ Kcal}}$ Ans.

ENTHALY OF IONISATION

It is the amt. of heat absorbed when one mole electrolyte will be dissociated into its ions.

E.g:- $AB \longrightarrow A^+ + B^-$ $(\Delta H > 0)$

Enthalpy for phase change

(At constant temp. & pressure)

(i) ENTHALPY OR HEAT OF FUSION

$A_{(solid)} \longrightarrow A_{(liquid)} \longrightarrow \underset{(fusion)}{\Delta H} > 0$ —— ①

The reaction is "endothermic."

When one mole of solid is converted into its liquid state, amt. of heat absorbed is called "Heat of fusion."

(ii) ENTHALPY OR HEAT OF VAPOURISATION

When one mole of liquid is totally converted into its gaseous state, amt. of heat absorbed is called "Heat of Vaporisation."

$A_{(l)} \longrightarrow A_{(g)} \longrightarrow (\Delta H_{vap} > 0)$ —— ②

(iii) ENTHALPY OR HEAT OF SUBLIMATION

When one mole of solid is totally converted into gaseous state, heat absorbed is called "Heat of sublimation."

$$A_{(s)} \longrightarrow A_{(g)}$$

$$\boxed{\Delta H_{(sub)} = \Delta H_{fusion} + \Delta H_{vap}}$$

$$\boxed{\Delta H_{sub} > 0}$$

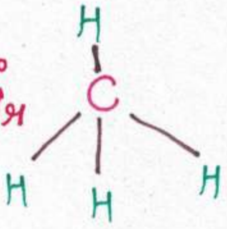
$$\boxed{\Delta H_{(sub)} = \Delta H_{fusion} + \Delta H_{vap}}$$

BOND ENERGY – It is the avg. amount of energy to break all type of bonds in one mole molecule.

It is denoted by "ε"

E.g:-

(i) $CH_{4(g)} \longrightarrow C_{(g)} + 4H_{(g)} \longrightarrow \Delta H^\circ_{r}$

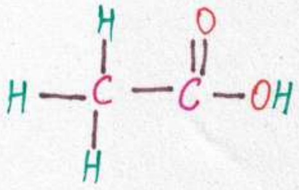


B.E of CH bond $= \dfrac{\Delta H^\circ_r}{4}$

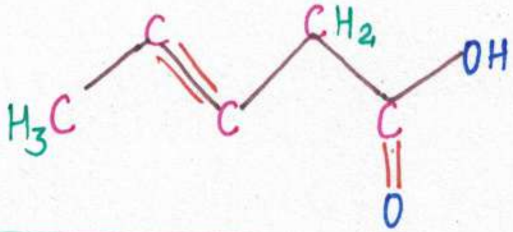
$$\boxed{\Delta H^\circ_r = 4\varepsilon_{CH}}$$

(ii) $CH_3COOH \longrightarrow 2C_{(g)} + 2O_{(g)} + 4H_{(g)}$

$$\boxed{\Delta H^\circ_r = 3\varepsilon_{C-H} + \varepsilon_{OH} + \varepsilon_{C=O} + \varepsilon_{C-O} + \varepsilon_{C-C}}$$



(iii)



$$\boxed{\Delta H^\circ_r = 3\varepsilon_{C-C} + 5\varepsilon_{C-H} + \varepsilon_{C=O} + \varepsilon_{C-O} + \varepsilon_{O-H} + \varepsilon_{C\equiv C}}$$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$CH_4 \longrightarrow C + 4H \quad (\Delta H = 4\varepsilon_{CH})$

$2O_2 \longrightarrow 4O \quad (\Delta H = 2\varepsilon_{O=O})$

$CO_2 \longrightarrow C + 2O \quad (\Delta H = 2\varepsilon_{C=O})$

$2H_2O \longrightarrow 4H + 2O \quad (\Delta H = 4\varepsilon_{C-H})$

For $C + 2O \rightarrow CO_2$

$\Delta H = -2\varepsilon_{C=O}$

For $4H + 2O \rightarrow 2H_2O$

$\Delta H = -4\varepsilon_{O-H}$

$$\Delta H^\circ = \left(4\varepsilon_{CH} + 2\varepsilon_{O=O}\right) - \left(2\varepsilon_{C=O} + 4\varepsilon_{OH}\right)$$

$$\boxed{\Delta H^\circ = \left(BE_{CH_4} + 2B.E_{O_2}\right) - \left(BE_{CO_2} + 2B.E_{H_2O}\right)}$$

$R \longrightarrow P$

$\Delta H^\circ_r = B.E$ of $R - BE$ of P

$C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$

$$\Delta H^\circ_r = \left(2\varepsilon_{CH} + \varepsilon_{C=C} + \frac{5}{2}\varepsilon_{O=O}\right) - \left(4\varepsilon_{C=O} + 2\varepsilon_{OH}\right)$$

LATTICE ENERGY – When one mole solid crystal is formed from its gaseous ions, energy released will be "Lattice Energy".

E.g:- $Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)}$

RESONANCE ENERGY

observed heat of formation − Actual heat of formation

Limitation of First Law of Thermodynamics

(i) No indication is available as regards the direction in which the change will proceed.

(ii) It gives no idea about the extent to which the change takes place.

★ These limitations can be understood from the following examples −

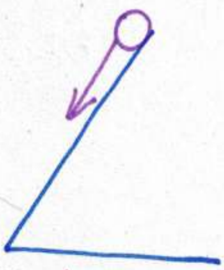
(iii) This Law can easily explain the bullet heating when it strikes a block due to conversion of kinetic energy into heat, but it fails to explain as to why heat in the block cannot be changed into kinetic energy of a bullet & make it fly back from inside of the block.

(iv) when a vessel of water is placed over fire, heat flows into the vessel. what prevents the heat from flowing from water into fire, & thereby cooling the water & ultimately converting into ice. Thus direction of (flow) change is not known from Ist Law.

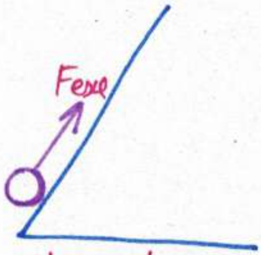
(v) It is practically found that whole of heat can never be converted into work. The first Law has no answer to this observation. Thus first Law falls to tell extent to which interchange of heat into work and vice versa is possible.

IInd Law of Thermodynamics

Spontaneous Reaction & Non spontaneous Process



Spontaneous
(feasible)



Non spontaneous
(Non feasible)

- All the natural process which occur without any external agent are "spontaneous".
- All the process which occur in presence of any external agent are "non-spontaneous".

ENTROPY – It is the degree of random ness. It is represented as "S".

- More arrangement of particles, less randomness, Therefore entropy is less.

$$S \longrightarrow L \longrightarrow G$$

- Therefore solids has least entropy due to more arrangement of particles so, entropy increases from solid to liquid to gas.
- It is "state function".
- It is "extensive property."

We can calculate absolute entropy for any substance.

$$R \longrightarrow P$$

$$\boxed{\Delta S = S_P - S_R}$$

$$aA + bB \longrightarrow cC + dD$$

$$\boxed{\Delta S = (cS_C + dS_D) - (b\,S_B + aS_A)}$$

ENTROPY CALCULATION FOR THERMODYNAMIC PROCESS

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

Mathematically, change in entropy is equal to –

$$\boxed{\Delta S = \frac{(dq)_{rev}}{T}}$$

$$dq = du + dw$$

$$\frac{dq}{T} = \frac{du}{T} + \frac{dw}{T}$$

$$dq = \int_{T_1}^{T_2} \frac{nC_v\,dT}{T} + \int \frac{P\,dv}{T}$$

$$\int_{T_1}^{T_2} \frac{nC_v\,dT}{T} \Rightarrow nC_v \ln\left(\frac{T_2}{T_1}\right)$$

$$PV = nRT$$

$$\frac{P}{T} = \frac{nR}{V}$$

$$\int \frac{P\,dv}{T} = \int_{V_1}^{V_2} \frac{nR\,dv}{V} \Rightarrow nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

We know that $\boxed{C_v = C_p - R}$

$$\Delta S = (C_p - R)\, n\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\left[-\ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right)\right]$$

$$\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\left[\ln\left(\frac{V_2 T_1}{V_1 T_2}\right)\right]$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{P_1}{P_2} = \frac{T_1V_2}{V_1T_2}$$

$$\boxed{\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)}$$

ENTROPY CALCULATION FOR ISOCHORIC PROCESS

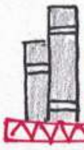
$$\Delta S = nC_v\ln\left(\frac{T_2}{T_1}\right)^{V_1=V_2} + nR\,\cancel{(\ln 1)}^{0}$$

$$\boxed{\Delta S = nC_v\ln\left(\frac{T_2}{T_1}\right)}$$

$$dq = du + \cancel{dw}^{0}$$

$$\frac{dq}{T} = \frac{nC_v dT}{T}$$

$$= nC_v\ln\left(\frac{T_2}{T_1}\right)$$



ENTROPY CALCULATION FOR ISOBARIC PROCESS

$P_1 = P_2$

$$\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) + nR\ln(1)$$

$$\boxed{\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right)}$$

$$dq = dv + dw$$

$$\frac{dq}{T} = \frac{nC_p dT}{T}$$

$$\frac{dq}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

ENTROPY CALCULATION FOR ISOTHERMAL PROCESS

$$dq = dv + dw$$

$$dq = dw$$

$$\frac{dq}{T} = \frac{P\,dv}{T} = \frac{nR}{V}\,dv$$

$$\frac{dq}{T} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\frac{dq}{T} = nR \ln\left(\frac{P_1}{P_2}\right)$$

NOTE:-

For adiabatic Process $dq = 0$

Therefore $\boxed{\Delta S = 0}$ since $\Delta S = \frac{dq}{T} = 0$

ENTROPY CHANGE DURING PHASE CHANGE

ENTROPY OF FUSION

The entropy change when one mole of a solid substance completly changes to its liquid state at its "melting point."

$$A_{(s)} \longrightarrow A_{(l)} \Longrightarrow \Delta H_{fusion}$$

$$\boxed{\Delta S = \frac{\Delta H^{\circ}_{fusion}}{T}}$$

T = melting Point

ENTROPY OF VAPOURISATION

The entropy change when one mole of a liquid substance completely changes into its gaseous state at its boiling point.

$$A_{(l)} \longrightarrow P_{(g)} \Longrightarrow \Delta H^{\circ}_{vap.}$$

$$\boxed{\Delta S = \frac{\Delta H^{\circ}_{vap}}{T}}$$

ENTROPY OF SUBLIMATION

When one mole of solid is completly changed to gaseous state, the entropy change is the entropy of sublimation.

$$A_{(l)} \longrightarrow P_{(g)} \Longrightarrow \Delta H_{sub.}$$

$$\boxed{\Delta S = \frac{\Delta H_{sub}}{T}}$$

ENTROPY OF PHYSICAL TRANSITION

$$C_{graphite} \longrightarrow C_{diamond}$$

$$\boxed{\Delta S = \frac{\Delta H_{Transition}}{T_{Transition}}}$$

Entropy change during chemical reaction

$R \longrightarrow P$

E.g:- $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

If $\Delta n > 0$, $\Delta S \uparrow$ randomness $\uparrow$
$\Delta n < 0$, $\Delta S \downarrow$ randomness $\downarrow$

If $\Delta n = 0$, we cannot predict.

E.g:- $H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$

Second Law of Thermodynamics

- All spontaneous process are thermodynamically irreversible.
- Without the help of an external agency, a spontaneous process cannot be reversed.
  E.g:- Heat cannot by itself flow from colder to hotter body.
- The complete conversion of heat into work is impossible without leaving some effect elsewhere.
- All spontaneous process are accompanied by a net increase of entropy.
- The entropy of universe is increasing.
- The entropy is a time arrow.

a. $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

b. $N_{2(0)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

c. $PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$

d. $H_2(g) + Cl_2(g) \longrightarrow 2HCl_{(g)}$

e. $NH_4HS_{(s)} \longrightarrow NH_{3(g)} + H_2S_{(g)}$

a. entropy ↑ b. entropy ↑ c. entropy ↑

d. entropy ↓ e. Cannot predict

➤ $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

Heat given = Heat taken

$q_{system} = -q_{surrounding}$

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

$$\Delta S_{surr} = -\frac{q_{sys}}{T}$$

$$T\Delta S_{surr} = -q_{sys}$$

$$T\Delta S_{universe} = T\Delta S_{sys} + T\Delta S_{surroundings}$$

$$T\Delta S_{universe} = T\Delta S_{sys} - \Delta H_{sys.}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{-T\Delta S_{universe} = \Delta G}$$

ΔG = Gibb's free energy / Max' useful work

ΔH = enthalpy or heat

ΔS = entropy

T = Temperature

➤ $\Delta S_{universe} > 0$

(i) $\Delta G < 0$, spontaneous

(ii) $\Delta G > 0$, non spontaneous

(iii) $\Delta G = 0$, at equilibrium

FOR THERMODYNAMICS PROCESSES

1. $\Delta H < 0, \quad \Delta S > 0$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = ⊖$

$\boxed{\Delta G < 0}$ spontaneous

2. $\Delta H > 0, \quad \Delta S < 0$

$\Delta G = ⊕$

$\boxed{\Delta G > 0}$ "Non spontaneous at all temperatures

3. $\Delta H > 0, \quad \Delta S > 0$

CASE-I (i) Low temperature

$\Delta G = \Delta H - T\Delta S$

T is very less

$\boxed{\Delta G > 0}$ Non spontaneous

CASE - II (ii) High temperature

$$\Delta G = \Delta H - T\Delta S$$

T is very high

$\boxed{\Delta G = 0}$ "Spontaneous"

(iv) $\Delta H < 0$ & $\Delta S < 0$

$$\Delta G = \Delta H - T\Delta S$$

(i) Law temperature

$$\Delta G = \Delta H - T\Delta S$$

$\boxed{\Delta G > 0}$ "Non Spontaneous"

➤ $\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$

ΔG° = Gabb's energy at standard condition's.

Q = Reaction Quotient

At equilibrium, $\Delta G = 0$

$\boxed{\Delta G^\circ = -RT \ln K}$

$\boxed{\Delta G^\circ = -nFE}$ where n = no. of e^- transferred in all reaction

F = Faraday

1 Faraday = charge of 1 mole e^-

$= 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$

$\boxed{1 \text{ Faraday} = 96500\,C}$

E = E.M.F of cell

E.M.F = electromative force

CARNET CYCLE

Efficiency of cycle or engine.

efficiency is represented as "η" (eta).

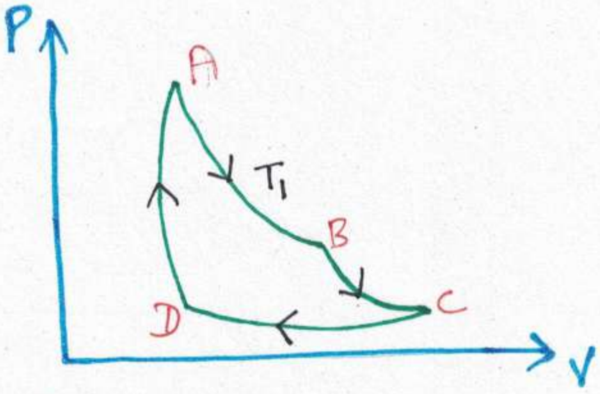
$$\eta = \frac{\text{work}}{\text{Heat given}}$$

$$\eta = \frac{Q_g - Q_r}{Q_g}$$

$$\boxed{\eta = 1 - \frac{|Q_r|}{Q_g}}$$

Q_r = heat rejected

Q_g = heat given



AB = isothermal

BC = adiabatic

CD = isothermal

AD = adiabatic

$$Q_g = nRT_1 \ln\left(\frac{V_B}{V_A}\right) = \oplus$$

$$Q_r = nRT_2 \ln\left(\frac{V_D}{V_C}\right) = \ominus$$

$$Q_r = nRT_2 \ln\left(\frac{V_C}{V_D}\right) = \oplus$$

$B \longrightarrow C$

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1} \text{———} ①$$

$D \longrightarrow A$

$$T_D V_D^{\gamma-1} = T_D V_A^{\gamma-1}$$

$$T_2 V_D^{\gamma-1} = T_1 V_A^{\gamma-1} \text{ ——— } ②$$

① % ②

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \text{ ——— } ③$$

$$\therefore \eta = 1 - \frac{|Q_r|}{Q_a} = 1 - \frac{nRT_2 \ln\left(\frac{V_C}{V_B}\right)}{nRT_1 \ln\left(\frac{V_B}{V_A}\right)}$$

$$\eta = 1 - \frac{T_2}{T_1} \frac{\ln\left(\frac{V_C}{V_D}\right)}{\ln\left(\frac{V_C}{V_D}\right)} \implies \boxed{\eta = 1 - \frac{T_2}{T_1}}$$

T_2 = sink temperature

T_1 = source temperature

Q. What is the percent efficiency of carnot source temperature is 127°C and sink

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400}$$

$$= 1 - \frac{3}{4} = 0.25$$

$\eta\% = 25\%$ Ans

$$1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1}$$

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

$$\boxed{\Delta S_1 = \Delta S_2}$$

b. What will be efficiency if sink temperature reduced to half of initial value?

$T_2 = \frac{27}{2} = 13.5°C$

$T_2 = 286.5°C$

$\eta = 1 - \frac{286.5}{400} = \frac{113.5}{400} = \boxed{0.28}$